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Characterization and reproducibility of some Chevrel-compound samples: $SnMo_6S_8$ and $PbMo_xS_8$ ($x = 6.00$, 6.20, and 6.35)

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A series of samples of $SnMo_6S_8$ and $PbMo_xS_8$ ($x = 6.00$, 6.20, and 6.35) were made with standardized techniques. The samples were characterized with x-ray diffraction, optical microscopy, scanning electron microscopy, and electron microprobe work. The superconducting transition temperatures of six $SnMo_6S_8$ samples had a standard deviation of 39 mK. The superconducting transition temperatures of four $PbMo_xS_8$ samples had a standard deviation of 20 mK for $x = 6.00$, 16 mK for $x = 6.35$, and 165 mK for $x = 6.20$. These standard deviations are about a factor of 5 less than those in the literature for the $x = 6.00$ and 6.35 materials and slightly less than those in the literature for the $x = 6.20$ material. The temperature dependence of the upper critical field, H_{c2}, was measured up to 30 kG. The graphs of $H_{c2}(T)$ show a positive curvature below 10 kG for all of the samples.

I. INTRODUCTION

In 1971 a class of materials of the general form $M_yMo_6S_8$ (M=metal) was discovered by Chevrel and coworkers.[1] A year later Matthias *et al.* reported that some of these compounds were superconductors.[2] Some had critical temperatures greater than 10 K, and one remained superconducting in fields above 500 kG. This last compound, $PbMo_6S_8$, is one of the more frequently studied Chevrel compounds because it has the highest known upper critical field. Yet even now there appears to be no standard way to prepare it. For this compound or ones stoichiometrically near to it, transition temperatures reported in the literature range from 11.3 K (Ref. 3) to 14.7 K (Ref. 4). For another frequently studied compound, $SnMo_6S_8$, or ones stoichiometrically near to it, transition temperatures of 10.8 K (Ref. 5) to 13.66 K (Ref. 6) have been reported. Thus different experimenters obtain rather different transition temperatures. Very seldom has any researcher reported on a series of nominally identical samples. In the cases where such a series has been described, a scatter of ±200 mK (Ref. 7) or larger has been seen. We report here on several sets of samples which are reproducible to better than ±40 mK. We had originally set out to study the effects of magnetic dopants on $SnMo_6S_8$ and $PbMo_6S_8$. Early on we realized that the scatter in the values of the transition temperature T_c of a set of nominally identical samples would obscure the effect of the dopants. Hence, we undertook a program to decrease this scatter.

Many factors affect the transition temperature of Chevrel compounds.[7] Among these factors are the following: (1) the purity of the starting materials, (2) the reaction temperature and time, (3) the pressure at which the samples are pressed, (4) the sintering temperature and time, (5) the quartz-tube volume and the type of quartz used, and most importantly (6) the nominal composition of the sample. Control of these factors requires the careful characterization of the samples. It is vital to know both the type and amounts of impurities present in them.

We address both the problem of reproducibility and that of characterization. We carefully standardized our procedures for making and characterizing our samples and for measuring some of their superconducting properties, viz., the transition temperature T_c and the upper critical field H_{c2}.

II. SAMPLE PREPARATION

Two sizes of transparent quartz tubes were used. The large size (18.7 cm^3) was used for reacting a sample, while the smaller (3 cm^3) tube was used in the sintering operation. The large tubes were ultrasonically cleaned for 10 min in a mixture of detergent (Alconox) and water. The tubes were then rinsed with deionized water and ultrasonically cleaned in acetone for 10 min more. This was followed by ultrasonic cleanings in water, acetone, and water, each for 5 min. A reagent-grade acetone rinse was then performed, and the tubes were loosely covered with tissue paper and dried in air. The small sintering tubes were cleaned in a similar way.

We made samples of $SnMo_6S_8$ and $PbMo_xS_8$ (where $x = 6.00$, 6.20, and 6.35). They were prepared with SnS (Alfa, 99.9% pure, crystals), PbS (Alfa, 99.9% pure, 200-mesh powder), Mo (A. D. Mackay, 99.95% pure, 325-mesh metal powder), and S (A. D. Mackay, 99.999% pure, coarse crystals). We had tried using the metals rather than their sulfides as starting ingredients in making some samples, but we found that regions of unreacted metal appeared in the finished samples when they were made that way.

The SnS was ground in a smooth ceramic mortar and sifted through a clean 200-mesh stainless-steel sieve before it was used. The PbS used would pass through the 200-mesh sieve and therefore required no grinding. Appropriate amounts of the metal sulfide, molybdenum, and sulfur were chosen to make 10-g batches. All chemicals were weighed out on a balance to the nearest 100 μg. Chemicals were always handled with weighing paper. When the chemicals were transferred to the large quartz reaction tube, any material left on the paper or on the upper walls of the tube was gently pushed down into the lower part of the tube with compressed freon gas and action of ultrasound. The ultrasound caused the small particles adhering to the tube's surface to become dislodged and fall to the lower section of the tube. After all of the chemicals were in the bottom of the tube, it was pumped out to a pressure of 10^{-5} Torr and sealed with a hydrogen-oxygen torch. A piece of water-soaked asbestos paper wrapped around the tube prevented the heat of the sealing operation from prereacting the chemicals.

A group of four such tubes, each with 10 g of chemicals, comprised a set of samples. All samples were prepared identically but separately (up to this step) by the procedure given above.

The chemicals in the four tubes were simultaneously reacted in a Lindberg box furnace (absolute accuracy ±5 °C, stability less than ±1 °C). In order to keep the tubes from exploding, we reacted chemicals at a series of temperatures, as other investigators have done. We chose temperature steps from 300 to 850 °C. The furnace was first preheated to 300 °C. The four tubes of a given set were then placed in the furnace. We reacted the chemicals at 300 °C for 3.5 h, 400 °C for 5 h, 550 °C for 15.5 h, and 850 °C for 9 h. (All of these periods were accurate to ±10 sec.) At the end of this time the furnace was shut off and the samples were allowed to cool down slowly in the unopened furnace. After approximately 15 h the furnace was opened and the tubes (now at 25 °C) were removed.

Each tube could be identified with a given sample by its recorded position in the furnace, its length, and by the peculiar shape of the neck it acquired when it was sealed. After first scribing and cleaning each neck, it was broken under vacuum to minimize the amount of chipped quartz that would be introduced into the sample tube.

A smooth ceramic mortar and pestle was cleaned with aqua regia, soap and water, and then ethyl alcohol. It was dried in air. Each sample was ground with the mortar and pestle and sifted through a clean 200-mesh stainless-steel sieve. The resulting uniform powder size helped to make the pressing and sintering steps (described below) that much more reproducible. We noted that the $\mathrm{PbMo_{6.20}S_8}$ samples formed semimalleable lumps and were therefore difficult to grind. The other compositions gave samples which formed either powders or brittle lumps and were comparatively easy to grind. The mortar and pestle and sieve were always cleaned before another sample was ground.

A 4.816-mm-diam bore die was used to press 1.5508 g of the powder under $(8.57\pm0.30)\times10^8$ Pa pressure. The pressure was reached in under 10 sec and was maintained for 300±1 sec. The die and pressing pistons were carefully cleaned with soap and water, rinsed in ethyl alcohol, and dried before another sample was pressed.

After each pressing, the now cylindrical samples were sealed under vacuum at a pressure of 10^{-5} Torr in the small quartz tubes described earlier. Again a wet asbestos sheet was used to protect the samples from the heat of the hydrogen-oxygen torch used for sealing the tubes. The samples were never heated above 100 °C during the sealing operation.

After preheating our box furnace to 1100 °C, all four samples, each in its own tube, were placed in the furnace. They were sintered at 1100 °C for 24 h. The furnace power was then shut off and the tubes cooled. It took typically one day for the tubes to reach room temperature in the unopened furnace. They were then removed from the furnace. Each tube was then scored and broken in air. The samples were placed in individual Teflon-stoppered bottles which had been cleaned with soap and water, rinsed with ethyl alcohol, and dried in air.

The length and diameter that the samples had before the sintering step were approximately 15 and 4.82 mm, respectively. Sintering the samples caused them all to expand. The percentage increase in length (α_l) and diameter (α_d) were as follows: $\alpha_l=7\%$ and $\alpha_d=5\%$ for $\mathrm{SnMo_6S_8}$, $\alpha_l=19\%$ and $\alpha_d=14\%$ for $\mathrm{PbMo_{6.00}S_8}$, $\alpha_l=17\%$ and $\alpha_d=12\%$ for $\mathrm{PbMo_{6.20}S_8}$, and $\alpha_l=15\%$ and $\alpha_d=8\%$ for $\mathrm{PbMo_{6.35}S_8}$.

III. SAMPLE CHARACTERIZATION

A single sample from each set of four was characterized by x-ray diffraction, optical microscopy, and electron microscopy. Electron microprobe work was also done on all but the $\mathrm{PbMo_{6.20}S_8}$ sample. This sample was characterized after we had learned to identify the main impurities by optical and electron microscopy alone. We determined the types and amounts of impurities in our samples as well as their form and distribution.

X-ray diffraction analysis was performed with a Phillips diffractometer. Filtered Cu $K\alpha$ radiation was used. A scanning speed of $\frac{1}{2}$ degree per minute (in 2θ) was satisfactory for resolving details of the diffraction pattern. In order to detect the low-intensity peaks which would be associated with small amounts of impurities, we made an additional run of the diffraction pattern using a sensitivity 10 times as great as that used in recording the strongest lines.

X-ray diffraction specimens were prepared from finely ground pieces of the sintered cylinders (described in a previous section). The powder was sifted onto a glass slide covered with double-sided sticky tape. A thick layer of this powder was carefully pressed onto the tape with the edge of a microscope slide. Excess powder was scraped off with a smooth uniform motion, producing a flat surface. The final thickness of the powder was always kept great enough so that it did not affect the line intensities.

Quantitative analysis was possible through the use of x-ray standards of β-$\mathrm{Mo}S_2$, $\mathrm{MoO_2}$, and Mo. These were placed on tape-covered slides in the same way as the Chevrel samples. The ratio of the intensity of a given impurity peak in a Chevrel sample to that of the same peak in a standard sample of the impurity is related to the percentage by weight of that impurity in the Chevrel sample. All intensity data for a given sample were taken on the same day with the same machine, with the use of identical settings, in order to minimize errors. The intensity of a given peak was determined by carefully adjusting the angle of the x-ray detector for maximum signal at the peak. A scaler was then allowed to count for 100 sec. This procedure was repeated three times to minimize the effect of any setting errors. Backing the detector off of the peak, we then took counts of the background on each side of the peak for 100 sec. The average of the three on-peak readings minus that of the mean of the background was taken as the intensity of the peak. Our estimated uncertainties for this technique, including the effects of counting statis tics, reproducibilities of the results, and background noise are given in Table I.

We were able to calculate the amount of impurities in our samples with the technique of Klug and Alexander.[8] The sensitivity of the technique would allow us to detect as little as 0.1 wt.% β-MoS_2, 0.5 wt.% MoO_2, and 0.04 wt.% Mo. As we were unable to obtain any Mo_2S_3 for use as a standard sample, the concentration of this impurity could only be estimated. Experience with the other impurities allowed us to estimate that we should be able to detect Mo_2S_3 concentrations as small as 0.1–0.5 wt.%. Table I contains information on the concentration of impurities in our samples. By subtracting the amount of the impurities from the starting (nominal) composition, we estimated the composition of the Chevrel phase of our samples to be as follows: $SnMo_{5.88\pm0.01}S_{7.75\pm0.02}$ for the $SnMo_6S_8$ samples, $PbMo_{5.00\pm0.05}S_{7.35\pm0.03}$ for the $PbMo_6S_8$ samples, $PbMo_{6.08\pm0.02}S_{7.96\pm0.03}$ for the $PbMo_{6.20}S_8$ samples, and $PbMo_{6.04\pm0.02}S_8$ for the $PbMo_{6.35}S_8$ samples. The uncertainties in the estimated Chevrel-phase compositions are due to the uncertainties in both the known starting compositions and the amounts of impurities present. Samples prepared with the first two (stoichiometric) starting compositions contained β-MoS_2 impurities. Samples prepared with excess Mo contained no β-MoS_2 and had estimated compositions of the Chevrel phase that were nearer to the stoichiometric composition than were those of samples prepared with stoichiometric starting compositions. None of the samples had estimated final compositions that matched the perfect stoichiometric values. Several other researchers have also reported nonstoichiometric compositions for Chevrel compounds,[9] some including studies relating T_c to the nonstoichiometry.[10–12]

We calculated the lattice constants of our samples from the positions of the 101, 211, 223, 006, and 321 x-ray diffraction peaks of the $SnMo_6S_8$ sample and the 101, 122, 223, and 321 x-ray diffraction peaks of the $SnMo_xS_8$ sample and the 101, 122, 223, and 321 peaks of the $PbMo_xS_8$ samples. We scanned through each peak three times to minimize the effect of any setting errors. We chose the peak position to be the middle of the peak at half of the maximum height. This position was measured to the nearest ±0.01 deg in 2θ. We calculated lattice constants (see Table II for our samples) using a least-squares-fit computer routine.[13]

Optical microscopy, scanning electron microscopy, and electron microprobe work were all performed on polished slices of the same samples that yielded powder for the x-ray work. Each slice was mounted in a hole in an aluminum block and held in place with flexible silver paint (which also electrically connected the sample to the holder) and Torr seal. The slice was then polished on a flat surface with a succession of emery cloths, and was lapped with 1-μm diamond powder followed by 0.3-μm aluminum oxide powder.

Optical microscopy with an unpolarized Cs arc light revealed different phases by their different reflectivities. Our samples showed white areas (indicating the Chevrel phase), gray areas (which were identified as β-MoS_2), violet areas (MoO_2), and bright white areas (Mo). Qualitatively, the $SnMo_6S_8$ sample contained only a small number of gray areas (β-MoS_2) and no other phases. The $PbMo_6S_8$ contained more and larger regions of β-MoS_2 than did the $SnMo_6S_8$. MoO_2 crystals as large as 10 μm × 10 μm were also seen in the $PbMo_6S_8$, although most were much smaller than this, being barely resolvable at a magnification of 400. Our $PbMo_{6.20}S_8$ and $PbMo_{6.35}S_8$ samples also exhibited qualitative agreement between the x-ray diffraction data and the optical microscopy results.

A scanning electron microscope with an energy-dispersive x-ray analyzer confirmed our identification of the various regions seen under the optical microscope. Semiquantitative results from the electron microprobe showed that the violet-red areas had Mo concentrations that matched those of MoO_2.

We performed an experiment to determine where the MoO_2 came from. Pure Mo powder (as determined by x-ray analysis) was placed in a large quartz reaction tube, cleaned as described earlier. The tube was sealed at 10^{-5} Torr and heated at the same temperatures and for the same times as would be used in preparing a Chevrel sample. X-ray analysis of the resulting powder showed 2.5 wt.% MoO_2. We concluded that the molybdenum reacted with the oxygen in the SiO_2 tube walls. The appearance of

TABLE I. Composition and superconducting properties of the samples.

Nominal composition	$SnMo_6S_8$	$PbMo_6S_8$	$PbMo_{6.2}S_8$	$PbMo_{6.35}S_8$
Impurities				
Mo	<0.1 wt.%[a]	<0.1 wt.%[a]	0.07±0.014 wt.%	1.3±0.1 wt.%
MoO_2	<0.5 wt.%[a]	8.2±0.4 wt.%	1.0±0.1 wt.%	2.0±0.1 wt.%
β-MoS_2	2.1±0.2 wt.%	4.9±0.25 wt.%	<0.1 wt.%[a]	<0.2 wt.%[a]
Mo_2S_3	<0.1 wt.%[a]	<0.1 wt.%[a]	0.1–0.5 wt.%	<0.1 wt.%[a]
T_c (K)	11.788±0.039	13.385±0.020	12.584±0.156	11.806±0.018
δT_c (mK)	113±11	317±16	238±66	151±29
dH_{c2}/dT (kG/K)	−32.87±0.37	−44.39±0.19	−44.82±0.51	−38.16±0.79

[a] Detection limit (none of this impurity was found).

TABLE II. Hexagonal lattice parameters of the samples.

Nominal composition	$SnMo_6S_8$	$PbMo_6S_8$	$PbMo_{6.2}S_8$	$PbMo_{6.35}S_8$
a (Å)	9.1608±0.0020	9.1961±0.0057	9.1896±0.0073	9.1944±0.0076
c (Å)	11.3439±0.0032	11.432±0.031	11.433±0.041	11.404±0.041
V_H (Å^3)	824.44±0.39	837.2±1.7	836.9±2.2	834.9±2.3

MoO_2 may partially explain the dependence of the superconducting transition temperature on the quality and size of quartz tubes.

IV. SUPERCONDUCTING PROPERTIES

Before we cut up our samples for the characterization work, we measured some of their superconducting properties. The transition temperature (T_c) was measured inductively, with T_c defined as the midpoint of the transition. The transition width (δT_c) was also defined in the usual way as the temperature difference between the 10% and 90% points of the transition. All temperatures were measured with a germanium resistance thermometer. The thermometer was also calibrated for use in magnetic fields up to 30 kG. A capacitance thermometer (which is insensitive to magnetic fields) was used as a transfer standard. All temperatures are accurate to ±4 mK and refer to the T58 temperature scale. The temperature was kept stable to better than 0.1 mK by a temperature controller. The magnetic field was provided by a superconducting solenoid capable of reaching 30 kG. Using a Hall-effect probe, we were able to measure fields to ±0.05 kG. We were thus able to measure the upper critical field H_{c2} as a function of temperature. Transition curves were taken by sweeping the temperature through the transition at a rate less than 0.3 mK/sec with the magnetic field held fixed. Two curves were always taken, the first while the sample was warmed up, the second while it was cooled down. In all cases T_c's determined from the two curves agreed to better than ±10 mK.

Transition temperatures for $SnMo_6S_8$ were made on six samples, of which four were made in one set and the other two in two other sets. The transition-temperature measurements of the lead-based Chevrel samples were made on four samples of the same set for each composition. Table I contains the T_c data. The uncertainty given with each mean is the standard deviation of the individual T_c values. The sample with the transition temperature (in zero field) that was closest to the mean of the T_c's of the samples in a given set was chosen for further study. For this sample, values of H_{c2} were determined at a number of temperatures. The transition temperatures of all samples were measured at both 0 and 30 kG. We compared the standard deviation of the transition temperatures at both of these fields. If these standard deviations were within a factor of 2, we assumed that the $H_{c2}(T)$ curves of these samples would also agree with each other along their entire length to within the larger standard deviation. The critical field data are presented in Figs. 1 and 2.

Note that in Figs. 1 and 2 there is a positive curvature of $H_{c2}(T)$ below about 10 kG. This is similar to the curvature seen also by Tulina,[14] although our curves do not bend and then become linear again at low fields as his do. This type of curvature is sometimes attributed to sample inhomogeneities. However, we know of no systematic studies of the effect of inhomogeneities on the linearity of $H_{c2}(T)$ near T_c in type-II superconductors. It has been

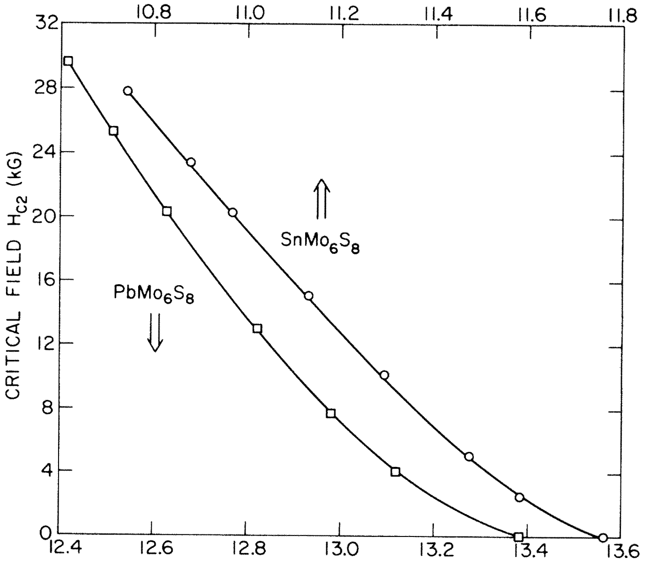

FIG. 1. Upper critical field (H_{c2}) as a function of temperature for $SnMo_{6.00}S_8$ and $PbMo_{6.00}S_8$.

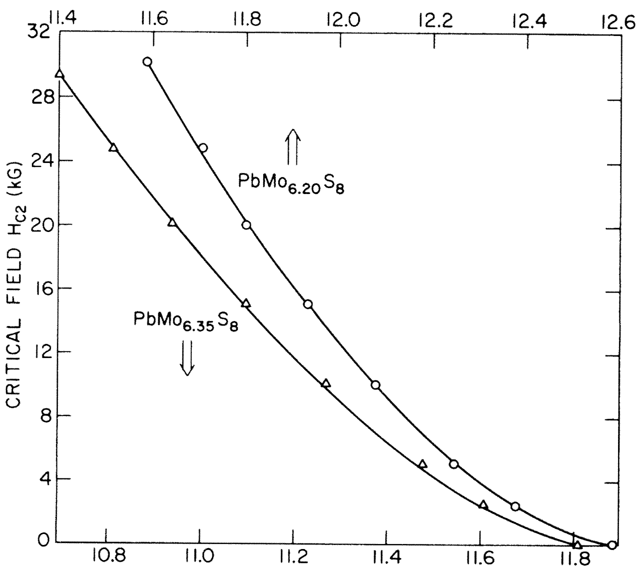

FIG. 2. Upper critical field (H_{c2}) as a function of temperature for $PbMo_{6.20}S_8$ and $PbMo_{6.35}S_8$.

shown in general that anisotropy of the Fermi surface can affect the shape of $H_{c2}(T)$ of bulk type-II superconductors.[15] Such Fermi-surface anisotropy is possible in light of the 20% directional anisotropy of H_{c2} found in $PbMo_6S_8$ and other Chevrel compounds.[16]

Because of the curvature below 10 kG, we determined all of the dH_{c2}/dT values (quoted in Table I) by linear-regression fits to the points at fields above the region of this curvature. Our values for dH_{c2}/dT are lower than those quoted in the literature. Typical values range from 37 kG/K (Ref. 6) to 47 kG/K (Ref. 17) for bulk samples of the tin-based compound and from 50 kG/K (Ref. 12) to 60 kG/K (Ref. 18) for bulk samples of the lead-based compound.

V. SUMMARY

Our purest lead-based samples had a formula of $PbMo_{6.20}S_8$. They contained 1.0 wt. % MoO_2 and less than 1 wt. % total of all other impurities. We had difficulty in grinding these samples because they were semimalleable; this difficulty may be related to the lower reproducibility of the transition temperature for this composition, as compared to that of the other samples.

Our samples of $SnMo_6S_8$ and $PbMo_xS_8$ ($x = 6.00$ and 6.35) exhibited transition temperatures with reproducibilities at least 5 times better than those found in the current literature. Our $PbMo_{6.20}S_8$ samples had transition temperatures as reproducible as those found in current literature. All samples also had reasonably narrow transition widths (a few hundred mK). We believe that the final quality of our samples relative to those described in the literature is a result of two factors: (1) our use of SnS or PbS rather than Sn or Pb, respectively, for starting materials, and (2) the sifting of the ground samples to provide a more uniform powder size before these samples were pressed and sintered.

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