CHAPTER 2

X-ray Methods in High-Intensity Discharges and Metal-Halide Lamps: X-ray Induced Fluorescence

John J. Curry^a, Walter P. Lapatovich^b, and Albert Henins^a

^aNational Institute of Standards and Technology, Gaithersburg, MD 20899, USA ^b51 Pye Brook Lane, Boxford, MA 01921, USA

Contents	1.	Introduction	66
	2.	High-Intensity Discharges and Metal-Halide	
		Lamps	68
	3.	Why X-ray Methods?	75
	4.	Interaction of X rays with Atoms	77
	5.	X-ray Induced Fluorescence Spectroscopy	
		(XRIF)	85
		5.1 Density Measurements	85
		5.2 Temperature Distributions	97
		5.3 Chemical Partitioning	99
		5.4 Demixing	102
		5.5 Equilibrium Vapor Pressures	107
		5.6 Accuracy	112
	6.	Summary	113
	Glos	sary	114
	Refe	erences	115

Abstract We describe the use of x-ray induced fluorescence to study metal-halide high-intensity discharge lamps and to measure equilibrium vapor pressures of metal-halide salts. The physical principles of metal-halide lamps, relevant aspects of

Advances in Atomic, Molecular, and Optical Physics, Volume 60, Copyright © 2011 Elsevier Inc. ISSN 1049-250X, DOI: 10.1016/B978-0-12-385508-4.00002-4. All rights reserved.

x-ray–atom interactions, the experimental method using synchrotron radiation, and x-ray induced fluorescence measurements relevant to metal-halide lamps are covered.

1. INTRODUCTION

Just over 10 years ago, x-ray induced fluorescence (XRIF) was used for the first time to measure and map gas-phase densities in a commercial highintensity discharge (HID) lamp (Curry et al., 2001). This work opened up a new window on important processes affecting lamp performance. It may also have been the first successful use of XRIF to measure vapor densities below 10¹⁷ cm⁻³. The success of those measurements owed much to an x-ray source that had just become available at the then relatively new Advanced Photon Source. Since then, XRIF has been used several more times to further explore the physics of metal-halide high-intensity discharge lamps and related processes. This chapter describes that work, all of which has been in collaboration with the lighting industry.

High-intensity discharges, also referred to as high-pressure arcs, play a role in many technologies including general purpose lighting, materials processing, sterilization, environmental remediation, and spectrochemistry. The focus here will be on high-intensity discharges used for lighting applications. Metal-halide high-intensity discharge (MH-HID) lamps, or metal-halide lamps for short, are among the most advanced general purpose light sources available (Hong et al., 2002 and 2005). These lamps combine a high luminous efficacy¹ with excellent color rendering² and are used in a number of places where intense sources are needed.³ The desires of lighting companies to produce more profitable lamps, of government agencies and public utilities to reduce energy consumed by lighting, and of scientists to improve general knowledge of plasma physics have made metal-halide lamps a topic of considerable scientific and engineering interest for at least the last few decades (ALITE, 2006; ICF, 2006). This interest has motivated the development and refinement of a number diagnostic methods in search of better and more detailed information about these complex systems. Diagnostics utilizing x rays are a small subset of the available methods, but a very powerful subset.

The combination of terms "x ray" and "high-intensity" frequently produces an initial misconception that the "x rays" are produced by

¹A quantitative measure of the illuminating efficiency of a light source (see Luminous efficacy in the Glossary for more detail).

²A quantitative measure of the ability of a light source to properly render all colors (see Color rendering in the Glossary for more detail).

³Metal-halide lamps are used to illuminate streets and parking lots, buildings and monuments, stadiums, large indoor spaces, and even high-end retail merchandise.

the "high-intensity" discharge; one thinks of laser-produced plasmas or pulsed-power discharges, from which x rays are indeed emitted by the plasma and are also used for diagnostic purposes. High-intensity discharges are high-pressure plasmas in which electrons and heavy particles have the same or nearly the same temperature, with that temperature generally being less than a few electronvolts. In metal-halide lamps, these temperatures are usually less than one-half an electronvolt,⁴ far too low to generate a substantial amount of ultraviolet radiation, to say nothing of x rays. The x-ray methods used to study high-intensity discharges and metal-halide lamps utilize external sources of x rays. X-ray absorption imaging has been demonstrated with both synchrotron radiation (Curry et al., 2004) and with commercial x-ray tubes (Curry et al., 1998), whereas x-ray induced fluorescence (XRIF) relies on synchrotron radiation (Curry et al., 2003b). The latter is the subject of the present discussion.

XRIF is neither new nor unfamiliar to the broader scientific community, but its application to the study of metal-halide lamps is novel and presents some special challenges. The densities of atoms being detected are small compared to typical applications; we are interested in densities as low as 10¹⁵ cm⁻³. Such sensitivities are made possible by the availability of third-generation synchrotron sources, such as the Advanced Photon Source (APS) at Argonne National Laboratory. It is possible to obtain spatially resolved measurements of relatively low vapor densities in a matter of tens of seconds.

An intense, laser-like beam of high-energy photons like that obtainable at the APS is not required for XRIF measurements but is so powerful that it makes measurements with lesser sources relatively insignificant. Unfortunately, the considerable effort and resources required to competitively obtain access to and operate a remote experiment at an appropriate synchrotron facility put such measurements beyond the reach of many. Most synchrotrons are publicly funded institutions with a responsibility and mission to serve scientific and industrial endeavors, but they are still a limited resource.

X-ray methods are far from being the answer to all questions in metalhalide lamps. They are, however, a considerably different set of tools with capabilities that are both powerful and complementary to existing methods. As will be seen, they can answer questions that are important and cannot be answered with other methods. In some ways, the significance of the answers they provide has not been fully appreciated because the theoretical approaches and interpretations have for so long been focused

⁴The electronvolt (eV) is a non-SI unit of energy equal to 1.60217733 × 10⁻¹⁹ J. It is accepted for use with the International System of Units (SI) by the International Committee for Weights and Measures (CIPM).

on the answers that are provided by existing methods. This situation has changed slowly, but we hope the change will continue.

At present, the lighting industry is undergoing somewhat of a revolution in technology. The development of blue, green, and even ultraviolet light-emitting diodes (LEDs) has led to the development of LEDs as general purpose light sources to compete with other traditional technologies like metal-halide, fluorescent, halogen, and incandescent lamps. There are a number of medium- to low-wattage LED lamps on the market that exhibit good luminous efficacy and color rendering. Much of the excitement in the industry and the public arises from the rapid rate of improvement in LED lamps over the last decade and the hope that eventually LEDs can be fabricated to meet any desired performance specification at competitive cost. If that hope becomes reality, LEDs may displace all existing technologies. Although LEDs have already made significant inroads into the lamp market and will probably continue that trend for some time as additional advances occur, a complete displacement of all existing technologies is no closer than a couple of decades and, in our opinion, is not likely to ever happen. The historical lesson in the lighting industry is that the market has always been diverse, matching the diverse performance of various light sources to the exacting requirements of customers. Candles and oil lamps, as an extreme example, are still made and marketed for their ambiance as well as muted illumination.

There is still much that can be learned about high-intensity discharges and metal-halide lamps. X-ray methods have and will continue to play a role in that process. Furthermore, the techniques themselves are not static and will experience development. It is our hope that this chapter encourages more work in this area.

We begin this chapter by discussing metal-halide high-intensity discharge lamps; the motivation for the use of XRIF and x-ray methods in general derives directly from the characteristics of the lamps themselves. An understanding of the physical structure and operational regimes of the lamps will enable an appreciation for many of the points to be made regarding XRIF. This is followed by a review of the atomic physics relevant to understanding how the technique works. Finally, we review applications of XRIF to measurements in operating metal-halide lamps and to the measurement of equilibrium vapor pressures of metal halides in vapor cells.

2. HIGH-INTENSITY DISCHARGES AND METAL-HALIDE LAMPS

High-intensity discharges (HID) are arc-like plasmas formed by a relatively intense concentration of power in a high-pressure vapor (typically the ambient pressure and above). The term is frequently associated with lamps and electroded discharges but rightfully applies to a more general class that also includes some electrodeless radio-frequency excited discharges and other plasma sources not used for lighting. In fact, electrodeless high-intensity discharges found use in atomic spectroscopy (Corliss et al., 1953) before metal-halide lamps became commercially available in the 1960s (Reiling, 1964). More recently, the lighting industry has seen the development and patenting of electrodeless HID lamps (Hochi et al., 2001; Palmer & Lapatovich, 2000; Turner et al., 1997), but they have not yet been developed into widespread products because of limitations on available power electronics.

High-intensity discharges for practical lighting applications include mercury arc lamps, high-pressure sodium (HPS) lamps, and metal-halide lamps. The vapor in all of these lamps is primarily mercury but also includes a lesser amount of a rare gas such as argon, which plays an important role during startup. Mercury arc lamps have no further additives and, as such, are somewhat inefficient and prone to producing a bluish-white light with rather poor color rendering properties. HPS lamps contain sodium metal in addition to mercury, and the rare gas used is xenon. These are very efficient lamps with luminous efficacies of 120–150 lm/W. However, the radiated light is largely from the pressure-broadened wings of the yellow sodium "D" lines. At 589 nm and 590 nm, these lines closely match the peak of the eye sensitivity curve (see Figure 1) near 550 nm, accounting for the high luminous efficacy. The domination of the yellow "D" lines gives HPS lamps poor color rendering (30 to 40) (de Groot & van Vliet, 1986).



Figure 1 The eye sensitivity curve defines the number of lumens produced by 1 W of light at a given wavelength. It represents the response of a human eye to electromagnetic radiation.

Metal-halide lamps are a particular type of high-intensity discharge lamp widely used in general illumination applications where high illumination levels or exceptional color rendering are necessary. These lamps contain, in addition to elemental mercury and a rare gas, some metalhalide salts.⁵ Metal-halide salts are a mechanism for introducing various metals into the discharge for the purpose of improving the luminous efficacy and color rendering of the lamp. Metal-halide salts are used in preference to elemental metals themselves because the vapor pressures of the salts are much higher than that of the metals. This permits the metal-halide lamp to operate at lower temperatures than would otherwise be necessary. The iodide salts are almost exclusively used in electroded lamps because of the limited reactivity of iodine with metal electrode components. In electrodeless lamps, bromides, chlorides, interhalogenated compounds, and oxyhalides may be used since there are no metallic electrodes in the discharge with which to react.

Our work has been focused on metal-halide lamps, and therefore this chapter will be as well. Much of what is discussed, however, may be applied to the broader class of high-intensity discharges. There are a number of excellent general articles on the operation and characteristics of metal-halide lamps (Ingold, 1987; Lister & Waymouth, 2002; Sugiura, 1993; Waymouth, 1971, 1991). A particularly good one is the general review of discharge lamps by Lister et al. (2004). An older article by Dakin et al. (1989) titled "Anatomy of a vertical metal-halide discharge" is also highly recommended.

A schematic of a typical, modern metal-halide lamp appears in Figure 2. The heart of a metal-halide lamp is the ceramic or vitreous silica arc tube. Lamps with the latter are often referred to as quartz lamps. Ceramic arc tubes are almost always constructed of densely sintered alumina grains with an average size between 0.02 mm and 0.05 mm. The sintered material is called polycrystalline alumina (PCA). Its hexagonal crystal structure results in a translucent arc tube. In contrast, vitreous silica makes a transparent glass arc tube. For applications requiring a transparent ceramic arc tube, cubic material such as yttrium oxide or dysprosium oxide may be sintered to transparency (Rhodes & Reid, 1979; Wei et al., 2008).

The arc tube is a sealed vessel, equipped with two opposing electrodes as shown in Figure 2. Before the tube is sealed, it is dosed with several milligrams of mercury, a few milligrams of a combination of metal-halide salts, and approximately 10⁴ Pa of a rare gas. The arc tube is mounted

 $^{^5\}mathrm{Hg}\text{-}free$ metal-halide lamps have been developed and are commercially available but have a much smaller market share than mercury-based metal-halide lamps.



Figure 2 Schematic of a typical low to medium wattage metal-halide high-intensity discharge lamp.

inside a hard glass jacket that absorbs ultraviolet radiation (produced during startup), provides thermal management for the arc tube, and provides some mechanical protection in case of failure of the arc tube. Sometimes, an internal shroud is used in close proximity to the arc tube to provide additional control and safety. The UV starting aid shown in Figure 2 shortens lamp ignition times by producing ultraviolet photons that enter the arc tube and ionize a few rare gas atoms, thus providing the initial electrons for discharge breakdown.

Modern metal-halide lamps are almost entirely driven by electronic ballasts that ignite the discharge with a high-voltage pulse or radiofrequency pulse train and drive the discharge with an audio frequency square wave or modified square wave. Some ballasts employ sinusoidal driving waveforms at a few MHz. The lamps are made and marketed in a wide range of sizes, from 10 W to 10s of kilowatts.

The vapor pressure of mercury at room temperature is a few tenths of a pascal, so if the lamp is ignited under these conditions, the discharge is initially a low pressure Hg glow discharge, much like that in a fluorescent lamp. At low pressure, Hg emits copious amounts of ultraviolet light at 254 and 185 nm (this is the basis for the fluorescent lamp). Ultraviolet protection by the glass jacket is absolutely essential if the lamp is located near people. The voltage across the discharge is relatively low at this point, so the power deposited is not at its full value. Nevertheless, heat from the discharge is sufficient to evaporate additional mercury, thereby increasing the mercury vapor pressure and consequently the power deposited in the discharge. At some point (usually when the mercury pressure is above 10⁵ Pa and at wall temperatures of around 800 K), the diffuse low-pressure discharge will constrict and transition to a high-pressure arc or high-intensity discharge. Before the lamp reaches final operating temperature, the mercury is typically completely evaporated, with final pressures in the arc tube in the range of a few or more times atmospheric pressure, depending on the lamp design. As the temperature continues to increase (>900 K), the arc tube becomes hot enough to raise the metalhalide vapor pressures to significant levels. The metal-halide molecules evaporate from the solid or liquid salt and diffuse into the discharge. The introduction of the metal-halide salts into the arc stream alters the discharge in many ways. The average ionization energy of the plasma species decreases, and the plasma core temperature drops. This results in reduced heat flux to the wall, and the arc tube temperature begins to level off. The cold spot, or cold zone, temperature reaches a steady state at approximately 1200 K. More importantly, the radiation output increases (more electrical power is converted to light and less into heat) and the color changes from the "blue-white" characteristic of mercury to a more pleasing "warm-white" with greatly improved color rendering as radiation from the metal additives fills out the spectrum.

Electric power is deposited along the axis of the lamp, between the electrode tips, where the electrical conductivity is highest. This establishes a radial temperature gradient in the approximately cylindrical lamp geometry as the input power is partitioned between thermal energy and radiation that escapes the lamp. In warmer regions of the discharge, salt molecules are dissociated to varying degrees. In the core of the arc, where temperatures are the highest (\leq 5300 K), the molecules are completely dissociated, releasing metal atoms into the vapor. Temperatures are even high enough to ionize a large fraction of the metal atoms. Those free metal atoms and their ions are largely responsible for the high luminous efficacies and excellent color rendering characteristic of metal-halide lamps.

Specific metals are used in the salts because of their strong emission in the visible range of the spectrum. Some common examples of metal-halide salts appearing in commercial lamps are given in Table 1. The rare-earth elements are prominently represented because they have rich visible spectra. Dysprosium, holmium, thulium, and scandium have been widely used for at least a couple of decades. More recently, cerium has produced dramatic improvements in luminous efficacies. A number of one- or twoelectron type atoms such as sodium, cesium, calcium, and indium are also used. These atoms tend to have strong resonance transitions as opposed to the complex spectra of the rare earths. Typically, a combination of these salts is used in a given lamp to optimize luminous efficacy and color rendering or produce a certain color temperature. The operation of a lamp depends strongly on the vapor pressures of the salts. These vapor pressures are often strongly modified by the presence of other salts in the melt

Metal-Halide Salt	Comments
NaI	Resonance emission near peak of eye sensitivity curve; improves efficacy; reduces core temperature.
DyI ₃	Multiline atomic spectrum and molecular continuum; improves efficacy and color rendering; reduces core temperature.
HoI ₃	Multiline atomic spectrum and molecular continuum; adjusts color temperature; improves efficacy.
TmI ₃	Multiline atomic spectrum and molecular continuum; adjusts color temperature; improves efficacy.
CeI ₃	Multiline atomic spectrum and molecular continuum; dramatically improves efficacy and color rendering.
CaI ₂	Dilution agent and filler; adjusts viscosity of liquid fill.
ZnI_2	Alternative to Hg for high electrical impedance.

Table 1Some common metal-halide salts used in metal-halide lamps and commentson their function.

and in the vapor phase. Formation of complexes (weakly-bound combinations of molecules) between different metal halides in the vapor phase can increase the vapor pressures of some salts sufficiently to improve spectral output or modify temporal behavior (warm-up time) of the lamp.

The temperature in the core of the discharge in a metal-halide lamp is in the same range as the photosphere of the Sun: 4500-6000 K, with the lower end being more typical of lamps having a high alkali content. Moving outside the core, into the mantle of the discharge, temperatures decrease rapidly-approximately quadratically-and the lamp geometry is chosen so that temperatures at the wall do not exceed the capability of the arc tube while it is under the extreme pressures produced by the mercury vapor. For polycrystalline alumina (PCA) arc tubes, the maximum wall temperature is about 1300 K. For fused quartz, it is only 1120 K. In a vertically operating lamp, the metal-halide salts eventually accumulate in the coolest parts of the arc tube, usually in a lower corner, or in the sealing area where the electrode enters the arc tube. The liquid salts are viscous and wet the interior surface of the arc tube but have a consistency more like honey. Droplets of salt can adhere to regions of the arc tube and resist gravity. The lamps are symmetrical with respect to the geometrical equator, so the colder areas near the lower electrode are replicated near the upper electrode seal region despite internal convection. The notion of a cold *spot* is too simplistic as the salts are always observed to cover a substantial area within the arc tube. The salts reside in a cold zone with a distribution of temperatures. Consequently salts are frequently observed in the upper and lower portions of the arc tube, although gravity tends to pool the salts in the lower part of the tube. Temperatures in the cold

zones are typically in the range of 1020–1200 K. The highest cold zone temperature determines the vapor pressures of the metal-halide salts in the surrounding volume. If the lamp were in complete equilibrium, these vapor pressures would be a constant throughout. Plasma and hydrodynamic effects frequently conspire to produce spatially dependent vapor pressures, as well as differences between various metals. The latter phenomenon is referred to as demixing and is almost always detrimental to the operation of the lamp.

Mercury, being at high pressure, is the most abundant constituent in the metal-halide arc. However, it produces only a small fraction of the radiation because temperatures in the core are too low to excite the resonance levels of mercury. The role of mercury is to increase the electrical and thermal resistivities of the arc. A large electrical resistivity makes it possible to dissipate a high level of power in the arc without increasing current. Mercury's relatively large electron impact momentum transfer cross section enhances the electrical resistance of the arc. The large cross section also facilitates equilibration of kinetic energy between heavy particles and electrons. Although some work has shown a modest divergence of electron and heavy particle temperatures (Elloumi et al., 1999; Karabourniotis, 2002, and references therein) in some regions of metal-halide arcs, the massive particles can be considered to be in local thermal equilibrium with each other. Mercury's low thermal conductivity reduces thermal transport across the large thermal gradients between the core and the arc tube wall, thereby reducing a significant power loss mechanism.

An essential aspect of metal-halide lamp design is the regenerative halogen cycle. This cycle begins with a parent molecule, e.g., DyI_3 , being vaporized from a liquid condensate in the cold zone and entering the discharge; as the molecule diffuses into warmer regions of the arc, the molecule dissociates to varying degrees; in the core of the arc, where temperatures are highest, the metal atom is completely liberated and may even be ionized; the metal atoms and ions are excited to radiating states by collisions with electrons and subsequently produce radiation. When the metal atom migrates to cooler regions, it recombines with halogen atoms; if a reassembled parent molecule comes in contact with a liquid condensate, it may recondense back into the liquid, ready to begin the cycle again.

Recombination near the wall is assisted by the high density of neutral Hg atoms, which act as collision partners to absorb the binding energy of the forming polyatoms. The latter is often viewed as an effective increase of radial thermal conductivity in the mantle. The halogen, after dissociation, rarely participates in the radiation process since its excitation potential is generally similar to or greater than that of Hg.

The halogen cycle is essential to the lifetime of metal-halide lamps. Processes that interrupt this regeneration can drastically reduce life and performance. For example, reactions of electrode components with dissociated halogens remove halogens from the vapor and produce a metal–rich plasma. If the metal cannot find halogen partners with which to recombine, it will condense on the arc tube wall. The temperature of the wall is insufficient to vaporize the pure metals, and these atoms are forever lost to the discharge. The presence of rare-earth metals on the alumina surface may precipitate formation of rare-earth aluminates, reducing the lifetime of the arc tube. Continued sequestering of halogens eventually depletes the discharge of metals entirely. Iodide salts are commonly used since iodine is the least reactive of the halogens.

The high pressures in metal-halide arcs lead to a high degree of radiation trapping in some regions of the spectrum. When the vapor is optically thick in a given wavelength range and local spatial volume, the radiation field equilibrates with the massive particles. This leads to radiation levels that saturate at the blackbody curve of the local vapor temperature. This is particularly true in the wavelength range surrounding the 254-nm resonance line of Hg, for which the mean free path is on the order of microns. Radiation emitted by the lamp in this range can only come from the very edge of the arc, but the temperature there is too low to allow any significant blackbody emission. Thus, ultraviolet radiation is greatly suppressed. This effect occurs to lesser extent in other regions of the spectrum, depending on the constituents of the vapor. Infrared radiation losses are not as effectively suppressed by optical opacity because the infrared blackbody limit is less severe than the ultraviolet limit.

3. WHY X-RAY METHODS?

The development and use of optical diagnostics to study high-intensity discharge lamps have been long and successful (see Lister et al., 2004 for a review). The reasons for this are quite obvious. The metal atoms in the discharge are chosen specifically because they and their singly-charged ions have radiative transitions in the visible range of the optical spectrum, and conditions in the discharge are engineered to maximize excitation of those transitions. Atoms, ions, and molecules of other species are also active in the optical range and may exhibit strong emission or absorption of optical radiation.

Optical emission spectroscopy has been used to confirm the presence or absence of particular species, obtain discharge temperatures (Herd & Lawler, 2007; Karabourniotis, 1986; Schneidenbach & Franke, 2008), and even measure Hg densities (Lawler, 2004). Excitation of optical transitions with an external continuum source (Bonvallet & Lawler, 2003) or a laser (Beks et al., 2008) has been used to measure densities and distributions of particular species. Many other optical measurements can be found in the literature.

It will become clear in the following pages that x-ray techniques require a somewhat different set of knowledge than the optical methods cited earlier and also require equipment that is not normally present in the laboratory of a lighting scientist. In fact, for XRIF, one has the additional burden of applying for beam time and conducting an experiment at a remote facility in order to access synchrotron radiation. Given these hurdles, one might be led to ask the question "Why is it useful to go to such lengths?"

The primary motivations for the use of x-ray diagnostics to study high-intensity discharge lamps arise from the nature of the lamps themselves and the impediments the lamps raise to traditional methods. Most HID lamps are relatively small. They contain the high-intensity discharge inside a sealed arc tube that is made of translucent PCA or fused silica that is generally not of optical quality; optical access is limited by the strong curvature and optical defects of the arc tube, with practically no spatial resolution being possible in PCA arc tubes, which are translucent. The sharp gradients in temperature restrict optical emission to the core of the arc where temperatures are sufficiently high; the mantle of the discharge is largely dark.

The need to "see through" the translucent PCA of most modern metalhalide lamps while still maintaining good spatial resolution is a strong motivation for the use of x rays. X-ray methods have also proved very capable in quartz arc lamps. In fact, it is possible to pull an arbitrary metal-halide lamp off a store shelf and make excellent x-ray measurements without the need for any modifications to the lamp. This makes it possible to study and learn about real lamps, not just model lamps. This is possible because high-energy x rays can penetrate both the glass jacket and arc tube with only a small amount of scattering and no additional deformation of the x-ray beam.

As will be discussed in the following section, x rays are used to probe inner shell electrons, electrons whose quantum states are not much perturbed by external conditions, such as valence excitation or binding with other atoms in a molecule. As an important consequence, x-ray techniques can be used to measure and understand what is happening in all regions of the arc, even in the dark regions where little optical excitation occurs; they are spatially comprehensive diagnostics.

A third important motivation follows from the preceding discussion: x rays are not just another way to measure the same parameters that traditional methods might be used to measure if not impeded by the limitations cited earlier. Instead of measuring the density of a particular valence level of a particular molecular species, both x-ray absorption and x-ray induced fluorescence measure the number densities of specific

nuclei (mercury, dysprosium, iodine, etc.). This is particularly useful for measuring metal additives in metal-halide lamps where the metal may be distributed over many molecular and atomic species. X-ray induced fluorescence is complementary to optical spectroscopy in this regard.

4. INTERACTION OF X RAYS WITH ATOMS

All of the optical methods discussed in the preceding section are based on interactions between radiation and valence electrons with binding energies of a few electronvolts or less. In contrast, the x-ray methods discussed in this chapter are based on the interaction of high-energy radiation with core electrons; electrons whose binding energies are several thousand electon volts and higher! This fact has two important, and favorable, consequences for the study of metal-halide lamps. First, the photon energies are orders of magnitude greater than anything produced by the high-intensity discharge. Thus, the isolation of the x-ray signal from the intense optical radiation produced by the discharge and from the noise of the thermal background is excellent. Second, the problem of translucent or poor optical quality arc tubes is avoided. Although scattering of highenergy x rays does occur, such interactions are much weaker than optical refraction. This enables x-ray methods to achieve good spatial resolution in lamps with translucent PCA or fused quartz arc tubes of poor optical quality.

There are three principal types of interactions between x rays and atoms that are relevant to the work described in this chapter. All of them involve interactions with the electrons orbiting atoms. They are photoelectric absorption, Compton scattering, and coherent scattering. The basis of XRIF is photoelectric absorption, but Compton and coherent scattering also have an impact on measurements. All three of these processes will be described in more detail in this section.

Figure 3 is a spectroscopic energy level diagram that may be used to visualize excitation of core electrons. Potassium is chosen as an example because it is simpler than, though not qualitatively different from, the heavier atoms that are typically of interest in metal-halide lamps. At the very bottom of the diagram is the ground level, corresponding to the lowest electronic energy levels filled by the 19 atomic electrons of the neutral potassium atom. This ground level and the bound valence levels (short horizontal lines in the expanded diagram) between it and the $4s_{1/2}$ ionization limit at 4.3 eV form the traditional level diagram of optical spectroscopy. These levels are excited when a valence orbital is occupied by the electron initially in the $4s_{1/2}$ orbital. The 4s ionization limit, on the other hand, corresponds to the energy required to eject the 4s electron from the atom. All of the levels between the ground level and the 4s level



Figure 3 Excited levels of the potassium atom, whose ground configuration is $1s^22s^22p^63s^23p^64s$, arising from excitation of a bound electron. The wide lines are ionization energies for each of the bound electrons; the initial orbital is given on the right of each line and the ionization energy in electronvolts is given on the left. It is also possible to excite one of the electrons to a valence orbital; these are indicated in the expanded view on the left of the figure by short lines; they are too close to the ionization limits to be visible on the right. Excitation of any of the levels above the 4s limit corresponds to an empty core orbital. (Deslattes et al., 2003; Ralchenko et al., 2010; Thompson et al., 2001).

correspond to an empty 4s orbital. The next higher set of levels is qualitatively similar in appearance and corresponds to excitation or ionization, not of the 4s electron, but of a $3p_{3/2}$ electron. All of these levels correspond to an empty $3p_{3/2}$ orbital.

Above the 4s and $3p_{3/2}$ ionization limits lie additional, similar sets of energy levels that correspond to single excitation of the other core electrons that lie increasingly deeper in the Coulomb potential of the nucleus. Other core orbitals in the potassium atom include $3p_{1/2}$, $3s_{1/2}$, $2p_{3/2}$, $2p_{1/2}$, $2s_{1/2}$, and $1s_{1/2}$. Values of n = 1, 2, 3, ... are often referred to by the letters

 K, L, M, \ldots , and excitation of one of the two $1s_{1/2}$ electrons is referred to as K-shell excitation. Excitation of closely spaced levels just below the ionization limits (short horizontal lines in the expanded diagram) produces the near-edge fine structure observed in some x-ray spectra.

The levels in Figure 3 can be excited by sufficiently energetic photons or by impact with sufficiently energetic massive particles. The former process is referred to as photoelectric absorption. The photon is annihilated and any excess energy is imparted to the ejected electron. Figure 4 gives the photoabsorption cross section σ for dysprosium as a function of photon energy *E*. The general dependence of the cross section on energy follows from some of the principles already discussed. Discontinuous jumps in the cross section occur at the minimum (threshold) energy required to eject an inner shell electron from the atom. Edges due to the three nondegenerate orbitals of the L-shell ($L_1 \leftrightarrow 2s_{1/2}$, $L_2 \leftrightarrow 2p_{1/2}$, $L_3 \leftrightarrow 2p_{3/2}$) are visible. The K-shell presents only one edge corresponding to the two degenerate $1s_{1/2}$ orbitals. Not visible in this graph is the fine structure just below each threshold energy that corresponds to excitation of a core electron to a valence orbital.

The photoabsorption cross section decreases relatively slowly with energy ($\sim E^{-7/2}$) above each threshold because the electron is ejected into



Figure 4 Cross sections for photoabsorption (-), coherent scattering (-), and Compton scattering (\cdots) of high energy photons by a dysprosium atom as a function of photon energy. The L_i-edges (i = 1, 2, 3) and K-edge in photoabsorption are noted. (Berger et al., 1998).

the continuum and can absorb any excess energy. This slow falloff has the effect that a monochromatic beam of x rays can simultaneously excite a large number of atoms and transitions, provided the photon energy is above the corresponding edges. Thus, several species can be observed simultaneously with XRIF.

The curve in Figure 4 gives the total cross section for photoabsorption. For photon energies above the K-shell threshold, this includes the cross section for absorption by all the other shells as well. The ratio of the K-shell cross section to that for all other shells is approximately independent of energy and may be determined at the K-edge.

All of the levels above the 4s ionization limit correspond to creation of an empty orbital, or hole, in the core. These levels will typically relax spontaneously to the 4s ionization limit, the ground level of the singly charged ion. The hole in the core is filled by some combination of three major processes that rearrange the remaining bound electrons. These processes are spontaneous radiative relaxation, Auger decay, and the Koster–Kronig process. The relative importance of these three processes is determined by the atomic number of the atom and the principal quantum number (n) of the excited level. Only the first of these, radiative decay, is of interest here because it is the process that produces characteristic fluorescence and is the basis of x-ray induced fluorescence.

Figure 5 shows the energy level diagram for dysprosium with the major radiative transitions from an excited K-shell, along with the traditional notation for the various lines. The radiative transitions involving core orbitals are subject to the same selection rules as optical transitions, so the most probable decay paths are electric-dipole transitions, i.e., transitions for which $\Delta l = \pm 1$ and $\Delta j = \pm 0, 1$. Thus, radiative decay from the 1s level is dominated by transitions to $np_{1/2,3/2}$ levels. Overlap of the orbitals is also a factor in the strength of transitions, so $\Delta n = 1$ transitions are stronger than the corresponding $\Delta n > 1$ transitions. The $K\alpha_1$ line is stronger than the $K\alpha_2$ line because the degeneracy g = 2j + 1 of the $3p_{3/2}$ level is greater than that of the $3p_{1/2}$ level. (Since excitation of levels in this diagram corresponds to a hole in the indicated orbital, the initial level for the electron involved in spontaneous decay is the lower level.)

The probability that a core-shell excitation will decay radiatively is referred to as the fluorescence yield. Figure 6 shows that the K-shell fluorescence yield *Y* increases with atomic number *Z* and for atoms heavier than Z = 55, Y > 0.9. The relative probabilities of the different radiative transitions originating in a given level are referred to as branching fractions. Branching fractions for major K-shell lines as a function of atomic number are given in Figure 7.

Photoabsorption involving K-shell electrons in heavy elements is only weakly affected by the valence electron(s). The so-called chemical effects



Figure 5 Radiative electric-dipole transitions from a K-shell excited dysprosium atom. (Deslattes et al., 2003).

(arising from molecular bonding) typically affect the absorption cross sections only near edges, where virtual transitions to valence states can have a noticeable influence. Observation of near-edge structure, and shifts in this structure due to molecular bonding and ionization of the valence electron, typically requires spectral resolutions of order 1 eV or better. The work described here has employed a much coarser energy resolution ($\approx 100 \, \text{eV}$) and has avoided absorption edges.

The considerations in the preceding paragraph lead to a very important point regarding the densities measured by XRIF. Since the inner shell processes are not significantly influenced by chemical bonding or ionization, XRIF is proportional to the density of atoms of a particular atomic number *Z*, regardless of the range of chemical states in which those atoms



Figure 6 K-shell fluorescence yield as a function of atomic number. (Krause, 1979).



Figure 7 Branching fractions for K-shell fluorescence lines η as a function of atomic number: $\eta = \alpha_1$ (-), $\eta = \alpha_2$ (- -), and $\eta = \beta = \sum_i \beta_i$ (· · ·). (Salem et al., 1974).

may find themselves! Thus, our measured densities $n_{\Sigma Z}$ are summations over all molecular and ionic species *M* that contain an atom of atomic number *Z*,

$$n_{\Sigma Z} = \sum_{i} c_{Zi} M_i \tag{1}$$

where c_{Zi} is the relevant stoichiometric coefficient. The $n_{\Sigma Z}$ are sometimes referred to as elemental densities, and for clarity, we usually replace the subscript *Z* with the one- or two-letter symbol for the element.

Coherent scattering and Compton scattering are generally of no significance for the atoms we are interested in observing with XRIF. However, scattering from the solid arc tube can be important. First, scattering causes a small, but finite, reduction in the transmission of x rays through the arc tube. Second, scattering from the arc tube into the detector can easily overwhelm the fluorescence signal being observed. This occurs because the density of the arc tube is many orders of magnitude higher than the vapor densities in the arc.

Compton scattering describes the interaction between a high-energy photon and a free electron. Electrons bound to an atom can react as free electrons to some extent if the photon energy is greater than the electron binding energy. Compton scattering is typically more of a problem than coherent scattering. The Compton cross section is generally larger and the shift in photon energy that accompanies Compton scattering often leads to interference between scattered photons and fluorescence lines in the observed spectrum.

Considering only the conservation of momentum and energy during the relativistic interaction between a high-energy photon and a free electron, it is relatively easy to derive the scattered photon energy E_f as a function of the scattering angle θ and the incident energy E_0 ,

$$E_f = \frac{E_0}{1 + \alpha (1 - \cos \theta)} \tag{2}$$

where $\alpha = E_0/m_0c^2$ is the ratio of the incident photon energy to the electron rest energy. This shows that the change in energy is small when the photon energy is relatively small compared with the electron rest energy of approximately 500 keV. A more complete treatment of the photon–electron interaction including the electric field of the photon leads to the Klein–Nishina formula for the cross section for Compton scattering of polarized radiation by a free electron (Evans, 1958). Additionally, the bound electrons of an atom react as free electron's binding energy. The binding energy has a small effect on the energy shift, but the cross section can be modified considerably. In addition, the kinetic energy of the bound electrons broadens the energy distribution of scattered photons. The effect of binding energy on the cross section must be calculated separately for each type of atom and is accounted for by multiplying the Klein–Nishina result with the incoherent scattering function *S*(θ) (Hubbell et al., 1975).

The differential Compton cross section then has the form

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega} = \left(\frac{r_{\mathrm{e}}}{1+\alpha(1-\cos\theta)}\right)^2 \left[1-\sin^2\theta\cos^2\phi + \frac{\alpha^2}{2}\cdot\frac{(1-\cos\theta)^2}{1+\alpha(1-\cos\theta)}\right] S(E,\theta)$$
(3)

where r_e is the classical electron radius, ϕ is the azimuthal angle about the incident photon wave vector with $\phi = 0$ parallel to the direction of polarization, and $d\Omega = \sin \theta \ d\theta \ d\phi$ is the differential solid angle. A surprising result is that the cross section does not go to zero along the direction of polarization, although it is a minimum.

Figure 8 gives the total Compton cross section for an Al_2O_3 unit cell as a function of incident photon energy. For photon energies greater than about 45 keV, Compton scattering is the dominant interaction. At approximately 3×10^{-23} cm², the Compton cross section for PCA is about two orders of magnitude smaller than the photoabsorption cross section for Dy. However, the density of PCA (and of fused quartz) is about five orders of magnitude larger than the vapor densities of interest. As a result, Compton scattering from arc tubes and vapor cells can have greater intensity than fluorescence if it is not minimized by an appropriate detection geometry.



Figure 8 Cross sections for photoabsorption (-), coherent scattering (-), and Compton scattering (\cdots) of high-energy photons from a unit cell of Al₂O₃ as a function of photon energy. (Berger et al., 1998).

Coherent scattering describes the correlated response of atomic electrons to an electromagnetic wave. As photon energy becomes comparable to and exceeds the binding energy of an electron, that electron ceases to contribute to the coherent response, so coherent cross sections decrease with photon energy. In addition, there is no significant shift in energy of the scattered photon. Cross sections for coherent scattering from dysprosium and PCA are given in Figures 4 and 8, respectively.

5. X-RAY INDUCED FLUORESCENCE SPECTROSCOPY (XRIF)

5.1 Density Measurements

X-ray induced fluorescence measurement of vapor-phase densities in metal-halide lamps was first attempted by Fohl et al. (1993). They reported having successfully measured iodine fluorescence signals, but they did not report iodine densities. Fohl et al. did not use photon energies high enough to detect the lanthanide rare-earth metals. The first reported densities measured with XRIF in a metal-halide lamp did not come until 2001 (Curry et al., 2001). Since then, XRIF has been used to measure densities of metal additives, iodine, and Hg in operating metal-halide lamps (Curry et al., 2003a,b; Nimalasuriya et al., 2007). More recently, XRIF has been used to measure equilibrium vapor pressures of metal-halide salts in vapor cells (Curry et al., 2011). All of this work has involved lighting industry scientists, including work done as part of the two Electric Power Research Institute-sponsored ALITE consortia that existed between 1995 and 2005 (ALITE, 2006). All of the cited measurements, except those by Fohl et al., were conducted at the Advanced Photon Source, Argonne National Laboratory because of the ideal source parameters that are available on Beamline 1-ID.

Beamline 1-ID combines an undulator and Si crystal double monochromator (Shastri et al., 2002) to produce a laser-like x-ray beam with high intensity, narrow bandwidth, wide tunability, low divergence, and small size. The beam photon energy can be tuned anywhere in the range between 50 keV and 130 keV with an energy resolving power of better than 600. A typical photon flux at the experiment is $\Phi = 10^{12} \text{ s}^{-1}$ with horizontal and vertical divergences of $\leq 10 \,\mu$ rad.⁶ Without focusing, the beam cross section is approximately 1 mm by 1 mm and polarization is >95% in the horizontal plane. The tunability of the beam photon energy makes it possible to observe atoms as heavy as thallium (90 keV) or to maximize the absorption cross section of lighter elements with photon energies as low as 50 keV.

 $^{^{6}}$ A 60 keV photon flux of 10^{12} s⁻¹ gives an average beam power of approximately 10 mW.



Figure 9 Apparatus for x-ray induced fluorescence measurements in a high-intensity discharge lamp, including a pair of crossed tungsten slits (S) and apertures (A_1 and A_2) defining the field of view of the detector. The coordinate system used in this chapter is also defined.

The tabletop arrangement for an XRIF measurement of densities in a metal-halide lamp is shown in Figure 9. A pair of crossed, electronicallyadjustable tungsten slits (S) is used to eliminate any halo around the beam and can be used to reduce the beam size. (Halos arise from scattering by air molecules and windows, as well as imperfections in beamline optics.) Next, an atmospheric pressure nitrogen ionization chamber measures the photon flux transmitted by the slits. A small number of photons transiting the ionization chamber are absorbed or scattered by the nitrogen atoms, creating electron-ion pairs in the gas. A pair of electrodes collects the resulting current, which can be calibrated to determine absolute fluxes. Immediately following the ionization chamber is the test lamp, mounted on a five-dimensional translation stage that allows the lamp to be moved in the three orthogonal linear dimensions, as well as rotation around the two horizontal axes. Rotation is sometimes required to improve the vertical alignment of the lamp and arc tube.

The fluorescence signal induced by the x-ray beam in the lamp discharge is observed by a solid-state Ge detector. The detector consists of a cryogenically cooled Ge crystal across which a voltage is applied. When a photon is absorbed by the crystal, the electrodes collect the charge pairs created by the deposited energy and the resulting current pulse is amplified and fed to a pulse height analyzer. Ideally, the pulse height is proportional to the energy of the absorbed photon. By processing a number of sequentially absorbed photons, a spectrum is constructed count-by-count. The energy scale for such a spectrum must be determined independently. ¹⁰⁹Cd, which produces an 88-keV γ ray and Ag characteristic x-ray fluorescence between 22 keV and 25 keV, has proved useful for this purpose.

Ge detectors typically have a flat response curve for a range of energies that extend from below 10 keV to about 90 keV, depending on the specific detector being used. The low energy cutoff is determined by the transmission of the window in front of the crystal, usually beryllium, sometimes polyimide. The detector response at high energy begins to decrease when the mean free path for photoelectric absorption becomes comparable to the crystal, and photons have a finite probability of passing through the crystal without interaction. A thicker crystal can extend this range but also reduce the maximum count rate because it increases the "dead time," or time required to collect the charge created by a photon. Dark current is greatly reduced by keeping the crystal at cryogenic temperatures.

Limitations of a finite crystal size, a finite pulse processing time, and crystal imperfections lead to spectral artifacts, limited spectral resolution, and noise (Knoll, 2000). Sometimes, so-called escape peaks can be seen in fluorescence spectra, and care must be taken to avoid misidentification. Escape peaks are created when some of the energy of the absorbed photon escapes the crystal as Ge K-shell fluorescence. A count is registered at an energy equal to the difference between the absorbed photon energy and the Ge fluorescence energy, instead of the absorbed photon energy. Pulse processing time is adjustable, with longer times producing better energy resolution but longer dead times. For high count rates, corrections must be made to account for dead time (Knoll, 2000). A typical energy resolution is a couple of hundred electronvolts.

The Ge detector is aligned to observe fluorescence emitted along the direction of polarization of the beam. This orientation suppresses scattering from the vapor into the detector. The detector's field of view is defined by two apertures, one at the detector and one close to the lamp. The detector aperture is formed by a pair of crossed, adjustable tungsten slits, typically open several millimeters wide. The lamp aperture is placed as close to the beam as possible, allowing just enough room for the lamp over its full range of movement. This aperture is typically a submillimeter circular hole in a 2-mm-thick tungsten plate. Because the lamp aperture is much smaller than the detector aperture, the field of view of the detector can be approximated as a projection of the detector aperture through the pinhole of the lamp aperture. This projection is shown in Figure 10 for some typical dimensions. The intersection of the field of view with the beam determines what will be referred to as the viewing volume, i.e., the volume from which fluorescence is collected by the detector. Typically, this volume is approximately 1 mm by 1 mm by 1 mm, although it has been



Figure 10 Fluorescence collection optics and x-ray beam. The detector (represented by a circle) sits to the right of A_2 . The field of view of the detector can be approximated by projecting A_2 back through the pinhole A_1 . The intersection of the field of view with the x-ray beam determines the viewing volume *V*, the region of space from which XRIF is observed by the detector.



Figure 11 Fluorescence spectra acquired from a metal-halide lamp with different beam photon energies.

substantially less on occasion because of a smaller beam size. Obviously, the axis of the field of view must be aligned to intersect the beam. Spatially resolved XRIF spectra are obtained by step scanning an operating lamp in the x - y plane.

A few typical spectra are shown in Figure 11 for beam photon energies of 60 keV, 70 keV, 81 keV, and 85 keV. The data were acquired from a lamp containing Hg, DyI₃, and CsI (Curry et al., 2003b). In all the spectra, narrow fluorescence lines from I and Dy are seen. In the spectrum excited by 85 keV, very strong fluorescence lines from Hg are also present. The Hg K-edge occurs at 83.102 keV; the lower beam energies are insufficient to excite Hg. The considerably larger magnitude of Hg fluorescence relative to Dy and I is mostly due to the much greater abundance of Hg, 2 to 3 orders of magnitude greater than I. Additionally, the photoabsorption cross section for Hg is about 4 times larger than that for I. Not labeled, but also present in each spectrum are fluorescence lines from Cs. The *K* α lines for Cs appear between the I *K* α and I *K* β peaks and are most apparent in the spectrum excited by 60-keV photons. All of these fluorescence lines appear at the same energy regardless of the excitation energy. Weak escape peaks originating from the Hg *K* α lines appear near 59 and 61 keV, the energies of Hg *K* α_1 and *K* α_2 minus the energies of Ge *K* α_1 and *K* α_2 .

Scattered photons are also apparent in each of the spectra. The narrow peaks at each of the beam photon energies are due to coherent scattering. The broad, multipeaked features that extend over many kilo-electronvolts are the result of Compton scattering from the arc tube. Figure 12 shows a cross section of the arc tube cylinder and the four possible paths by which photons can scatter into the detector with only two scattering events. (Single Compton scattering from the arc tube into the detector cannot occur because the field of view, beam, and arc tube do not all overlap at



Figure 12 The four possible paths involving double scattering from a cylindrical arc tube that can lead to a beam photon entering the detector.

any point in space.) One path involves scattering from point A through angle θ_1 followed by scattering from point B through angle θ_2 ; another from point A through θ_3 followed at point D through θ_4 ; another from points C and B through θ_5 and θ_6 , respectively; and the last from points C and D through θ_7 and θ_8 , respectively. The final photon energy after such sequential scatters is

$$E_{ij} = \frac{E_0}{\left[1 + \alpha (1 - \cos \theta_i)\right] \left[1 + \alpha (1 - \cos \theta_j)\right]}$$
(4)

where the cosines of each of the eight angles, as well as *x* and *R*, are defined in Figure 12. Thus,

$\cos \theta_1 =$	$\frac{1}{\sqrt{2}}\sqrt{(1-\rho)}$	
$\cos\theta_2 =$	$-\frac{1}{\sqrt{2}}\sqrt{(1+\rho)}$	
$\cos\theta_3 =$	$\frac{1}{\sqrt{2}}\sqrt{(1+\rho)} =$	$-\cos\theta_2$
$\cos \theta_4 =$	$\frac{1}{\sqrt{2}}\sqrt{(1-\rho)} =$	$\cos \theta_1$
$\cos \theta_5 =$	$-\frac{1}{\sqrt{2}}\sqrt{(1-\rho)} =$	$-\cos\theta_1$
$\cos \theta_6 =$	$-\frac{1}{\sqrt{2}}\sqrt{(1+\rho)} =$	$\cos\theta_2$
$\cos\theta_7 =$	$-\frac{1}{\sqrt{2}}\sqrt{(1+\rho)} =$	$\cos\theta_2$
$\cos \theta_8 =$	$\frac{1}{\sqrt{2}}\sqrt{(1-\rho)} =$	$\cos \theta_1$

with $\rho = x/R$. Only three Compton peaks are produced because E_{12} and E_{78} are always the same. Figure 13 plots the energies of the 3 peaks for $E_0 = 70 \text{ keV}$ as a function of ρ , and Figure 14 plots the Compton-shifted energies as a function of E_0 for $\rho = 0$. These calculations do not take into account the broadening of the energy distribution of the scattered photons arising from the kinetic energy distribution of the scattering electrons and from the range of possible scattering angles due to the finite field of view of the detector. Figure 11 shows that the Compton peaks are quite broad compared with fluorescence lines, with each Compton peak having a different shape. It can also be seen that increasing the beam energy is not very



Figure 13 Final energies for 70-keV photons doubly scattered from a cylindrical arc tube along the paths shown in Figure 12 as a function of ρ , the distance between the beam and arc axis, normalized by the radius of the arc tube.



Figure 14 Final energies for photons doubly scattered from a cylindrical arc tube along the paths shown in Figure 12 as a function of beam photon energy E_0 for $\rho = 0$, the beam intersecting the arc axis.

effective in reducing interference with fluorescence lines, but just spreads the Compton peaks over a wider spectral range. Fortunately, the breadth of the Compton features is a considerable help in separating scattering from characteristic fluorescence.

The count rate *C* observed by the detector within a given K-shell fluorescence line $K\eta$ is

$$C_{Z}^{\kappa_{\eta}} = \frac{\Phi}{A} \sigma_{Z}^{\kappa}(E_{0}) Y_{Z}^{\kappa} B_{Z}^{\kappa_{\eta}} \frac{\Omega}{4\pi} V T(E_{0}) T(E_{Z}^{\kappa_{\eta}}) Q_{d}(E_{Z}^{\kappa_{\eta}}) n_{\Sigma Z}$$
(5)

where Φ is the incident photon flux, A is the beam cross-sectional area, $\sigma_Z^{\kappa}(E_0)$ is the K-shell photoabsorption cross section for an atom of atomic number Z at the energy of the incident beam photons E_0 , Y^{κ} is the Kshell fluorescence yield, $B^{\kappa_{\eta}}$ is the branching fraction for the K-shell η line, Ω is the solid angle observed by the detector, V is the viewing volume (see Figure 10), T is the transmission of x rays of fluorescence energy $E_Z^{\kappa_{\eta}}$ through the arc tube, or other, wall, Q_d is the detector efficiency, and $n_{\Sigma Z}$ is the number density defined by Equation 1.

Equation (5) allows the determination of elemental densities $n_{\Sigma Z}$ from the intensity of observed fluorescence lines. The values for the atomic parameters σ , Y, and B have been discussed in Section 4. The beam flux density Φ is continuously measured during the experiment by the ionization chambers as the beam passes through them. Transmission of beam and fluorescence photons through the arc tube wall is determined from cross sections of the relevant materials. Transmission through 1 mm of fused silica and transmission through 1 mm of PCA are shown in Figure 15 as a function of energy. Attenuation of beam photons is typically small because their energy is usually greater than 60 keV. Attenuation of fluorescence photons, however, can be more severe and gets larger as the element being observed gets lighter and the fluorescence energy decreases. There is no hard cutoff for what can be observed, but as the fluorescence photon energy decreases, the measurement signal-to-noise ratio decreases. In addition, the correction factor for finite transmission becomes larger and more sensitive to the exact thickness and density of the arc tube or cell wall. It is difficult, in practice, to observe elements with atomic numbers less than Z = 40 inside the types of arc tubes and cells being used and



Figure 15 Transmission through 1 mm of PCA (- -) and fused silica (\dots) as a function of photon energy, not including scattering.

at the densities typical of metal additives in MH-HID lamps. This precludes observation of the important additives sodium and scandium, or the mercury substitute zinc in Hg-free lamps.

The transmission curves in Figure 15 reflect attenuation due to photoabsorption only. An additional attenuation results from coherent and Compton scattering. This component must be calculated for each situation because a significant fraction of scattered photons is scattered at such small angles that the event is irrelevant. The fraction of photons scattering from 1 mm of PCA is shown by the top curve in Figure 16. This is an upper limit on the attenuation due to scattering. The lower curve gives the fraction of photons scattered by Compton scattering only. The atomic form factor concentrates coherent scattering in the forward direction, while the incoherent scattering function goes to zero in the forward direction (Curry, 2010). Consequently, the Compton cross section gives a reasonable first approximation for attenuation by scattering, which is increasingly accurate with increasing energy.

The measured value *C* is the count rate in a fluorescence line. Lineshapes for spectra measured by a Ge detector depend on a number of factors including processing time and photon energy (Knoll, 2000). As a result, *C* may be just as accurately obtained by straight integration as by line fitting if care is taken to integrate over the entire line and to adequately account for the baseline. Figure 17 demonstrates how this can be done using the Dy $K\alpha_1$ and $K\alpha_2$ doublet blended with a Compton feature as an example. The background, including the Compton signal, is determined by fitting a single second-order polynomial to the noncontiguous baseline segments on each side of the fluorescence line. These regions are indicated



Figure 16 Fraction of photons scattered by 1 mm of PCA as a function of photon energy. The top curve includes both Compton and coherent scattering. The bottom curve includes only Compton scattering.



Figure 17 Finding the baseline under Dy $K\alpha$ lines. The thin horizontal lines indicate the ranges over which a second-order polynomial is fit to the baseline on each side of the fluorescence peaks. The thick horizontal line indicates the range over which the spectrum is integrated after the fitted baseline (shown) is subtracted.

in the figure by thin horizontal black lines. Contributions from Compton scattering, as can be seen in Figure 11, change slowly over the width of most fluorescence features. The fitted background is subtracted from the entire spectral region, and the line feature is integrated. The region of integration is shown in the figure by a thick horizontal black line. The regions of integration and baseline fitting can be chosen individually for each line but should remain the same across all spectra. The statistical uncertainty σ_c in the number of counts can be estimated as

$$\sigma_{\rm C} = \sqrt{p \, \sigma_{\rm fit}^2 + q} \tag{6}$$

where *p* is the number of points over which the integration is performed, σ_{fit} is the rms deviation of the data from the fit in the fitting regions, and *q* is the number of counts in the line integral. The first term in the radical is an estimate of the statistical error due to fluctuations in the true baseline, whereas the second term represents shot noise in the line integral. For Figure 17, the measured density is 6.7×10^{15} cm⁻³ and the statistical uncertainty is about 2%. The data were acquired with an integration time of 600 seconds.

The concept of two separable geometric parameters Ω and *V* is only an approximate way of representing geometric effects in Equation (5). In fact, Ω is a complicated function of position and should be integrated over the volume *V*. Nevertheless, one can deal with these parameters in an exact way by comparison of fluorescence signals from a lamp to fluorescence signals from a known standard. Fused silica cells or PCA cells filled with



Figure 18 Schematic of x-ray induced fluorescence measurements in a gas-filled calibration cell.

a comparable density of Xe have proven to be useful for this purpose. The measured lamp is simply replaced by a calibration cell as in Figure 18, and a fluorescence spectrum is acquired in the same manner as for the lamp. A ratio of counts then leads to an absolute density

$$n_{\Sigma Z} = \frac{C_Z^{K\eta}}{C_{Xe}^{K\alpha}} \frac{\Phi_{Xe}}{\Phi_Z} \frac{\sigma_{Xe}^K(E_0)}{\sigma_Z^K(E_0)} \frac{Y_{Xe}^K}{Y_Z^K} \frac{B_{Xe}^{K\alpha}}{B_Z^{K\eta}} \frac{T_{\text{cell}}(E_0)}{T_{\text{lamp}}(E_0)} \frac{T_{\text{cell}}(E_{Xe}^K)}{T_{\text{lamp}}(E_Z^{K\eta})}$$
(7)

if the Xe $K\alpha$ lines are used for calibration and the detector efficiency is flat over the range of energies considered.

Typically, lamp measurements are entirely automated, and the lamp position will be stepped through a predetermined matrix of positions such that the desired spatial range is covered. Once the lamp has settled at each position, data acquisition is triggered and persists for a predetermined period, usually for a period in the range of 10–100 seconds. At the end of this period, a time-integrated spectrum and a time-integrated incident flux are electronically saved along with all other relevant measurement parameters. Though changes in the beam intensity over tens of seconds are generally quite small, any changes that do occur are automatically taken into account because the flux signal and fluorescence signal are integrated simultaneously. Some examples of XRIF measurements of density distributions in a metal-halide lamp appear in Figure 19. These include essentially complete spatial distributions of the principle components of a lamp containing 16 mg of Hg, 6.8 mg of DyI₃, 1.2 mg of CsI, and 12 kPa (90 Torr) of Ar (Curry et al., 2003b). The only component not measured was Ar because the K-shell fluorescence lines of Ar have energies of less than 3.2 keV,



Figure 19 Density distributions measured by XRIF in a metal-halide high-intensity discharge lamp containing 16 mg of Hg, 6.8 mg of Dyl₃, 1.2 mg of CsI, and 12 kPa (90 Torr) of Ar (Curry et al., 2003b). The coordinate system is defined in Figure 9.

too low to be observed through an arc tube. It is worth noting that this lamp was equipped with an outer glass jacket in addition to a translucent ceramic arc tube. The x-ray transmission of the jacket must be taken into account but represents no serious impediment to XRIF measurements.

The measurements in Figure 19 were acquired at the vertices of the grid superposed on the data. The spatial resolution for each measurement was $\Delta x \approx 1$ mm, $\Delta y \approx 1$ mm, and $\Delta z \approx 1$ mm. Measurements were not acquired over the full range of -x because of the assumption of cylindrical symmetry. In the figure, the positions of the electrodes and arc tube walls are shown in blue on the $n_{\Sigma Z} = 0$ plane. The arc tube was operated vertically with the bottom of the arc tube at y = 0 on the right side of each graph. The range of densities measured in this lamp extends from 1×10^{16} to 5×10^{19} cm⁻³.

The density of Hg is the largest of any constituent of the arc, more than an order of magnitude larger than the second most abundant constituent, iodine. Cs has the smallest density of all. Its presence in the arc is primarily to broaden the main current channel. Two properties of Cs help achieve this goal. First, the ionization potential of Cs is lower than that of Dy. Therefore, Cs is ionized at larger radii than Dy. Second, resonance radiation produced by Cs in the core is heavily self-absorbed, thereby heating the vapor by collisional de-excitation wherever atomic Cs exists. Such broadening or fattening of the arc is necessary in lamps containing strong multiline radiators like the rare earths. Metals like Dy are so efficient at producing and emitting radiation that they cool the vapor in the core of the arc. In order to maintain sufficient ionization for a given input power, the volume of the current channel must decrease. If the current channel becomes too thin, magnetic instabilities begin to make the arc precess slowly about the arc axis like a vertical jump rope. Such an effect is highly detrimental to lamp appearance and performance and is avoided by adding a small amount of Cs or a similar resonance radiator.

5.2 Temperature Distributions

The primary contributor to the shapes of the density distributions in Figure 19 is the temperature variation in the arc. As the measurements make clear, Hg is the dominant component. It exists almost completely in monatomic form. Thus, the relationship of the Hg density $n_{\Sigma Hg}$ to the vapor temperature *T* can be described by the Ideal Gas Law

$$p = n_{\Sigma Hg}(\vec{r})kT(\vec{r}) \tag{8}$$

where *p* is the total vapor pressure, \vec{r} is spatial location, and *k* is Boltzmann's constant. Spatial variation does occur in the total vapor pressure, either because of convective flow or in the form of acoustic waves driven

by the alternating current in the arc. Pressure variations associated with convective flows are too small to be of significance in this context (Lowke, 1979; Zollweg, 1978). Pressure variations from acoustic waves are of order 1% and occur at frequencies exceeding 10 kHz (Baumann et al., 2009; Dreeben, 2008). The time-averaged vapor pressure is constant and spatially homogeneous in a normally operating lamp. As a result, the spatially dependent arc temperature may be determined if the Hg density and vapor pressure are both known

$$T(\vec{r}) = \frac{p}{kn_{\Sigma \text{Hg}}(\vec{r})}.$$
(9)

Alternatively, the temperature of core of the arc can be determined from optical emission measurements (Karabourniotis, 1986). The spatially independent vapor pressure is determined from the combination of a local Hg density and the corresponding local temperature. Then, spatially comprehensive temperature maps can be obtained from Hg density distributions. Some examples can be found in Curry et al. (2005) and Curry et al. (1998). Using a design operating pressure of 10⁶ Pa (10 atm), the Hg density shown in Figure 19 is converted to the temperature distribution in Figure 20. Optical determination of core temperatures in ceramic lamps has been discussed in the literature (Karabourniotis & Drakakis, 2002) but was not applied to this lamp.

The density distributions in Figure 19 and the temperature distribution in Figure 20 show that the arc is hottest in the core where the electrical



Figure 20 Temperature distribution derived from the Hg density distribution in Figure 19 using a design operating pressure of 10^6 Pa (≈ 10 atm). The coordinate system is defined in Figure 9.

current provides direct heating of the gas. Somewhat less apparent is the general trend of increasing temperature from bottom to top as the heated gas rises. Within a couple of hundred microns or less of each electrode, the temperature distribution is determined by different factors. The convergence of the current to meet the electrode tip produces a relatively rapid increase in the gas temperature, but the temperature of the tungsten electrode tip itself cannot exceed the melting point of tungsten. These two effects produce a local maximum in excess of 5000 K in front of each electrode, followed by a steep drop to 3683 K or less at the tip. These near-electrode effects are more clearly seen from high-resolution x-ray imaging of the Hg density (Curry et al., 1998) than in the lower resolution XRIF measurements.

Temperatures in the core of the arc are typically in the range of 4500–6000 K, depending on the lamp. Outside the core, the temperature must drop quickly to the maximum operating temperature of the arc tube wall material, 1100–1400 K. The shape of the temperature drop depends greatly on the type and density of radiating species in the core. If radiation trapping is sufficiently large, the temperature distribution becomes fatter and most of the temperature drop occurs in the outer third of the discharge radius. This leads to very large temperature gradients near the wall. Another important area for lamp operation is the area below the bottom electrode. This is often the coolest part of the arc because the cooler, heavier gas sinks to the bottom. The greater densities in this region are clearly seen in the distributions of Figure 19. The metal-halide salts also reside in this region, and the temperatures here determine the equilibrium vapor pressures of the salts.

Temperatures throughout the core of the arc can be obtained directly from optical emission measurements. However, optical emission is of little help for regions outside the core where the temperature is too low to produce significant emission in the visible. Thus, comprehensive temperature maps, as in Figure 20, are practically impossible to obtain by any method other than x rays. Such complete maps are essential to determining and understanding the chemical distribution in the arc. Although the dark region of the lamp contributes no visible radiation to the lamp output and would appear to be of little interest, the molecular species that exist in these regions can have a substantial impact on infrared radiation transport and do play an important role in the transport of metal additives into the core. The latter can be a determining factor in the luminous efficacy and color rendering.

5.3 Chemical Partitioning

As pointed out earlier in this chapter, the densities shown in Figure 19 and those obtained by XRIF are elemental densities, a summation over all atomic and molecular species. In the lamp of Figure 19, there are only five

elements present, the four shown and Ar. What are not shown are the 10 or more significant molecular species into which these elements may combine over the range of temperatures that occur in the lamp. A few of these species may be detected by optical means. Given a temperature distribution, densities of a few more may be inferred from optical measurements. Alternatively, one may infer all of the species densities by combining the elemental densities with the corresponding temperature map. For a system in thermal equilibrium, the partitioning of elements across different species is a function only of the elemental densities present, the equilibrium temperature, and the thermodynamic parameters of all possible atomic and molecular species. Although lamp discharges are not in full equilibrium, a local chemical equilibrium is achieved. The densities of individual molecular species are those that are mutually consistent and minimize the free energy of the system. Those densities can be determined for a given set of input parameters by an iterative calculation (Cruise, 1964). As an example, the chemical distribution for a system containing a Hg number density of 3×10^{19} cm⁻³, a DyI₃ density of 1×10^{17} cm⁻³, and a CsI density of 5×10^{16} cm⁻³ has been calculated as a function of temperature and is shown in Figure 21. The shift from heavy molecular species at the lower temperatures to lighter molecular species at increasing temperatures, then to atoms, and eventually to electrons and ions at the highest temperatures is evident.

In contrast to Figure 21 where the elemental densities are held constant, the elemental densities and temperature in a lamp will be a function of position. An example of the chemical partitioning in a real lamp appears



Figure 21 An example of equilibrium molecular densities as a function of temperature for a system containing a Hg number density of 3×10^{19} cm⁻³, a Dyl₃ number density of 1×10^{17} cm⁻³, and a Csl number density of 5×10^{16} cm⁻³. (Curry et al., 2003a).

in Figure 22 (Curry et al., 2003a). These are the equilibrium molecular densities in the midplane of the arc calculated from the measured elemental densities in Figure 19 and the temperature distribution in Figure 20. This figure illustrates the complexity of the chemistry of a metal-halide high-intensity discharge, even though only the major Dy species are plotted. It is interesting to note the localization of certain molecular species like DyI_2 . Given sufficient atomic data, the radiative output of the discharge could be calculated from the information presented in this graph. Practically, the calculation of radiation production and transport remains a challenge because of the large size of the parameter space and the nonlocal nature of some portion of the radiation transport.

The measurements and calculations behind Figure 22 are a way to determine a comprehensive picture of the chemical distribution in a metalhalide lamp. The weakness of such calculations is the lack of experimental measurements of thermodynamic parameters for many of the species of interest, at least at the temperatures relevant to lamps. Free energies can, in principle, be calculated from basic principles and spectroscopic data in a straightforward way (Chase, 1998). However, the key to accurate results at higher temperatures lies in the appropriate treatment of the lowering of ionization energy for each species. This is where different calculations begin to diverge, and experimental measurements are needed to distinguish the most accurate methods. In Section 5.5, we will discuss the use



Figure 22 Equilibrium molecular densities calculated from measured elemental densities and the inferred temperature distribution in the mid-plane of a metal-halide lamp. The elemental densities are from Figure 19 and the temperature distribution is from Figure 20. The total Dy density (black, \Box) is given along with the major Dy molecular species Dyl₃ (×), Dyl₂ (gray, \Box), Dyl (\circ), Dy (Δ), and Dy⁺(\diamond). Also shown are monatomic I (+) and the negative ion I⁻ (∇) (Curry et al., 2003a). The coordinate system is defined in Figure 9.

of XRIF to measure some of the needed basic thermochemical data. Without experimentally confirmed data, thermochemical calculations can still be useful in clarifying the relative importance of different species and processes.

5.4 Demixing

An interesting phenomenon that can be observed in some metal-halide high-intensity discharge lamps is demixing of the metal additives (Dakin & Shyy, 1989; Fischer, 1976; Stormberg, 1981). The impact of demixing on lamp performance is deleterious. Severe cases that are immediately obvious to any observer may produce color and brightness variations along the length of a lamp (Nimalasuriya et al., 2007). Less severe demixing may not be apparent to the naked eye but still have a negative impact on luminous efficacy and color rendering.

Demixing refers to the segregation of minority constituents to different parts of the discharge. Molecular and atomic species are, of course, segregated simply because certain molecular species are thermodynamically preferred at certain temperatures, and a wide range of temperatures exists within a high-intensity discharge lamp. Demixing is the much more comprehensive spatial segregation of an elemental constituent that extends across all of the atomic and molecular forms in which that element may be found. Thus to observe demixing, the densities across all such species must be measured. It is also necessary to measure the overall density of the vapor because demixing is a relative change in density. Large changes in absolute density are always present for all elements in a high-intensity discharge because of the large range of temperatures. Demixing has a much smaller impact on absolute densities than do temperature variations. The most obvious way of observing demixing is to look at the so-called mixing ratios (Dakin et al., 1989; Shaffner, 1971), that is, the ratios of the elemental densities to the Hg density, the latter being an excellent approximation to the overall vapor density. The mixing ratios are independent of chemical partitioning and of the overall density variation of the vapor. Spatial variations in the mixing ratios represent demixing. XRIF, as discussed already, directly measures the elemental densities required to determine the mixing ratios, something difficult to achieve with other methods.

Mixing ratios for Dy, Cs, and I obtained from the data in Figure 19 are shown in Figure 23. These plots give the radial variations of the mixing ratios in the midplane of the arc, along with the temperature profile (Figure 20). Radial demixing is evident for the metal additives Dy and Cs, being most pronounced for the latter. On and near the discharge axis, the metal atoms have been significantly depleted. A depletion of this kind generally reduces luminous efficacy, simply because there are fewer



Figure 23 Mixing ratios in a ceramic metal-halide lamp for Dy (\triangle), Cs (\circ), and I (\Box), as well as the temperature distribution (\times) obtained from the data in Figure 19 and an estimated lamp pressure of 10⁶ Pa. The ratios have been normalized so that their asymptotic value at the wall is 1. The coordinate system is defined in Figure 9.

radiators present. Outside the core near |x| = 2 mm, there is a relative enhancement in the mixing ratio of both Dy and Cs as compared with the asymptotic value at the wall. I, on the other hand, shows little or no demixing.

The origin of demixing is the differences in diffusion velocities for different atomic and molecular species and the range of temperatures present in a high-intensity discharge. Two principal classes of demixing are referred to as radial demixing and axial demixing. The former involves radial transport velocities, whereas the latter involves both radial and axial (convection) transport.

The radial depletion seen in Figure 23 can be explained by considering the different types of radial transport at work. Considering Dy in Figure 22 near the axis as an example, singly ionized dysprosium Dy⁺ has a density maximum on axis and diffuses away from the axis due to that density gradient. Dy, DyI, and DyI₂ have a minimum on axis and diffuse toward the axis. In steady state, the net transport rate is zero and the inflow of neutral molecules must balance the outflow of the ion

$$\Sigma_i D_i \nabla n_i(\vec{r}) = -D_+ \nabla n_+(\vec{r}) \tag{10}$$

where the summation is over all the neutral particles i, D is the diffusion coefficient, and n_+ is the ion density. If the diffusion coefficients of all species are the same and the spatial dependence of the coefficients is ignored, this leads to

$$n_{\Sigma D y}(r) = n_{\Sigma D y}(0). \tag{11}$$

In other words, the dysprosium elemental density is independent of *r* and there is no demixing.

When the diffusion coefficients are different for different species, the picture changes. The diffusion coefficient for the Dy ion is generally much larger than the coefficients for the neutral particles because of the presence of the radial ambipolar electric field. Such a field arises in finite-sized plasmas in order to balance the loss of positive charge and negative charge. The lighter, more mobile electrons escape at a faster rate than the more massive positive ions, creating a space-charge electric field. The field grows until it is large enough to balance the loss of positive and negative charges by speeding up the loss of positive charges and slowing down the loss of negative charges. When ion and electron temperatures are the same, the ambipolar field has the effect of doubling the diffusion coefficient for positive ions over its value in the absence of a field (Krall & Trivelpiece, 1986).

The larger diffusion coefficient for positive ions increases the transport rate of ions away from the axis resulting in a relative depletion of the elemental density near the axis if an element is ionized there. The solution of Equation (10) is then

$$n_{\Sigma Dy}(r) = n_{\Sigma Dy}(0) + n_{+}(0) - n_{+}(r).$$
(12)

The elemental density of Dy is clearly a function of *r* if $n_+(r)$ is. In addition, it is also clear that the elemental density on axis is less than the elemental density at the wall (r = R)

$$n_{\Sigma \mathrm{Dy}}(R) > n_{\Sigma \mathrm{Dy}}(0) \tag{13}$$

as long as the ion density on axis $n_+(0)$ is greater than the ion density at the wall $n_+(R)$. This simplified analysis does not take into account the change in temperature between the axis and the wall, nor the differences in diffusion coefficients for different molecules, but those effects do not qualitatively change the conclusions drawn.

The extent of ambipolar depletion experienced by an element increases with ion density on axis, with the result that more easily ionized species will see a greater level of demixing. Accordingly, Cs having an ionization potential 35% lower than Dy exhibits a greater level of depletion on axis. Iodine, with an ionization potential 75% larger than Dy, shows very little or no depletion on axis.

Both Dy and Cs, in addition to exhibiting depletion on axis, show a local maximum in their mixing ratios just outside the core of the arc. This feature is not explained by the reasoning in the preceding paragraphs, nor has such a feature been previously observed. Curry et al. (2003a)



Figure 24 Distribution of negative charge corresponding to the densities and temperatures in Figure 23. The coordinate system is defined in Figure 9.

calculated the chemical equilibrium from their measured elemental densities and temperatures and found that the distribution of negative charge was as shown in Figure 24. The negative charge in the core is dominated by electrons, but off axis, where the temperature begins to drop, the negative charge consists primarily of I⁻, negative iodine ions. The iodine ions do not have the light mass of the electrons; their mass is only slightly smaller than that of Dy and Cs ions. Therefore, the ambipolar field must quickly disappear where the negative charge becomes dominated by I⁻, and so must the excess transport that leads to depletion. A detailed explanation of the observed maxima remains to be provided.

Axial demixing involves the radial diffusion mechanisms described earlier but also involves axial convective flow. Axial demixing can often be observed in lamps for which convective and radial diffusion velocities are comparable. A major convective cell that rises along the axis and falls along the arc tube wall circulates the mercury vapor and entrained additives axially. At the same time, radial diffusion transports constituents between the upward and downward flowing parts of the convective cell. If radial transport is faster in the outward direction than the inward, and comparable to convective transport, constituents riding the upward flowing vapor on axis will short-circuit the convective cell by diffusing outward to the downward flowing vapor before they reach the top (see Figure 25). This leads to a steady state in which the constituents subject to strong radial depletion will also show depletion at the top of the arc, whereas elements less subject to radial demixing are relatively more abundant there. Axial demixing is considerably reduced if the convective velocity is either much smaller than or much larger than radial diffusion velocities. Fischer (1976) showed that there is a convective velocity for



Figure 25 Typical convective flow in an HID lamp.



Figure 26 The mixing ratio for Dy in a Dyl₃-Hg metal-halide lamp plotted versus radial coordinate for several axial positions. The percentages given in the key are the percentages of the total distance from the lower electrode to the upper electrode. Data points at each wall are off the scale of the figure. Both radial and axial demixing are apparent. The coordinate system is defined in Figure 9. (Nimalasuriya et al., 2007).

which axial demixing is a maximum. Larger convective velocities reduce, rather than increase, demixing because additives are transported upward faster than they can be transported away from the axis by radial diffusion.

A study of axial demixing was made by Nimalasuriya et al. (2007) using both XRIF to measure elemental densities and laser absorption to obtain distributions of atomic Dy (Flikweert et al., 2005). The XRIF measurements showed clear examples of both radial and axial demixing (Figure 26). In addition, the two complementary diagnostic techniques made it possible to evaluate specific terms in the radial diffusion equation presented there.

5.5 Equilibrium Vapor Pressures

After seeing the capabilities of XRIF in the measurement of metal and iodine densities in metal-halide lamps, Walter Lapatovich (then of OSRAM SYLVANIA INC) suggested that XRIF might be a solution to the longstanding problem of obtaining accurate measurements of the equilibrium vapor pressures of metal-halide salts. By "equilibrium vapor pressure," we mean the pressure that equilibrates with a solid or liquid condensate when the vapor and condensate are in a closed system in full thermodynamic equilibrium. Although the observations of demixing, discussed already, make clear that actual vapor pressures in metal-halide lamps are not everywhere in equilibrium with a condensate, those pressures are a strong function of the equilibrium vapor pressures of the salts. Ab initio numerical modeling of metal-halide lamps must incorporate reasonably accurate values for equilibrium vapor pressures, even though small errors are self-correcting.⁷ Unfortunately, very few, if any, of the relevant vapor pressures have been measured anywhere in the temperature range of interest for metal-halide lamps (>1000 K). The calculated and/or extrapolated values currently used may be in error by an unacceptable amount.

In addition to the need for the equilibrium vapor pressures of simple metal-halide salts, knowledge of the vapor pressures in equilibrium with salt *mixtures* has become increasingly important. The lighting industry has sought to exploit the phenomenon of vapor-phase complexing between dissimilar salts to increase the density of the radiating metal in the arc at a given temperature, or equivalently, obtain the same density at a lower temperature.

Complexing refers to a relatively weak bonding of two or more stable molecules, which may be identical (homocomplex) or different (heterocomplex) (Hastie, 1975). The use of complexing in lamps typically involves pairing a high vapor pressure salt with a low vapor pressure salt in order to increase the partial pressure of the metal atoms in the lower vapor pressure salt. Thermochemical calculations suggest that some combinations of salts can produce increases in the partial pressures of some metals by up to two orders of magnitude (Lapatovich & Baglio, 2001). Again, very few or no measurements have been made of this effect in the temperature range relevant to metal-halide lamps.

The principal impediment to obtaining measurements of equilibrium vapor pressures in the temperature range of interest is the difficulty in not only reaching those high temperatures but also in making accurate

⁷For example, a slightly too high vapor pressure leads to greater radiative losses, a cooling of the lamp, and hence a lowering of the vapor pressure.

measurements in that pressure range. The Knudsen cell method is based on the measurement of time-integrated mass loss from a small hole in an equilibrium vapor cell. The hole must be small enough that the flow of vapor does not substantially perturb the vapor pressure in the cell, i.e., the mean free path of the molecules must be much greater than the diameter of the hole. The technique is often referred to as the effusion method. This requirement typically limits the maximum pressures that may be investigated to something of the order of 100 Pa and less. The pressure range relevant to metal-halide lamps is 10² Pa to 10⁴ Pa.

The Knudsen method also involves an open system in which some of the vapor is lost through the effusion aperture. When measuring salt mixtures whose components have greatly different vapor pressures, this involves a change in the system content with time.

The use of XRIF for the measurement of equilibrium vapor pressures has many aspects in common with the measurement of metal distributions in operating arc lamps. The metal-halide salts are typically the same. The vapor densities are in the same range. And one can use vapor cells identical or similar to the arc tubes used in lamps. There are some critical differences, however. First, one would like to measure equilibrium vapor pressures over the widest range possible. Hence, there is an incentive to increase the dynamic range of XRIF as much as possible. Second, if one intends to obtain quality reference values for the measured vapor pressures, absolute accuracy and understanding of systematic errors becomes essential. (In lamps, relative pressures can be of great importance.) Thus, the measurement of equilibrium vapor pressures tests the limits of XRIF.

The sensitivity of XRIF measurements in operating lamps is limited by Compton scattering of beam photons from the arc tube into the detector. These Compton features frequently interfere with fluorescence lines in observed spectra. Although the broad shape of those Compton features makes it possible to distinguish them from line fluorescence, the Compton counts contribute to statistical noise in integrated line intensities. In Section 5.1, we described the paths by which photons scattered from an arc tube can reach the detector. These paths all require at least two scattering events. A vapor cell geometry that reduces Compton scattering further by requiring at least three scattering events to reach the detector is shown in Figure 27. Except for a several millimeter long, sealed filling stem, the PCA cell is cylindrically symmetric. It is surrounded by a cylindrical tantalum jacket whose primary purpose is to absorb scattered photons. It also serves the purpose of providing reasonably good heat conduction along the outside wall of the cell, thus reducing temperature gradients when the cell is heated in the oven. The jacket has two holes to accommodate the entrance and exit of the beam, and a third hole through the side of the cylinder through which x-ray fluorescence is observed. This hole is one of the defining apertures determining the solid angle from which



Figure 27 The PCA vapor cell and tantalum jacket used for vapor pressure measurements with XRIF.



Figure 28 Schematic of the oven used for measuring equilibrium vapor pressures of metal-halide salts with XRIF.

photons are collected by the detector. The jacket has two holes (only one is visible in Figure 27), which accommodate thermocouples for monitoring the cell and jacket temperature.

Measurement of equilibrium vapor pressures with XRIF was recently demonstrated using the vapor cell described above (Curry et al., 2011). Several vapor cells were dosed with a salt or salt mixture and filled with 500 Pa of Ar. They were sealed by fusing a PCA plug into the filling tube with a frit. A vapor cell and the tantalum jacket were fit into a graphite bushing and placed into a cylindrical oven as shown schematically in Figure 28. The experimental arrangement shown there is not too different

from that used for measurements in a metal-halide lamp discussed in Section 5.1. The oven is aligned so that the x-ray beam travels unobstructed through the oven. The detection of fluorescence remains along the direction of polarization of the incident beam to minimize scattering directly from the vapor into the detector. The field of view of the detector is determined by the viewing hole in the tantalum jacket and the crossed slits in front of the detector. Nitrogen-filled atmospheric pressure ionization chambers monitor the beam flux immediately preceding and following the oven and are used to normalize the measured fluorescence signal and determine corrections for attenuation of the beam by the vapor at the highest vapor pressures.

Absolute vapor densities are obtained by comparison with fluorescence observed from calibration cells containing a known pressure of xenon (see Section 5.1). These cells are placed in the oven in the same manner as the salt-filled cells. Vapor pressures p(T) corresponding to the measured densities n(T) are then determined from the Ideal Gas Law

$$p(T) = n(T)kT \tag{14}$$

where *T* is the temperature of the cell as determined by thermocouple measurements. It is important to remember that n(T) is defined by Equation (1). Accordingly, the corresponding vapor pressures p(T) have sometimes been referred to as elemental vapor pressures.

A weakness of the calibration approach described earlier is the susceptibility to movement of the tantalum jacket and the limiting aperture through which fluorescence is observed, particularly as the oven changes temperature. A remedy may be to dose each vapor cell with a calibration gas so that the calibration is obtained simultaneously with each measurement.

Measurements of equilibrium vapor pressures for Dy over DyI_3 and Tm over TmI_3 are shown in Figures 29 and 30 where the logarithm base 10 of the pressure *P* is plotted versus 1/T (Curry, 2010). Plotting in this manner allows one to compare the data visually against the expected linear dependence predicted by

$$\ln P = \frac{\Delta S}{k} - \frac{\Delta H}{kT} \tag{15}$$

where ΔS and ΔH are the changes in entropy and enthalpy under standard conditions when a mole of molecules evaporates, and *k* is Boltzmann's constant (Mahan, 1975). A distinct change in slope in each graph occurs at or near the predicted melting point of each salt shown by a vertical dashed line. Such a change is expected since the enthalpy of evaporation from a solid should be more than that from a liquid.



Figure 29 Equilibrium vapor pressure of Dy over Dyl_3 as measured with XRIF (Curry, 2010). The solid line is an analytic expression for the vapor pressure, and the dashed line is the melting temperature, both given by Hansen et al. (1998, 2000).



Figure 30 Equilibrium vapor pressure of Tm over Tml_3 as measured with XRIF (Curry, 2010). The solid line is an analytic expression for the vapor pressure, and the dashed line is the melting temperature, both given by Hansen et al. (1998, 2000).

The dynamic range of these measurements extends over nearly three orders of magnitude. At the upper end of the range, the vapor density is high enough to produce significant absorption of the x-ray beam and corrections were made for this effect. The lower end of the range overlaps with the upper end of the range of applicability of the effusion method, and several measurements of the vapor pressure of both DyI₃ and TmI₃ have been made for pressures below 100 Pa. These existing measurements have been compiled by Hansen et al. (1998, 2000) who have produced recommended analytic expressions for the vapor pressures of

the triiodide molecule over each salt. These expressions are also shown in Figures 29 and 30 by solid lines for their range of expected applicability. The XRIF results are 50% and 10% higher for DyI₃ and TmI₃, respectively. At this point, sufficient work has not been completed to understand possible systematic errors and their origins. The XRIF results are for the total Dy vapor pressure, summed over all possible molecules, as opposed to Hansen's expressions for the triiodide molecular vapor pressure, but there is no expected significant difference in these two values in the range of temperatures where the comparison is being made.

Now that the use of XRIF to measure equilibrium vapor pressures has been demonstrated, a more thorough understanding of the absolute accuracy of the method is needed. There are many possible sources of systematic error. Chief among these are: (1) possible contamination of the metal-halide salts and/or cells during preparation, (2) an inaccurate filling of the Xe pressure in the calibration cells, and (3) variations in fluorescence collection efficiency due to movement of the tantalum jacket with temperature or when cells are changed. Inconsistencies in initial data indicate errors in the range of 20%. Discrepancies with Hansen's recommended values indicate errors may be larger.

5.6 Accuracy

Some of the data presented already have statistical error bars associated with many of the XRIF measurements. These are frequently dominated by photon statistics. Thus, smaller uncertainties could, in most cases, be obtained by integrating for a longer period of time. Harder to understand are systematic errors. With respect to measurements on lamps, there has not been a strong incentive to make measurements with uncertainties less than 5%. For measurement of basic data, such as vapor pressures, there is always merit in reducing uncertainties, if not for present applications, then for future ones.

Calibration of XRIF signals using a gas-filled standard is a primary source of systematic uncertainty because independent measurements of the pressures of the standards have not been made. The densities of Xe, for example, have been determined entirely by a single pressure and temperature measurement of the cell maker prior to sealing of the cell. The process of sealing a cell opens the possibility of significant changes in the density from the measured value. Independent measurements of Xe densities could be made in sealed cells using x-ray absorption. Such measurements should give a good scale for the consistency and accuracy with which standard cells can be made.

There are several atomic parameters in Equation (7) including absorption cross sections, fluorescence yields, and branching fractions. These values are almost always based on semiempirical or ab initio calculations rather than direct measurements. Thus, their uncertainty is not always a matter of common agreement. Nevertheless, a few points can be made. Uncertainties in the cross sections are largest for photon energies close to energy edges where resonances can have a large impact. Uncertainties are generally much smaller away from the edges. The cross sections appearing in most tabulations are total cross sections, meaning the cross section for energies greater than the K-shell threshold includes absorption by the L- and lower shells. In order to obtain the K-shell only cross section, the ratio of cross sections at the K-edge is taken as a constant and used to determine the K-shell component at higher energies. This inevitably involves additional error. Thus, it may be wise to consider the K-shell photoelectric cross section values to be no better than 5%. Veigele (1973) puts uncertainties for some of the rare-earth K-shell cross sections as high as 10%. The branching fractions used here are estimated to have errors between 2% and 5% (Salem et al., 1974). Uncertainties in the relevant fluorescence yields are estimated as 1% to 2% depending on the atomic number (Krause, 1979).

Determination of the transmission factors T in Equation (7) follows from total absorption cross sections of the relevant material, so the discussion in the preceding paragraph applies here as well. In addition, there is Compton and coherent scattering from the materials, which also effectively attenuates the x-ray beam. The treatment of scattering was discussed in Section 5.1 where the total effect was shown to be 11% at 20 keV, decreasing to less than 7% at 90 keV. The suggested approximation of using Compton scattering but ignoring coherent scattering probably cuts the error by more than a factor of two.

Measurements of beam flux under normal conditions are not likely to be a significant source of error, mostly because it is the ratio of fluxes that enter into the calibration [Equation (7)]. Statistical fluctuations in the flux measurements are typically negligible.

6. SUMMARY

We have described the use of high-energy x rays to study the low temperature plasmas in high-intensity discharge lamps and to measure equilibrium vapor pressures at high temperatures. X-ray induced fluorescence (XRIF) is a well-known technique used for analysis in many fields, but its application to low-density vapors, as described in this chapter, appears to be unique. Spatially resolved vapor densities of less than 10¹⁶ cm⁻³ have been measured, in a reasonable time, with the use of high-flux synchrotron radiation.

Additive densities, temperature distributions, mixing ratios, and equilibrium vapor pressures have all been measured with a straightforward application of XRIF. More sophisticated variants of XRIF could prove useful in the future. These include nuclear resonance fluorescence for observing lighter elements, resolving near-edge fine structure to determine chemical bonding, looking at the very weak effect of the x rays on the plasma current to understand transport and equilibration times, and using Ge detector arrays to increase measurement sensitivity.

GLOSSARY

- **Ambipolar field** The weak electric field arising from unequal loss rates of positive and negative charges in a finite-sized plasma.
- **Coherent scattering** The scattering of electromagnetic radiation produced by the coherent response of all the bound electrons in an atom. This process is sometimes referred to as Rayleigh scattering.
- **Color rendering** The color rendering index is a quantitative measure of the ability of a light source to render all colors properly as compared to an ideal source, such as daylight. The color rendering index can have values between 0 and 100, with 100 indicating a perfect match between source and reference.
- **Complex** A molecule formed from the relatively weak association of two or more smaller molecules.
- **Compton scattering** The scattering of electromagnetic radiation by a free electron. The low-energy limit of Compton scattering is sometimes referred to as Thomson scattering. The response of a bound atomic electron has a Compton component if the photon energy is larger than the binding energy of the electron.
- **Demixing** The relative spatial separation of elements in metal-halide high-intensity discharge lamp.
- **Elemental density** The total number density of atoms of a particular element summed over all atomic and molecular species.
- **Equilibrium vapor pressure** The vapor pressure of a substance that is in equilibrium with a condensate in a closed system in full thermal equilibrium.
- **Escape peak** An anomalous signal from a crystal x-ray detector arising from the excitation and loss of the crystal material's characteristic fluorescence. It produces relatively small peaks that differ in energy from real signal peaks by an energy equal to the characteristic fluorescence energy.
- HID High-intensity discharge.
- **HPS** High-pressure sodium.
- **Luminous efficacy** Luminous efficacy is a measure of the illumination a light source provides per unit of input power. It typically has the units of lumens/ watt and is defined as the wavelength integral of the product of the eye sensitivity curve (lumens per watt of optical power) and the optical power per unit wavelength radiated by the lamp, all divided by the electrical power consumed by the lamp. The maximum luminous efficacy for a full-color white light source is generally considered to be in the range of 300 lm/W to 350 lm/W, depending on what is considered full-color.
- **XRIF** X-ray induced fluorescence.

REFERENCES

- ALITE. (2006). Program on technology innovation: advanced light source research: ALITE-II: losses in high-intensity discharge light sources. Tech. rep., Electric Power Research Institute, Palo Alto, CA, Philips Lighting Company, Somerset, NJ, General Electric Company, Niskayuna, NY, Osram Sylvania, Beverly, MA. Retrieved July 16, 2011, from www.epri.com
- Baumann, B., Wolff, M., Hirsch, J., Antonis, P., Bhosle, S., & Barrientos, R. V. (2009). Finite element estimation of acoustical response functions in hid lamps. *Journal of Physics D: Applied Physics*, 42, 225209.
- Beks, M. L., Flikweert, A. J., Nimalasuriya, T., Stoffels, W. W., & van der Mullen, J. J. A. M. (2008). Competition between convection and diffusion in a metal halide lamp, investigated by numerical simulations and imaging laser absorption spectroscopy. *Journal of Physics D: Applied Physics*, 41, 144025.
- Berger, M. J., Hubbell, J. H., Seltzer, S. M., Chang, J., Coursey, J. S., Sukumar, R., et al. (1998). NIST Standard Reference Database 8: Photon cross sections database. Retrived July 16, 2011, from http://www.nist.gov/pml/data/xcom/index.cfm
- Bonvallet, G. A., & Lawler, J. E. (2003). Optical absorption spectroscopy on a metal-halide high intensity discharge arc lamp using synchrotron radiation. *Journal of Physics D: Applied Physics*, 36, 1510.
- Chase, M. W. (1998). NIST-JANAF Thermochemical Tables, fourth edition, part I, Al-Co. Journal of Physical and Chemical Reference Data, Monograph No. 9, 17.
- Corliss, C. H., Bozman, W. R., & Westfall, F. O. (1953). Electrodeless metal-halide lamps. Journal of the Optical Society of America, 43, 398.
- Cruise, D. R. (1964). Notes on the rapid computation of chemical equilibria. *Journal of Physical Chemistry*, 68, 3797.
- Curry, J. J. (2010). Monte carlo simulation of photon scattering in x-ray absorption imaging of high-intensity discharge lamps. *Journal of Physics D: Applied Physics*, 43, 234001.
- Curry, J. J., Adler, H. G., Lee, W.-K., & Shastri, S. D. (2003a). Direct observation of de-mixing in a ceramic metal-halide arc lamp. *Journal of Physics D: Applied Physics*, 36, 1529.
- Curry, J. J., Adler, H. G., MacPhee, A., Narayanan, S., & Wang, J. (2004). X-ray absorption imaging of Hg vapour in a ceramic metal-halide lamp using synchrotron radiation. *Plasma Sources Science and Technology*, 13, 403.
- Curry, J. J., Adler, H. G., Shastri, S. D., & Lawler, J. E. (2001). Minority additive distributions in a ceramic metal-halide arc lamp using high-energy x-ray induced fluorescence. *Applied Physics Letters*, 79, 1974.
- Curry, J. J., Adler, H. G., Shastri, S. D., & Lee, W.-K. (2003b). X-ray induced fluorescence measurement of density distributions in a metal-halide lighting arc. *Journal of Applied Physics*, 93, 2359.
- Curry, J. J., Estupiñan, E. G., Henins, A., Lapatovich, W. P., & Shastri, S. D. (2011). Measurement of vapor pressures using x-ray induced fluorescence. *Chemical Physics Letters*, 507, 52.
- Curry, J. J., Sakai, M., & Lawler, J. E. (1998). Measurement of the Hg distribution in a highpressure arc lamp by x-ray absorption. *Journal of Applied Physics*, 84, 3066.
- Curry, J. J., Sansonetti, C. J., & Wang, J. (2005). Temperature profiles and thermal losses in 150 W high-intensity discharge lamps. *Journal of Physics D: Applied Physics*, 38, 3086.
- Dakin, J. T., Rautenberg, T. H., Jr., & Goldfield, E. M. (1989). Anatomy of a vertical metal halide discharge. *Journal of Applied Physics*, 66, 4074.
- Dakin, J. T., & Shyy, W. (1989). The prediction of convection and additive demixing in vertical metal halide discharge lamps. *Journal of the Electrochemical Society*, 136, 1210.
- de Groot, J. J., & van Vliet, J. A. J. M. (1986). *The high pressure sodium lamp*. London: MacMillan Education LTD.
- Deslattes, R. D., Kessler, E. G., Jr., Indelicato, P., de Billy, L., Lindroth, E., & Anton, J. (2003). X-ray transition energies: new approach to a comprehensive evaluation. *Rev. Mod. Phys.* 75, 35, also available as NIST Standard Reference Database 128: X-ray Transition Energies. Retrieved from July 16, 2011, from http://www.nist.gov/pml/ data/xraytrans/index.cfm
- Dreeben, T. D. (2008). Modelling of fluid mechanical arc instability in pure-mercury HID lamps. *Journal of Physics D: Applied Physics*, 41, 144023.

- Elloumi, H., Kindel, E., Schimke, C., & Zissis, G. (1999). Experimental investigation of deviations from local thermodynamic equilibrium in high-pressure mercury discharges. *Journal of Applied Physics*, 86, 4134.
- Evans, R. D. (1958). Compton effect in Encyclopedia of Physics (Vol. 34, p. 218). Berlin: Springer-Verlag, Ch. Compton Effect.
- Fischer, E. (1976). Axial segregation of additives in mercury metal-halide arcs. *Journal of Applied Physics*, 47, 2954.
- Flikweert, A. J., Nimalasuriya, T., Grothuis, C. H. J. M., Kroesen, G. M. W., & Stoffels, W. W. (2005). Axial segregation in high intensity discharge lamps measured by laser absorption spectroscopy. *Journal of Applied Physics*, 98, 073301.
- Fohl, T., Kramer, J. M., & Lester, J. E. (1993). X-ray measurements of mercury density in arc discharge lamps during warm-up and following extinction. *Journal of Applied Physics*, 73, 46.
- Hansen, S., Getchius, J., & Brumleve, T. R. (1998). Vapor pressure of metal bromides and iodides, with selected metal chlorides and metals. Urbana, Illinois: APL Engineered Materials, Inc.
- Hansen, S., Steward, R., Getchius, J., & Brumleve, T. (2000). Supplement to vapor pressure of metal bromides and iodides. Urbana, Illinois: APL Engineered Materials, Inc.
- Hastie, J. W. (1975). High temperature vapors: science and technology. New York: Academic Press.
- Herd, M. T., & Lawler, J. E. (2007). Infrared continuum radiation from metal-halide highintensity discharge lamps. *Journal of Physics D: Applied Physics*, 40, 3386.
- Hochi, A., Hashimotodanl, K., & Katash, K. (2001). Vane-type electrodeless HID lamp. Matsushita Technical Journal, 47, 42.
- Hong, E., Conroy, L. A., & Scholand, M. J. (2002 and 2005). U. S. lighting market characterization (Vols. i and ii). Tech. rep., Navigant Consulting, Inc., Washington, DC.
- Hubbell, J. H., Veigele, W. J., Briggs, E. A., Brown, R. T., Cromer, D. T., & Howerton, R. J. (1975). Atomic form factors, incoherent scattering functions, and photon scattering cross sections. *Journal of Physical and Chemical Reference Data*, 4, 471.
- ICF. (2006). High-intensity discharge lighting technology: workshop report. Tech. rep., Prepared for the U.S. Department of Energy by ICF Consulting. Retrieved July 16, 2011, from http://apps1.eere.energy.gov/buildings/publications/pdfs/corporate/hid_workshopreport.pdf.
- Ingold, J. H. (1987). Radiative processes in discharge plasmas. Physics Volume 149 of NATO Advanced Study Institute Series B (p. 347). New York: Plenum Press, Ch. Metal-halide Sources.
- Karabourniotis, D. (1986). Self-reversed emission lines in inhomogeneous plasmas. In J. M. Proud & L. H. Leussen (Eds.), *Radiative processes in discharge plasmas* (pp. 171–247). Plenum, New York: Proceedings of a NATO Advanced Study Institute.
- Karabourniotis, D. (2002). Non-equilibrium excited-state distribution of atoms in dense mercury plasmas. *Journal of Applied Physics*, 92, 25.
- Karabourniotis, D., & Drakakis, E. (2002). Electron temperature and density in a metal-halide discharge lamp. In 2002 IEEE international conference on plasma science. Vol. Banff, Canada of IEEE conference record - abstracts (p. 315). Piscataway, NJ: IEEE.
- Knoll, G. F. (2000). *Radiation detection and measurement* (3rd ed.). New York: John Wiley and Sons.
- Krall, N. A., & Trivelpiece, A. W. (1986). Principles of plasma physics (Chap. 6.8). San Francisco: San Francisco Press, Inc.
- Krause, M. O. (1979). Atomic radiative and radiationless yields for K- and L-shells. *Journal of Physical and Chemical Reference Data*, 8, 307.
- Lapatovich, W. P., & Baglio, J. A. (2001). Chemical complexing and effects on metal-halide lamp performance. In *Proceedings of the 9th International Symposium on the Sci. and Tech. of Light Sources*, 12–16 Aug (p. 91). Ithaca, NY: Cornell University.
- Lawler, J. E. (2004). Resonance broadening of Hg lines as a density diagnostic in high intensity discharge lamps. *Plasma Sources Science and Technology*, 13, 321.
- Lister, G. G., Lawler, J. E., Lapatovich, W. P., & Godyak, V. A. (2004). The physics of discharge lamps. *Reviews of Modern Physics*, 76, 541.
- Lister, G. G., & Waymouth, J. F. (2002). Encyclopedia of Physical Science and Technology (3rd ed., Vol. 8, p. 557). San Diego: Academic Press, Ch. Light Sources.

- Lowke, J. J. (1979). Calculated properties of vertical arcs stabilized by natural convection. *Journal of Applied Physics*, 50, 147.
- Mahan, B. H. (1975). University chemistry (3rd ed., Chap. 8.). Reading, MA: Addison-Wesley.
- Nimalasuriya, T., Curry, J. J., Sansonetti, C. J., Ridderhof, E. J., Shastri, S. D., Flikweert, A. J., et al. (2007). X-ray induced fluorescence measurement of segregation in a DyI₃-Hg metalhalide lamp. *Journal of Physics D: Applied Physics*, 40, 2831.
- Palmer, F. L., & Lapatovich, W. P. (2000). Coaxial applicators for electrodeless high-intensity discharge lamps. U. S. Patent 6,107,752 and associated patents.
- Ralchenko, Y., Kramida, A. E., Reader, J., & the NIST ASD Team. (2010). NIST Standard Reference Database 78: Atomic spectra database. Retrieved July 16, 2011, from http://www.nist.gov/pml/data/asd.cfm
- Reiling, G. H. (1964). Characteristics of mercury vapor-metal iodide arc lamps. *Journal of the Optical Society of America*, 54, 532.
- Rhodes, W. H., & Reid, J. (1979). Transparent yttria ceramics containing magnesia and magnesium aluminate. U. S. Patent 4,174,973.
- Salem, S. I., Panossian, S. L., & Krause, R. A. (1974). Experimental K and L relative x-ray emission rates. Atomic Data and Nuclear Data Tables, *14*, 91.
- Schneidenbach, H., & Franke, S. (2008). Basic concepts of temperature determination from self-reversed spectral lines. *Journal of Physics D: Applied Physics*, 41, 144016.
- Shaffner, R. O. (1971). Theoretical properties of several metal halide arcs assuming LTE. Proceedings of the IEEE, 59, 622.
- Shastri, S. D., Fezzaa, K., Mashayekhi, A., Lee, W.-K., Fernandez, P. B., & Lee, P. L. (2002). Cryogenically-cooled bent double-Laue monochromator for high-energy undulator x rays (50-200 keV). *Journal of Synchrotron Radiation*, 9, 317.
- Stormberg, H. P. (1981). Axial and radial segregation in metal-halide arcs. *Journal of Applied Physics*, 52, 3233.
- Sugiura, M. (1993). Review of metal-halide discharge lamp development 1980–1992. *IEE Proceedings A*, 140, 443.
- Thompson, A. C., Attwood, D. T., Gullikson, E. M., Howells, M. R., Kortright, J. B., Robinson, A. L., et al. (2001). X-ray data booklet. Berkeley, CA: Technical and Electronic Information Department, Lawrence Berkeley National Laboratory.
- Turner, B. P., Ury, M. G., Leng, Y., & Love, W. G. (1997). Sulfur lamps: progress in their development. *Journal of the Illuminating Engineering Society*, 26, 10.
- Veigele, W. J. (1973). Photon cross sections from 0.1 keV to 1 MeV for elements Z = 1 to Z = 94. Atomic Data, 5, 51.
- Waymouth, J. F. (1971). Metal-halide lamps. Proceedings of the IEEE, 59, 629.
- Waymouth, J. F. (1991). LTE and near-LTE lighting plasmas. IEEE Transactions on Plasma Science, 19, 1003.
- Wei, G. C., Lapatovich, W. P., Browne, J., & Snellgrove, R. (2008). Dysprosium oxide ceramic arc tube for HID lamps. *Journal of Physics D: Applied Physics*, 41, 144014.
- Zollweg, R. J. (1978). Convection in vertical high-pressure mercury arcs. *Journal of Applied Physics* 49, 1077.