# Lattice vibrations and the energy landscape of the isoelectronic semiconductor series CuBr, ZnSe, GaAs, and Ge: The special case of CuBr and its *d*-level chemistry

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#### Abstract

We have examined the lattice vibrations and the energy landscape of the isoelectronic diamond and zincblende semiconductor series CuBr, ZnSe, GaAs, and Ge. Vibrations are found to be an increasing function of ionicity, with the cation sublattice always vibrating more strongly than the anion sublattice. These findings are consistent with density-functional-theory calculations of the energy landscape and temperature-dependent molecular-dynamics simulations of the atomic-position fluctuations. For CuBr, inclusion of the Cu 3*d* Hubbard-*U* term is found necessary to stabilize the zincblende structure and to bring its vibrational amplitudes into agreement with experiment. In addition, vibrations are found to strongly affect the CuBr near-edge x-ray absorption fine-structure that we have successfully modeled by including displacements in our theoretical Bethe-Salpeter equation calculations. Reverse Monte-Carlo structural refinements using large atomic configurations to simultaneously fit x-ray absorption and x-ray total-scattering

data support these conclusions, and they reveal strong Cu-Br first-neighbor correlations and asymmetric distributions of interatomic distances in the temperature ranges of both negative and positive thermal expansion. Delineation of the CuBr valence-band photoelectron spectrum into its Cu 3d and Br 4p states uniquely reveals their covalent mixing and further supports the density-functional theory results.

### Introduction

Lattice vibrations are a crucial aspect of solid-state physics, and they are responsible for many unique solid-state properties. These include thermal expansion, thermal resistivity, heat capacity, and a myriad of other collective phenomena such as ferroelectricity and superconductivity [1]. CuBr stands out as one of the most ionic of the zincblende tetrahedral semiconductors; its ionicity is 0.74 on the Phillips scale, well above the ionicities of many other ionic (or polar) semiconductors such as GaAs, InP, and ZnSe and close to the critical ionicity of 0.79 that typically delineates 4-fold and 6-fold coordination [2,3]. With its superionic conductivity [4,5] and asymmetric thermal vibrations [6], it is not surprising that CuBr has served as a benchmark, high-vibration material for x-ray absorption [6,7,8,9], x-ray [10] and neutron diffraction [11,12,13,14], Raman scattering [15,16], and several early theoretical studies based on density-functional theory (DFT) [17,18]. Despite these efforts, there has been no complete description of the thermal vibrations in CuBr: Structural refinements from neutron scattering find anharmonic vibrations with large displacements of the Cu<sup>+</sup> ions along the <111> bond directions [12,13], while early theoretical studies [17,18,19] find significant (and controversial [20,21]) concentrations of Cu defect clusters that are energetically favored by strong coupling between

neighboring Cu<sup>+</sup> ions, although this result has also been questioned by more recent DFT studies [22].

In this work, we combine extended x-ray absorption fine structure (EXAFS) - a technique that, unlike many other scattering techniques, is elementally specific to the x-ray absorbing atom - and total x-ray scattering methods to study the thermal vibrations of the isoelectronic zincblende and diamond semiconductor series CuBr, ZnSe, GaAs, and Ge. Our findings reveal that thermal vibrations depend strongly on ionicity, directly reflecting the rigidity of covalent versus ionic bonding [23], with significantly different cation-cation versus anion-anion distance fluctuations. Close examination of the energy landscape as calculated within DFT finds that the Cu defect clusters predicted by earlier theoretical studies are suppressed by inclusion of an on-site Coulomb interaction Hubbard-U term [24] for the Cu 3d electrons. Unique temperature-dependent changes in the near-edge x-ray absorption fine structure (NEXAFS) of CuBr are consistent with the large thermal fluctuations found both experimentally and theoretically, and we present a novel but straightforward method by which to include them in our Bethe-Salpeter equation (BSE) calculations [25]. Delineation of the photoemission valence-band spectrum of CuBr into its Cu 3d and Br 4p states reveals their contributions to the chemical bonding and that different values of the Cu 3d Hubbard-U correction are necessary to account for different spectral regions of the valence band. The NEXAFS measurements of the unoccupied density of states, on the other hand, do not necessitate inclusion of this parameter.

#### Experimental

All data were collected at the National Synchrotron Light Source-II (NSLS-II), Brookhaven National laboratory (BNL). EXAFS and NEXAFS spectra were recorded at the National Institute of Standards and Technology (NIST) beamline 6BM from finely ground crystalline CuBr, ZnSe, GaAs, and Ge powders, as previously described using the Si(311) reflection from the beamline's double-crystal monochromator [25]. Additional temperaturedependent data were acquired for both Ge and CuBr in a closed-cycle He cryostat. For the Cu and Br K edges, data from a copper foil and a bromophenol blue standard placed downstream of the CuBr sample were recorded simultaneously. EXAFS data manipulations and fits were performed using the Athena, Artemis, and IFEFFIT EXAFS data-analysis software [26].

Hard x-ray photoelectron spectra (HAXPES [27]) were collected at the NIST beamline 7ID-2 from finely ground CuBr powder using a hemispherical-electron analyzer and photon energies 2000 eV, 3500 eV, and 6000 eV from the Si(111), Si(220), and Si(333) reflections from the beamline's double-crystal monochromator as described previously [28]. Cu 3*p* and Br 3*p* core levels exhibited sharp, well-resolved doublets, with no indication of CuO formation [29]. The energy of each valence spectrum was aligned to the kinetic energy of the Cu 2*p* photopeak recorded at each photon energy, and the energy position of the valence-band maximum was determined by extrapolating the straight portion of the high kinetic-energy edge of the 2000 eV spectrum to zero electron emission. This procedure placed the valence-band maximum approximately 0.8 eV below the Fermi level of the analysis chamber.

Powder x-ray diffraction measurements were performed on CuBr at the NSLS-II beamline 28-ID-1 in a capillary transmission geometry using an amorphous-silicon area detector placed approximately 204 mm and 1006 mm downstream of the sample with 74.5 keV ( $\lambda = 0.1665$  Å) x rays. The diffraction patterns were radially integrated to obtain intensity vs scattering vector Q data using the pyFAI software package [30]. These data were processed using the xPDFsuite software [31] to obtain the total-scattering function and its Fourier transform ( $Q_{max} = 26 \text{ Å}^{-1}$ ) representing the pair-distribution function (PDF). Rietveld analysis verified that the CuBr powder sample was zincblende. Reverse Monte-Carlo (RMC) refinements were performed in RMCProfile [32] utilizing a 64,000-atoms CuBr configuration to simultaneously fit the x-ray total-scattering and EXAFS data, as previously described [33]. Combining x-ray total scattering with EXAFS improves the sensitivity of such refinements to the anion and cation sublattices given the otherwise relatively weak contrast between Cu and Br with x-ray and even neutron radiation.

#### **Density Functional Theory**

DFT based relaxations and molecular-dynamics (MD) calculations were used to model the lattice vibrations at different temperatures for the CuBr-ZnSe-GaAs-Ge semiconductor series, using the VASP code [34]. The projector-augmented wave (PAW) pseudopotentials [35] titled Cu, Zn, Ga, Ge, As, Se, and Br were used from the VASP5.2 PAW\_PBE pseudopotential library. The calculations were performed at the generalized-gradient approximation (GGA) level with nonlocal dispersion corrections [36], using the optB86b-vdW functional of Klimeš et al. [37]. While dispersion is commonly thought of as a surface and interface phenomenon, it is also present in bulk solids. Benchmarking of the optB86b-vdW and related functionals in bulk solids generally shows improved structural predictions [38] relative to the PBE functional [39].

*Ab initio* MD was used to compute the vibrational fluctuations in the semiconductor series. In each case, a 64-atoms supercell of the zincblende (diamond for Ge) structure was used, with a  $2x2x2 \ k$ -point scheme centered on  $\Gamma$ . The plane-wave cutoff energy was set to the largest augmentation charge cutoff among the pseudopotentials for the given system. The timestep was 5 fs. A Langevin thermostat [40] with a friction coefficient of 0.2 THz was used for thermal equilibrium. Systems were equilibrated for 40 ps and then simulated for up to 50 ps to collect vibrational information.

The initial MD runs on CuBr showed the formation of Cu clusters at low temperature, as was seen in some of the earlier computational studies on CuCl [18,19]. Recognizing the contradiction between this result and structural refinements showing that the zincblende phase remains stable down to cryogenic temperatures, we investigated the effect of a Hubbard-Ucorrection for the Cu 3d electrons. Applying a Hubbard-U correction helps correct for the tendency of "basic" DFT functionals to delocalize highly correlated d electrons in transition metals. In a calculation of U for Cu based on linear-response calculations for 51 copper-containing oxides [41], the mean and standard deviation of the fitted values were 7.6 eV  $\pm$  0.7 eV. For Zn, the corresponding values were 0.5 eV  $\pm$  0.8 eV. While the transferability of these results to the zincblende semiconductors CuBr and ZnSe is not known, we use these results, along with the fact that the Zn 3d contribution to the valence band is deep (8 eV below the valence-band maximum [42]) to limit our investigations of U corrections to the  $Cu^+$  ion. In [41], the mean fitted Cu Hubbard-J value and its standard deviation were  $1.1 \pm 1.1$  eV. As this value is small, we did not include it in our calculations. In another study [43], based on the local-density approximation (LDA) rather than the GGA, U = 6.1 eV and J = 0.8 eV were determined for Cu in CuBr.

#### **Results and Discussion**

To illustrate the intriguing thermal properties of the isoelectronic series and particularly those of CuBr, Figure 1 compares the Fourier transforms of the Cu and Br K-edge EXAFS of CuBr recorded at 8 Kelvin (K). (The "raw"  $k^3\chi(k)$  EXAFS data are shown in the inset.) The Fourier transforms display well-resolved backscattering peaks from the first, second, and third-coordination shells of the zincblende structure. Because EXAFS is chemically specific to the absorbing atom, the Cu and Br K-edge data both measure first and third-neighbor backscattering, while the Cu data uniquely measure Cu-Cu second-neighbor backscattering amplitudes of Cu and Br have similar strengths [25], the readily apparent > 50 % reduction in intensity of the second-neighbor Cu-Cu peak relative to the second neighbor Br-Br peak must reflect either (*a*) a significantly larger vibrational amplitude of the Cu<sup>+</sup> sublattice relative to the Br sublattice or (*b*) an anomalously large presence of localized Cu defects as previously suggested by DFT studies [18,19,20]. Note that in either case, this anomaly is prevalent even at temperatures close to absolute zero, where zero-point motion of the ions should dominate the thermal vibrations [1].

To interpret the results of Figure 1 for CuBr, as well as results derived from measurements of ZnSe, GaAs, and Ge, optB86b-vdW DFT calculations were performed to determine the energy landscape of each material. Figure 2 compares the resulting potential-energy displacement curves, i.e., the relative-energy cost of displacing either the cation or anion of each compound from its equilibrium position along a <111> bond direction. Note that the displacement potential for Cu away from Br is particularly soft. Indeed, in the DFT calculations with  $U_{Cu} = 0$  eV (henceforth referred to simply as *U*), the correlated displacements of Cu<sup>+</sup> to form Cu clusters in CuBr is energetically favored over the ideal zincblende structure. Consequently, we re-computed the energy landscape of CuBr with the inclusion of the Hubbard-*U* correction applied to the Cu 3*d*  states; these results are shown in the inset of Figure 2. (The curve plotted in the main body of the Figure for Cu<sup>+</sup> assumes a value of U = 8 eV.) Clearly, the inclusion of a Hubbard-*U* term increases the relative energy of the Cu displacements while systematically removing the secondary minimum in the Cu<sup>+</sup> displacement curve. A Hubbard-*U* correction of about 2 eV or greater ensures that the lowest-energy configuration is zincblende.

Several features of Figure 2 are noteworthy. First, the hardening of the Cu<sup>+</sup> displacement potential with U explains the conflicting results of early DFT studies that found substantial concentrations of  $[Cu_4]$  and other defects [17,18,19], as the earlier studies did not include U or other corrections. Our result is comparable to a recent DFT study that found a hybrid functional (rather than a U correction) stabilizes the zincblende structure [22]. Second, the curvature of the curves implies that vibrational amplitudes should be an increasing function of ionicity, with the cation sublattice always vibrating more strongly than the anion sublattice on account of the softer cation potential relative to the harder anion potential, and this bifurcation should also be an increasing function of ionicity. We attribute this result to the much larger -a factor of 2 – ionic radii of the anions compared to their "same-row" cations [44] and consequently the ease with which the cations can "roam" in their anion cages rather than vice versa [1] in addition to the s-d coupling [17] that will be examined further below. Third, the "hard-sphere limit" encountered at low r is observed for each material (as well as for each finite value of the Cu 3d Hubbard U). Lastly, although quantum effects on the lattice dynamics (notably zero-point motion) are not included in our DFT calculations, the significantly softer landscape for Cu than for Br in Figure 2, along with the smaller mass of Cu, will lead to significantly larger zero-point motion for Cu. The origin of the relatively small second-shell Cu-Cu peak in Figure 1 is thus resolved in favor of larger Cu<sup>+</sup> sublattice vibrations.

To explore the vibrational landscape in more detail, we performed *ab initio* MD simulations [45] to compute the atomic trajectories  $x_i(t)$  for each material at T = 77 K and T = 293 K. Here *t* denotes time, and *i* indexes the individual atoms for 64-atoms zincblende or diamond supercells. To make a connection with the EXAFS measurements, the mean-square deviations of interatomic distances (also referred to as Debye-Waller factors) corresponding to a particular coordination shell (species and symmetry-equivalent mean-separation vectors) were computed using

$$\sigma^2_{shell} = \langle (d_{ij}(t) - \langle d_{ij}(t) \rangle \rangle^2 \rangle \rangle_{t;i,j \in shell}$$

$$\tag{1}$$

with averages performed over time and atomic pairs *i* and *j* that correspond to a site type and coordination shell. For Cu in CuBr, different *U* values were also considered. Figure 3 compares the Debye-Waller factors calculated for CuBr at 293 K as a function of *U*. The values shift dramatically between U = 2 eV and U = 6 eV and stabilize for values exceeding 6 eV.

Figures 4 and 5 compare the results of the MD simulations to the experimental EXAFS results for each material at 77 K and room temperature (300 K experiment, 293 K theory). Excellent agreement is found for the first three coordination shells of ZnSe, GaAs, and Ge with no Hubbard-*U* correction, and for CuBr with U = 8 eV. (This value is close to the mean-estimated value of *U* in Ref. [41].) The data support the general notion that atoms are more rigidly held in place by directional covalent bonds than less directional ionic forces [23] as all fluctuations increase with the ionicity of the compound. They also demonstrate the greater amplitude of the cation-sublattice vibrations relative to the anion-sublattice vibrations suggested by Figure 2 and consistent with previous EXAFS studies [7,46,47,48]. We should mention that, unlike the other

materials, the contributions to the EXAFS from the higher shells in CuBr above 150 K were too weak to provide reliable information on the underlying distance distributions if considered alone; consequently, we found it necessary to simultaneously fit the EXAFS and x-ray total-scattering data of CuBr to obtain these quantities.

Figure 6 shows the x-ray total-scattering data, F(Q) = Q[S(Q) - 1], for CuBr and its corresponding pair-distribution function, G(r), obtained by Fourier transforming F(Q), at 34 K and 300 K. The smearing of higher-shell features with temperature is readily apparent: At 300 K, the Bragg peaks mostly disappear for Q > 12 Å<sup>-1</sup> with only sinusoidal oscillations of intensity remaining. The periodicity of these oscillations is  $\approx 2.6$  Å, which corresponds to the Cu-Br bond length of  $\approx 2.44$  Å. The persistence of these oscillations demonstrates that significant positive Cu-Br correlations still exist even at 300 K for the chemically bonded Cu and Br atoms [49]. These correlations are also indicated by the relatively sharp, first-neighbor peak in G(r), which contrasts the much broader peaks observed for higher-order neighbors that reflect significantly larger relative atomic displacements for such non-bonded pairs.

Figures 7, 8, and 9 compare the experimental data (black) and calculated traces (red) for CuBr at 34 K and 300 K. (Not shown are data and analysis at 150 K.) The calculated curves were determined from atomic coordinates in the 64,000-atoms configurations refined while simultaneously fitting all temperature-dependent datasets (x-ray total-scattering function, x-ray Bragg-peak intensity profile, x-ray PDF, and Cu and Br K-edge EXAFS). We emphasize that all calculated signals in Figures 7, 8, and 9 correspond to the same atomistic model at each temperature. Our RMC refinements therefore treat thermal disorder explicitly without effective parameters. They therefore provide a more complete mapping of the actual probability-density

distributions (PDDs) for the Cu and Br atoms and their displacement correlations, going beyond the Gaussian-type approximation of atomic-displacement parameters of Figures 4 and 5.

Figure 10 shows the resulting PDDs projected onto the {100} plane of the zincblende structure. The distributions were obtained by folding the CuBr atomic configurations refined against the x-ray total-scattering and EXAFS data (Figures 7, 8, and 9) onto a single crystallographic unit cell. At both 34 K and 300 K, the magnitudes of the Cu displacements are significantly larger than those for Br. At 34 K, the projections of Cu and Br exhibit a pronounced square-like shape, with larger displacements along the diagonal directions. At 300 K the projections appear more isotropic, but they are still non-Gaussian for Cu.

To further investigate the directional dependence of the thermal vibrations, Figure 11 plots stereographic-projection maps of the probability density for the directions of the Cu and Br displacements away from their average positions in the crystallographic unit cell at 34 K and 300 K. The results reveal the larger-magnitude, preferential displacements of the Cu cations along the <111> directions, with their PDDs being significantly anharmonic. A similar directional trend, but with smaller magnitudes of displacements and more harmonic distributions, is observed for the Br anions, again directly reflecting the correlated motion of the two chemically bonded species, but we note the blurring of the Br distribution at 34 K that may indicate transverse displacements at low temperature [14]. We find no indication of off centering of Cu<sup>+</sup> in its tetrahedral [Br<sub>4</sub>] coordination. Additionally, our results reveal a suppression of vibrations along the <100> directions for both sublattices.

Motivated by these findings, we repeated the DFT calculations of Figure 2 for displacements along the <100> directions. The bottom of Figure 11 compares the potential-energy curves for Cu and Br displacements along the <111> directions and along the <100> directions for

U = 8 eV. As expected, the <100> curves are symmetric and more harmonic than the <111> curves, but again the Cu displacements are softer than the Br displacements. However, the <100> curves are harder than <111> displacements that lengthen the Cu-Br bond length and softer than <111> displacements that shorten it. It is gratifying that the energy landscapes are consistent with the RMC refinements discussed above.

Turning now to the distance distributions themselves, Figure 12 shows the Cu-Br firstneighbor bond-length distribution recovered by the RMC analysis. It appears asymmetric, with the asymmetry skewed towards negative distances for 34 K, but to increasing positive distances for 150 K and 300 K. The asymmetry of the first coordination shell is also evident from EXAFS fitting performed using a parameterized small-cluster model in Artemis with the first coordinationshell cumulants  $C_3$  and  $C_4$  as shown in Figure 13 [50]. This parameterization clearly identifies the asymmetry of the underlying PDFs [51,52]. It has been demonstrated theoretically that  $C_3$  should be positive in the temperature range of positive thermal expansion and negative in the temperature range of negative thermal expansion [53]. A positive  $C_3$  has been identified previously in EXAFS studies at high temperatures [6,7,8], and the EXAFS itself has been integrated to determine asymmetric potential-energy curves that are consistent with Figure 2 [9]. However, this is the first time that a negative  $C_3$  has been identified at low temperature. Additionally, counter to previous EXAFS studies [54,55], our data suggest a contraction of the Cu-Br first-neighbor bond length in the region of negative thermal expansion (between 0 K and 50 K [56]) that is consistent with the negative asymmetry of the PDF observed in Figure 12 at 34 K.

Another important observation is the significant negative asymmetry of the Cu-Cu secondneighbor distribution at 300 K. Figure 14 shows this distribution, again recovered from the RMC analysis, to be significantly skewed to shorter distances, and this asymmetry is again found to be

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an increasing function of temperature. A positive asymmetry for the Cu-Br nearest neighbors indicates that the Cu is moving preferentially toward the triangular faces of their tetrahedral [Br<sub>4</sub>] cages, rather than toward the Br-atom vertices, consistent with the potential-energy curves of Figure 2. [If a Cu atom moves by a distance  $\delta$  toward a face of its [CuBr<sub>4</sub>] tetrahedron, it moves by a distance  $\delta$  away from the Br at the vertex opposite that face, but by only a distance  $\delta/3$  toward the Br atoms at the face corners (to lowest order in  $\delta$ ). Hence, the probability distribution of the Cu-Br nearest-neighbor distance extends three times further on its longer-distance side than on its shorter-distance side.] A negative asymmetry for the Cu-Cu second neighbors then is consistent with the correlated motion of four Cu atoms toward the center of the octahedral void bounded by the [CuBr<sub>4</sub>] tetrahedra. Such correlated motion is exactly what leads to Cu clustering in DFT studies that do not include U [18]. Apparently, these motions are energetically favored by the otherwise symmetry forbidden vibronic *s*-*d* coupling that occurs on neighboring Cu atoms when the local-site symmetry of a moving Cu atom is reduced from  $T_d$  to  $C_{3\nu}$  by displacement from its tetrahedral center [22]. This coupling is likely intrinsic to all the cations studied, albeit with significantly diminishing importance as the cation 3d levels fall further below the valence-band maximum and become more localized with increasing Z [42]. The Br-Br second neighbor distribution, on the other hand, is more symmetric than the Cu-Cu distribution at elevated temperatures, but it is still not Gaussian, likely from the correlated motion of the Cu<sup>+</sup> ions that forces the Br<sup>-</sup> ions at the base of the tetrahedra apart. Note that the Cu-Cu and Br-Br secondneighbor distributions are both sharp and symmetrical at 34 K.

As our theoretical calculations have demonstrated the need to include the Hubbard-U correction in the DFT calculations of CuBr, we will now examine the electronic structure of CuBr and the effects of U on its occupied and unoccupied electronic density of states. Figures 15 and

16 show the temperature dependence of the CuBr near-edge spectra. As described in detail previously [25], the Cu and Br K-edge NEXAFS are a sensitive measure of the Cu and Br unoccupied l = 1 angular-momentum resolved partial density of states that we calculate beginning with ground-state, equilibrium-geometry DFT calculations using the LDA and then solution of the BSE to include the excited-state electron-core-hole interaction [57]. This methodology has been demonstrated to accurately predict the NEXAFS for all seven K edges of the isoelectronic series [25], and it is required to reproduce changes in spectra resulting from the core-hole interaction that would otherwise be neglected in a simple DFT treatment of the unoccupied states. We expect, however, that DFT-based core-excited methods such as XCH [58] and other analogous treatments [59] would render spectra with similar core-hole-induced refinements of the near edge.

The near-edge spectra of CuBr sport unprecedented changes with temperature, and, because no phase transition of CuBr is expected to occur within this temperature range, they are solely attributed to thermal vibrations of the cation and anion sublattices. It is well known that the EXAFS Debye-Waller factors decrease spectral features by exponential terms with arguments proportional to the photoelectron wave-vector squared [60], which is typically assumed to be zero close to an absorption edge. Consequently, thermal vibrations are usually not considered in the interpretation of near-edge spectra [61]. Following original papers by Stern et al. [62] and Rehr and Albers [60], this assumption is in fact not correct, and we take the reference-energy zero for the wave vector to be the bottom of the valence band which is approximately 12 eV below the Fermi level for these materials [23]. Fourier transforming our theoretical near-edge spectra as functions of electron-wave vector to real-space in the spirit of more traditional, real-space multiple-scattering calculations [60], we can include Debye-Waller effects by convolving spectral contributions in contiguous, narrow ranges with normalized Gaussians reflecting the values of  $\sigma$ 

from our MD simulations prior to returning to the wave-vector/energy domain. For each spectrum,  $\sigma$  is a continuous function of path length and specific for either the Cu or Br K edge. This treatment thereby reproduces results familiar from traditional EXAFS analysis.

The insets of Figures 15a and 16a show reference data acquired simultaneously from either a Cu or Br standard downstream of the sample. The small ( $\approx 0.4 \text{ eV}$ ) edge shifts to lower photon energy observed for both the Cu and Br K edges likely reflect a reduction of the CuBr 1*s*-toconduction-band minimum separation with temperature [63], and we include these shifts in the theoretical spectra by aligning the edge jump recorded at each temperature to its experimental value. Likewise, the insets of Figures 15b and 16b show the different Debye-Waller factors for each atomic pair used in the calculations that were obtained from the MD simulations corrected for zero-point motion of the ions as determined from the EXAFS data recorded at 8 K. The overall agreement between theory and experiment displayed in Figures 15 and 16 coupled with the general simplicity of the above approximations supports the general conclusion that no additional physics must be invoked to explain the local structure of CuBr other than thermal vibrations.

While NEXAFS is sensitive to the unoccupied density of states of a crystal, photoemission is directly sensitive to its occupied states. Photoemission has therefore been used to experimentally determine chemical hybridization in the solid and consequently the nature of the solid-state chemical bond [64]. The ground-state electronic configurations of Cu and Br are  $[Ar]3d^{10}4s^1$  and  $[Ar]3d^{10}4s^24p^5$ , respectively. In a simple ionic picture, copper would therefore lose its 4*s* electron to bromine leaving it +1 charged and bromine -1 charged, and, consequently, both ions with noblegas-like outer shells. However, as detailed previously, the bonding between Cu and Br is significantly covalent [65]. As seen from the valence-photoemission spectra shown in Figure 17a, the valence band of CuBr consists of four lobes that make up two individual sub-bands with a significant bonding-antibonding gap between them. The dramatic intensity changes observed for the upper band relative to the lower band indicate that the former consists mostly of Cu 3dcharacter (the "Cu 3d band") while the latter consists mostly of Br 4p character (the "Br 4p band"), on account of the approximate factor of 4 variation in the ratio of their photoionization cross sections over this photon-energy range [66].

To isolate the individual Cu 3*d* and Br 4*p* contributions, we performed non-negative matrix factorization, a principal component analysis (PCA) technique, of the three valence-band spectra to obtain their two principal components. Figure 17b shows the resulting components that we assign to the occupied Cu 3*d* and Br 4*p* states. Note the significant *p*-*d* mixing that occurs across the bonding-antibonding gap as well as the one-to-one correspondence of valence features that indicates the sharing of electrons in a covalent bond [64]. Local  $T_d$  site symmetry splits the Cu 3*d* antibonding states into a lower-energy *e* set and a higher-energy  $t_2$  set on account of their orbital proximity to the negatively charged Br ions [67]. The  $t_2$  set forms both  $\sigma$  and  $\pi$  bonds with combinations of Br 4*p* orbitals of the same symmetry, so these states lie at higher energy and are spread into wider bands than the *e* set that forms only weaker  $\pi$  bonds. There is also significant contribution (as well as  $\sigma$ - $\pi$  splitting) to the Br 4*p* band from the Cu 3*d* states, and again this mixing is stronger at the higher energies.

To validate these conclusions and to directly assess the effect of the Hubbard-U correction on the chemical bonding of CuBr, Figure 18 shows the CuBr partial density of states calculated for U = 0 eV and U = 8 eV. Clearly, increasing U decreases the energy separation between the Cu 3d band and the Br 4p band, indicating a reduction in ionicity of the Cu-Br bond [23]. Increasing U also increases the width of the Cu 3d band while decreasing the width of the Br 4p band. Reducing the energy separation between the Cu 3d states and the Br 4p states directly increases their overlap, and consequently produces a stronger Cu-Br chemical bond, as evident from the increased mixing observed. In fact, for U = 8 eV there is a large contribution of Cu 3d states to the Br 4p band and vice versa. The reduction in energy of the Cu 3d states by U therefore is directly responsible for increasing the covalency of the Cu-Br bond, thereby explaining the seemingly surprising result that U (known to spatially localize the Cu 3d electrons [24]) reduces the lattice vibrations or Debye-Waller factors of the CuBr distances. Also note that the unoccupied states (in particular, the Cu 4p and Br 5p states) are not as sensitive to U as are the occupied states, only showing rigid band shifts to higher energies that follow the band gap. This latter result explains the successful treatment of the NEXAFS spectra with LDA that does not include Hubbard-U corrections. We note that, in an alternative approach [22], the inclusion of nonlocal-Fock exchange in a hybrid calculation of the CuBr electronic structure also shifts the occupied Cu 3d states downward as the amount of exchange is increased, without the inclusion of a U term.

While various aspects of the photoemission spectra are reproduced by the density of states calculations, no single value of U gives agreement with the entire band structure: U = 0 eV gives the best agreement with the energy and splitting of the Br 4p band, but U = 6 eV gives the best agreement with the energy and splitting of the Cu 3d band. Values determined for the band gap also evolve with U, increasing from  $E_g = 0.434$  eV for U = 0 eV to  $E_g = 2.26$  eV for U = 10 eV. These values are all below the 2.91-eV experimental value [68], but U still apparently increases the energy separation (level repulsion) between the occupied Cu 3d states (at the top of the valence band) and the unoccupied Cu 4s states (at the bottom of the conduction band) by an amount large enough to inhibit the pseudo Jahn-Teller s-d coupling believed to produce the Cu defect formation found previously [17,18,19,22]. The HSE hybrid functional [69], on the other hand, can reproduce the band gap of CuBr being superior to GGA+U in describing the CuBr electronic structure.

However, hybrid functionals are much more computationally expensive, and we have established by comparison of experiment and theory that GGA+U works well enough for the costly *ab initio* MD simulations.

#### Conclusion

We have examined the thermal vibrations of the isoelectronic semiconductor series CuBr, ZnSe, GaAs, and Ge with special emphasis on CuBr because of its unique physical and electronic properties. Vibrational amplitudes are found to be increasing functions of ionicity, with the cation sublattice always vibrating more strongly than the anion sublattice in agreement with DFT calculations of the energy landscape and temperature-dependent MD simulations of the localatomic fluctuations. For CuBr, atomistic structural refinements against combined x-ray totalscattering and EXAFS data find large thermal vibrations and asymmetric distributions of interatomic distances in the regions of both negative and positive thermal expansion with displacements preferentially along <111> directions and magnitudes which are considerably larger for Cu than for Br. The large thermal vibrations of CuBr strongly affect its NEXAFS spectra that we have also modeled theoretically. Furthermore, the Hubbard-U correction, when applied to the Cu 3d states, is found to stabilize CuBr in the zincblende structure by increasing both the covalency of the Cu-Br chemical bond and its level repulsion (band gap). These results are corroborated by the experimental delineation of the CuBr valence-band photoelectron spectrum into its Cu 3d and Br 4*p* states that uniquely reveals details of their chemical bonding.

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#### References

a) Reference to specific software packages is made to adequately specify the methodology used and does not represent an endorsement by the National Institution of Standards and Technology nor does it imply that the software identified is necessarily the best available for the purpose.

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real and imaginary parts of the Fourier transform in the range from 1 Å to 5 Å, and it included both single- and multiple-scattering paths. For the EXAFS cumulant fits, the *k* ranges were 3.00 Å<sup>-1</sup> to 19.60 Å<sup>-1</sup> for both Cu and Br and the Fourier transforms were computed in the range of 1.45 Å to 4.75 Å. Multiple scattering was not considered in the cumulant fits.

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## Figures



1) Magnitude of the Fourier transforms of the  $k^3$ -weighted EXAFS,  $k^3\chi(k)$ , of CuBr recorded at 8 K. Data recorded at the Cu K edge and the Br K edge as indicated. The inset shows the "raw"  $k^3\chi(k)$  EXAFS data for each edge. Also indicated are the scattering contributions from the first three coordination shells.



2) Relative change in energy (in eV) as a function of ion displacement from equilibrium in 64atoms cells along a <111> direction calculated by density-functional theory (DFT) for CuBr, ZnSe, GaAs, and Ge. For CuBr, a Hubbard U = 8 eV was assumed. Coordinates are scaled such that cation equilibrium is at x = 0 and anion equilibrium at x = 0.25. Note the hard-sphere limit that is encountered as either ion moves closer to the other. The inset shows the relative change in energy as the Cu<sup>+</sup> ion of CuBr is displaced along the <111> direction as a function of Hubbard U. Note that the curve steepens and the off-center secondary minimum near x = -0.175disappears with increasing U.



3) Results of the MD simulations for the mean-square relative displacements or Debye-Waller factors for the first three coordination shells of CuBr calculated as a function of  $U_{Cu}$  at 293 K.



4) Mean-square relative displacements or Debye-Waller factors for the first three coordination shells of CuBr, ZnSe, GaAs, and Ge at 77 K. a) Experiment. b) Theory. The theoretical curves do not include zero-point motion of the ions. Error bars represent a 1-sigma statistical error [26] and are often smaller than the data points shown.



5) Mean-square relative displacements or Debye-Waller factors for the first three coordination shells of CuBr, ZnSe, GaAs, and Ge at 300 K and 293 K. a) Experiment. b) Theory. The theoretical curves do not include zero-point motion of the ions. Error bars represent a 1-sigma statistical error [26] and are often smaller than the data points shown.



6) a) X-ray total-scattering function, F(Q), and b) x-ray pair-distribution function, G(r), for CuBr at 34 K (black) and 300 K (red). The pair-distribution function is obtained by Fourier transforming the F(Q) data.



7) a) [S(Q) - 1], and b) x-ray Bragg-peak intensity profile for CuBr at 34 K and 300 K. The black curves are data, and the red curves are the RMC fits (see text). The curves for the two temperatures have been offset for clarity.



8) X-ray pair-distribution function, G(r), at 34 K and 300 K. The inset shows an expanded view of its low-*r* region. The black curves are data, and the red curves are the RMC fits (see text). The curves for the two temperatures have been offset for clarity.



9) Magnitude of the Fourier transforms of the Cu and Br  $k^2$ -weighted K-edge EXAFS,  $k^2\chi(k)$ , recorded at 34 K and 300 K. The black curves are data, and the red curves are the RMC fits (see text). The curves for the two temperatures have been offset for clarity.



10) Atomic-probability density distributions (PDDs) for Cu (a, c) and Br (b, d) projected onto the {100} plane at 34 K and 300 K as indicated. The PDDs of Cu are anisotropic, with this anisotropy particularly prominent at 34 K. The PDD of Br exhibits some anisotropy at 34 K, but it is approximately Gaussian at 300 K. The magnitude of Cu displacements is always larger than the magnitude of Br displacements. (e) and (f) show line traces along the diagonal <110> (red) and horizontal <100> (blue) directions. Dashed lines 34 K, solid lines 300 K.



11) Stereographic-projection maps of the probability density for the directions of Cu and Br displacements away from their crystallographic positions at 34 K and 300 K: (a) Cu and (b) Br,

34 K. (c) Cu and (d) Br, 300 K. The projections demonstrate the preference for both the Cu and Br atoms to move along <111> directions and the relatively low probability for displacements along <100> directions. The similar directional preferences for both species along <111> directions indicate the correlated motion of the nearest-neighbor Cu and Br atoms that reflect a significant covalency of their chemical bond. (e) Theoretical potential-energy curves for Cu and Br displacements along <111> and <100> directions for U = 8 eV. For <111> displacements, positive (negative) Cu displacements shorten (lengthen) the Cu-Br bond length, and positive (negative) Br displacements lengthen (shorten) it. The theoretical calculations are consistent with the data in (a) – (d) (see text).



12) Cu-Br first-neighbor pair-distribution functions (PDFs) as determined by combined RMC fits using the EXAFS and total-scattering data at 34 K, 150 K, and 300 K. Note that the asymmetry of the distributions is positive at 150 K and 300 K, but it is negative at 34 K consistent with the EXAFS determination of  $C_3$  at these temperatures (see text). The inset shows the temperature dependence of the CuBr lattice constant taken from [53] that extends below 34 K.



13) Temperature dependence of the  $C_3$  and  $C_4$  cumulants of the Cu-Br first-neighbor bondlength distribution measured by EXAFS. The inset shows the EXAFS determination of the Cu-Br first-neighbor bond length (relative to its room-temperature value) in the temperature range of negative thermal expansion. Error bars represent a 1-sigma statistical error [26] and are often smaller than the data points shown.



14) a) Cu-Cu and b) Br-Br second-neighbor pair-distribution functions (PDFs) as determined by combined RMC fits using the EXAFS and total-scattering data at 34 K, 150 K, and 300 K. Note the significant negative asymmetry of the Cu-Cu distribution at 150 K and 300 K. The Br-Br distribution is more symmetrical, but it is not Gaussian at the higher temperatures.



15) Normalized temperature dependent Cu K-edge near-edge spectra (NEXAFS) from CuBr. a) Experiment. b) Theory. The inset in (a) shows the data recorded at 8 K and 300 K on an expanded energy scale together with a Cu-foil standard that was recorded simultaneously. The inset in (b) shows the Debye-Waller factors used in the simulations.



16) Normalized temperature dependent Br K-edge near-edge spectra (NEXAFS) from CuBr. a)Experiment. b) Theory. The inset in (a) shows the data recorded at 8 K and 300 K on anexpanded energy scale together with a bromophenol blue standard that was recordedsimultaneously. The inset in (b) shows the Debye-Waller factors used in the simulations.



17) a) Photoemission valence-band spectra of CuBr measured with photon energies 2000 eV, 3500 eV, and 6000 eV. The curves have been referenced to the valence-band maximum and have had a Shirley background removed. They have also been normalized to unit area. Not shown is the Br 4*s* level that peaks at -15.5 eV relative to the valence-band maximum. b) Non-negative matrix-factorization results for the Cu 3*d* and the Br 4*p* majority contributions to the valence

band. These curves have also been normalized to unit area. Note the one-to-one correspondence of the valence features, indicating the sharing of electrons in a covalent bond (see text).



18) Theoretical partial density of states (DOS) for CuBr calculated for (a) U = 0 eV and (b) U = 8 eV. Not shown is the Br 4s level that peaks at -15.96 eV and -14.63 eV for U = 0 eV and U = 8 eV, respectively. The valence-band maximum is set to 0 eV in each case.