LOW TEMPERATURE MAGNETIC BEHAVIOR OF "NONMAGNETIC" MATERIALS*

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ABSTRACT

Designs for many superconductor systems, ranging from large magnets to thin film devices, require a knowledge of the magnetic properties of a wide range of materials. Commercial "nonmagnetic" materials may show bizarre magnetic behavior as a function of temperature, changing from paramagnetic to diamagnetic, or vice versa, as the temperature is lowered, and sometimes even become ferromagnetic. In metallic alloys, whether these effects occur and at what temperature are often determined by the exact composition of the alloy, which is frequently correlated with its age. Furthermore, nonmetallic materials may have strong magnetic signatures which arise from magnetic impurities, such as inclusions of magnetite in the glass fibers of fiberglass epoxies. Here we summarize results of magnetic susceptibility measurements on a number of metallic alloys and some nonmetallic materials used in cryogenic applications. The data suggest that care should be taken in the use of many of these common materials, especially in the construction of sensitive magnetometer systems.

INTRODUCTION

The magnetic properties of materials used for low temperature instrument construction have always been of concern. A number of papers have appeared in the literature over the years in which magnetic properties of specific materials or groups of materials were investigated [1-7]. Detailed magnetic behavior of a few alloys as a function of temperature is available in handbook form [8]. More highly magnetic alloys for specific applications have also been treated [9]. I have written an earlier paper that discusses general magnetic effects at low temperatures in detail [10].

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The most serious consequences of magnetic misbehavior of materials occur in devices such as magnetometers, gradiometers, and susceptometers designed to detect low levels of magnetic flux. Especially susceptible are instruments based on Superconducting QUantum Interference Devices (SQUIDs). Materials problems contribute to excess noise, drift, and hysteretic effects that can place limitations on the achievable balance and sensitivity of many devices [11]. Materials used in the construction of these systems are obviously required to be "nonmagnetic." In this application, however, the term requires a strict definition. Not only should the materials be nonferromagnetic on a macroscopic scale, they should be so at the lowest levels of detection. Furthermore, knowledge of the intrinsic magnetic behavior, be it paramagnetism, diamagnetism, or any of a number of more exotic types, is often important even though the behavior is normally manifested at a much lower level than cooperative ferromagnetism. Similarly, the behavior of the magnetization as a function of temperature, or at least at the temperature of operation of the device, is necessary information. Little in the way of compiled data is generally available, although as mentioned above, a significant number of measurements have been made. As a result the choice of construction materials often involves a more-or-less random approach, heavily biased toward what is available and inexpensive.

In this paper we present a summary of results of measurements made on a large number of metallic alloys, some nonmetallic composites, and a few plastics. At low magnetization levels, many of these "nonmagnetic" materials behave in unexpected ways, especially at low temperatures. Surface and internal oxidation of low-level ferromagnetic impurities may lead to highly magnetic oxides, and common alloys may contain significant amounts of superconducting elements and compounds. Impurities and alloying elements that are weakly magnetic at one temperature may dominate the magnetic properties at another. All of these effects have the potential to cause problems in sensitive magnetic instrumentation, both because of their inherent magnetic properties and their role in hysteretic behavior.

Figure 1 shows the variety of common magnetic behavior observed in materials. It is the behavior of the magnetization of the material as a function of applied field that determines the designation of diamagnetism, paramagnetism, or ferromagnetism. Note the widely different scales on the two graphs. Ferromagnetism is the much stronger effect and the only one that results in a remanent magnetization (M_R) in the material after the field is removed. The magnetic susceptibility χ is defined (for dia- and paramagnetic materials) as the slope of the line (M/H) and is dimensionless in SI units. A common usage is to divide this value by the material density to get the mass susceptibility, $\chi_\rho = \chi/\rho$ [m^3/kg].

APPARATUS

The majority of our measurements are made with a homemade SQUID magnetometer. The sample is lowered through counterwound coils that make up the primary of a flux transformer, the secondary of which is a coil around the SQUID. The system allows sample sizes up to 1 cm in diameter and 3-4 cm in length. The applied field is provided by a small superconducting solenoid with a persistent-mode switch. External fields are reduced by an external high-permeability shield and a superconducting lead coating over the SQUID and pickup coil containers. Room temperature operation is provided by means of a small re-entrant dewar fitted into the bore of the pickup coils. For liquid helium measurements, the dewar is removed. Further data on the system are given in Table 1.

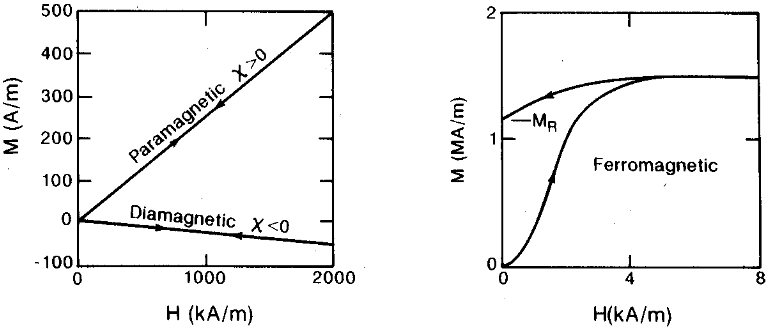

Fig. 1. Magnetization as a function of applied magnetic field for the major types of magnetic behavior in materials. Note the scale differences between the two graphs.

SAMPLES

We obtained samples of a large number of copper, brass, and bronze alloys from an industrial source. Furthermore, we had a good stock of alloys from earlier experimental programs in which electrical resistivity [12] and thermal expansion [13] were measured. In each case, the alloys are of known composition in that they are standard industrial alloys and, in some cases, analyses were available for the specific lot from which our samples came. Composite materials and plastics were all from standard commercial sources. All samples were machined to the shape of cylinders 6 mm in diameter by 12 mm long, given a light etch if appropriate, and carefully cleaned with distilled water and alcohol to remove surface contamination from the machining process. The mass and density of each sample was determined using an electronic balance set up for water/air weighing.

DATA ACQUISITION

Data were taken at both room temperature and with the samples in liquid helium. For each field point, the field value was set and the sample lowered through the susceptometer coils. The output of the SQUID electronics was plotted on an x-y plotter with a time base used for the x axis. The system calibration was determined by measuring a NIST aluminum standard and a series of artificial magnetic moments created by small coils. Moment data were taken at field points up to about 4 kA/m (50 Oe) and converted to magnetization using the measured sample volume. The slope of this magnetization versus field line is the magnetic

Table 1. Calibration data for magnetometer system.

<u>Sense Coils</u>	Calibration constant - high sensitivity: 6450 μA·m^2/V - low sensitivity: 13.8 μA·m^2/V	
	System accuracy: 5%	Detection limit: 200 nA·m^2
	System precision: 3%	Measurement time: < 1 min
<u>Magnet</u>	Coil constant: 2 x 10^{-4} m^{-1}	Maximum field: 50 kA/m
	Field reproducibility: < 0.1%	
	Field uniformity over sense-coil region: 4%	

susceptibility. In addition, the magnetization was measured at zero field both before and following the above sequence. The value measured in zero field after the sample has been taken to the maximum field is the remanent magnetization.

RESULTS

Susceptibility data were entered into a data base and converted to various systems of units. The tables which result are too detailed for publication here in their entirety. However, Table 2 presents data for a large subset of the data base and contains most of the more common materials. Only the SI volume susceptibility is given, but it is possible to convert to other common representations for susceptibility by using the listed density values. The "sample" column contains the NIST identification numbers for the samples. For common metallic alloys the first six characters are the Unified Numbering System (UNS) designations. Additional numerical characters indicate a specific sample number.

Table 2. Magnetic susceptibility of selected materials (SI units).

SAMPLE	COMMON NAME	DENSITY g/cm^3	VOL SUSC ROOM TEMP	VOL SUSC 4 K	TYPE
A00001	AL PURE	2.70	2.07E-5	2.52E-5	P
A03560H	AL 356 T6	2.66	1.80E-5	1.63E-5	P
A92014H	AL 2014	2.79	1.80E-5	1.72E-5	P
A92024	AL 2024	2.77	1.93E-5	2.74E-5	P
A95083H	AL 5083	2.67	1.68E-5	1.78E-5	P
A96061H	AL 6061	2.70	1.90E-5	2.42E-5	P
A97039H	AL 7039	2.75	1.63E-5	2.36E-5	P
A97075H	AL 7075 T6	2.81	1.57E-5	1.87E-5	P
C10100	OXYGEN FREE COPPER	8.94	-9.37E-6	-2.98E-6	D
C11000	ETP COPPER	8.92	3.22E-5	2.53E-5	P
C15000H	AMZIRC COPPER	8.89	-4.44E-6	4.96E-4	D-P
C16200M	DEOXIDIZED CADMIUM CU	8.97	7.47E-5	6.74E-5	P
C17200	BERYLCO 25	8.33	1.56E-3	1.82E-3	P
C18200	CHROME COPPER	8.94	-3.60E-6	7.51E-5	D-P
C18700M	DEOXIDIZED C18700	8.95	2.76E-4	-4.01E-3	P-D
C18900	HIGH COPPER ALLOY	8.89	2.36E-4	2.59E-3	P
C22000H	COMMERCIAL BRONZE	8.80	-5.69E-6	7.63E-6	D-P
C22600	JEWELRY BRONZE 87.5	8.83	-3.19E-6	1.26E-5	D-P
C230001	RED BRASS 85	8.76	-5.85E-6	3.38E-5	D-P
C260002	CARTRIDGE BRASS 70	8.52	-3.48E-6	-6.14E-5	D
C31600	LEADED BRONZE W NI	8.86	-7.86E-6	-1.26E-2	D
C34000	MEDIUM LEADED BRASS 64	8.48	9.42E-5	-8.36E-3	P-D
C35300	HIGH LEADED BRASS 62	8.50	3.36E-3	-2.37E-2	P-D
C36000	FREE CUTTING BRASS	8.52	1.12E-2	-1.40E-2	P-D
C44300	ADMIRALTY BRASS AS	8.55	-1.27E-5	-2.62E-5	D
C46400	NAVAL BRASS UNINHIBITED	8.43	6.64E-4	7.85E-3	P
C46400H	NAVAL BRASS	8.40	5.54E-4	1.17E-3	P
C48200	NAVAL BRASS MED LEAD	8.44	5.63E-5	-1.81E-3	P-D
C48500	NAVAL BRASS HIGH LEAD	8.50	5.80E-4	-2.21E-2	P-D
C50700	PHOSPHOR BRONZE 1.25	8.95	-5.98E-6	-3.98E-6	D
C51000	PHOSPHOR BRONZE 5 A	8.95	-5.86E-6	-5.56E-6	D
C61000	ALUMINUM BRONZE	7.88	-9.02E-6	-1.12E-5	D
C64700	SILICON BRONZE	8.91	4.04E-6	7.95E-5	P
C65100	LOW SILICON BRONZE B	8.75	2.85E-5	2.09E-3	P
C655001	HIGH SILICON BRONZE A	8.56	2.30E-4	8.02E-3	P
C65600	SILICON BRONZE	8.54	2.84E-4	8.67E-3	P
C66100	SILICON BRONZE	8.55	1.30E-4	4.48E-3	P
C77300	NICKEL SILVER	8.44	4.96E-6	1.42E-4	P
R564001	TI 6AL 4V	4.41	1.80E-4	-8.27E-6	P-D
R564002	TI C120 AV	4.42	1.80E-4	-8.42E-4	P-D
R56400M	TI C120 AV ELI	4.44	1.83E-4	-5.94E-3	P-D
R58010	TI B120 VCA	4.85	2.73E-4	2.62E-4	P
S316001	SS 316	7.98	3.04E-3	1.53E-2	P
FG10CR3	FEP G10CR	1.83	2.63E-6	5.34E-4	P
FG111	FEP G11	1.78	3.23E-5	5.18E-4	P
FG11CR3	FEP G11CR	1.90	2.59E-6	4.58E-4	P
FLINENPH	LINEN PHENOLIC	1.35	-4.26E-6	2.93E-6	D-P
QTZROD	QUARTZ	2.21	-1.03E-5	-9.27E-6	D
PACRYL1	ACRYLIC	1.05	-6.98E-6	-2.65E-6	D
PCHEMFL	PCTFE	2.12	-1.08E-5	-7.53E-6	D
PDELRIN1	ACETAL	3.45	-2.18E-5	-1.82E-5	D
PKELF	PCTFE	2.14	-1.10E-5	-7.41E-6	D
PNYLON1	NYLON	1.15	-9.04E-6	-7.46E-6	D
WOODH	HARDWOOD	0.63	6.09E-6	1.22E-5	P

Letters indicate some modification of the basic alloy involving heat treatment (H), drawing (D), or other modification such as oxidation (M). Identification numbers for the nonmetallics have no particular significance. In many cases a number of samples of the same material were measured. An effort has been made to choose a representative set of data for the table. A few materials showed large variations among samples, probably as a result of contamination, as discussed below. In any case, do not expect the susceptibility of a random sample of material to agree with these data within less than about 10% because of differences in alloy composition allowable under a given UNS designation and manufacturing variations in the other materials.

The column labeled "type" calls out the change in magnetic behavior on cooling from room temperature to 4 K. This can be determined from the numerical data, where diamagnetic susceptibilities are listed as negative, but it emphasizes the large number of materials that change character. Some large groups of materials are well behaved in this regard. All aluminum alloys, the silicon bronzes, and epoxy fiberglass materials remain paramagetic. All phosphor and aluminum bronze, and all plastics are diamagnetic at both temperatures. Brass in general is undependable in its magnetic properties. The brasses have a very wide range of compositions and frequently contain lead, which may become superconducting at 4 K. Similarly, the change to diamagnetism of the titanium alloys may be a result of the vanadium content. Materials, such as chrome copper, which change from diamagnetic to paramagnetic on cooling, are probably exhibiting the different temperature dependences of their component elements. This behavior is discussed and a table of temperature dependences presented in [10]. A few of the diamagnetic alloys, when measured in a drawn condition also showed an unexpected change to paramagnetism. We think that this indicates contamination of the sample surface from the drawing operation. None of these are included in the table. Also, a number of common alloys, such as Cu30Ni and stainless steels were measured, but proved to be too ferromagnetic. A less sensitive measurement system, such as a vibrating sample magnetometer, is more appropriate for these samples.

Table 3 lists the remanent magnetization observed on the samples after measurement of the susceptibility. Most materials show either a very small magnetization or none at all, much as we expect. A few, however, show medium to large moments, most likely indicative of a ferromagnetic contamination, either in the bulk or on the surface. Materials are listed here only if they exhibit a medium or large moment at some temperature. Remember that these magnetic effects are extremely small. By normal standards, every one of these materials is nonmagnetic.

Table 3. Remanent magnetization after susceptibility measurement.

UNS NO	COMMON NAME	RT	4 K
C36000	FREE CUTTING BRASS	M	M
C46400H	NAVAL BRASS	M	L
C48500	NAVAL BRASS HIGH LEADED	M	S
C51000	PHOSPHOR BRONZE 5 A	M	M
C61000	ALUMINUM BRONZE	M	L
C65600	SILICON BRONZE	M	S
R564001	TI 6AL 4V	N	L
R564002	TI C120 AV	N	M
R56400M	TI C120 AV ELI	N	M

Code: N - no moment observed; S - small, <10% of magnetization at maximum field, M - medium, 10-50%; L - large, >50%. RT - room temperature.

CONCLUSIONS

The magnetic behavior of common materials used in construction of low temperature apparatus may seriously affect the apparatus performance. This is especially true in the case of sensitive magnetic measurement systems based on SQUID devices or other low level detectors of field or moment. While the effects outlined here are all small, the fact that they exist at all argues for some care in the selection and handling of materials. Finally, we repeat the best advice of all: if you need to know the properties with great precision, measure them on samples from the specific lot of material that will be used in the construction.

The data in Table 2 range over many orders of magnitude. A complete analysis of the magnetic behavior of these materials must, therefore, take into account not only the gross effects outlined here, but also the more subtle effects related to the magnitude of the various susceptibilities such as the effect of the material shape used in a given application.

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