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Superconducting Properties, Chemical Compositions, and Lattice Parameters of Pb-, Sn- and $(Pb_{1-x}Sn_x)Mo_6S_8$

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Abstract: The values of critical temperatures for alloys of Pb- and $SnMo_6S_8$ were shown to be lower than those of the respective pure Chevrel phases. Chemical compositional analysis of the compounds revealed that the decreased T_c in the alloys are due to the off-stoichiometric compositions in the alloys. Although alloying slightly increased the values of the upper critical field H_{c2} over that for $PbMo_6S_8$, the H_{c2} values for these specimens were substantially lower than those which have been reported for $PbMo_6S_8$. Possible causes for these depressed values of H_{c2} are discussed.

I. INTRODUCTION

Over the last several years, the Chevrel phases, particularly $PbMo_6S_8$ and $SnMo_6S_8$, have received considerable attention as a possible superconducting material for production of very high magnetic fields. This is due to the fact that both $PbMo_6S_8$ and $SnMo_6S_8$ are reported [1][2] to have very large upper critical magnetic fields H_{c2}, 290 and 510 kG at 4.2 K, respectively even though their values of superconducting critical temperatures T_c (~14.5 K) are lower than that (~18 K) for Nb_3Sn. However, the extrapolated values of H_{c2} for wires or strips of $PbMo_6S_8$ have been substantially lower (e.g. ~350 kG) [3]-[6] than those which are reported for the powders [1][2] and the single crystals [7]. Since the values of H_{c2} have a strong influence on J_c at very high magnetic fields, relatively low J_c, which was found in the wires, were thought to be due to the low H_{c2}. Thus, we have explored the possibilities of increasing H_{c2} through formation of the pseudo-ternaries between Pb- and $SnMo_6S_8$ using a vapor-solid reaction method for the preparation. It was found that the critical temperatures decreased upon alloying from those for the pure phase compound. This decrease was then shown to be associated with the off-stoichiometric compositions in the alloys. The values of $H_{c2}(T)$ for these alloys were also measured. Although a slight increase in H_{c2} (4.2 K) was found, the maximum value, 405 kG, was significantly lower than the values for powders [1][2] and single crystals [7] of $PbMo_6S_8$. Possible sources for the depressed H_{c2} in the current specimens are discussed as well as the method of the chemical compositional analysis.

II. EXPERIMENTAL PROCEDURE, RESULTS, AND DISCUSSION

The Chevrel phase compounds for this study were prepared by reaction of Mo sheets with Pb and S vapors in sealed quartz tubes [3][4]. The procedure placed a couple of strips of Mo in a quartz tube with several pieces of metal chips, Pb, Sn, or (Pb + Sn) and MoS_2 flakes. (The compositions of the pseudo-ternaries were chosen by the relative amounts of Pb and Sn in the capsule.) The capsule was then heated for 20-40 h at 1030°C to grow 20-50 μm thick layers of the compounds on both sides of the Mo strips. As shown previously [8], it is crucial to minimize the amounts of oxygen inclusions in the compounds for synthesis of high T_c specimens of the Chevrel phase. For this reason, MoS_2 flakes were specially prepared by the reaction of Mo sheets with out-gassed sulfur particles.

The inductively measured critical temperatures for pure $PbMo_6S_8$ and $SnMo_6S_8$ specimens were 14.8 and 14.75 K, respectively, as defined by the midpoint of the transition. Since the c/a ratio of the compounds can be used as a measure of the quality of the compounds, particularly related to the oxygen contents [8], we have measured the lattice parameters of the compounds and compared that with the data of Hinks et al. [8]. This comparison indicated that the compounds made by this procedure were low in oxygen and crystallographically of high quality.

Establishing the high quality of the pure Chevrel phase compounds, we proceeded to prepare the alloys of Pb- and $SnMo_6S_8$ by placing appropriate amounts of Pb and Sn chips in quartz tubes and the combined materials were treated as before. The amounts of Pb and Sn in each capsule and the critical temperatures of the alloys as well as the lattice parameters for some of the compounds are listed in Table I. As shown in the table, the values of T_c decreased with increasing amounts of the incorporated Sn in $PbMo_6S_8$.

In order to determine the cause for the depression, a scanning Auger electron spectroscopy (PHI 600) was used for chemical analysis of the compounds. (Since the specimens contain fine precipitates of Pb and Sn, a standard electron microprobe could not be used to determine the compositions of the Chevrel phases.) The sensitivity factor, i.e., the strength of the Auger electron signal from each element, depends on its chemical environment. Thus, we measured the relative sensitivity factors for each metallic element, Pb, Sn, and Mo, against S using similarly prepared PbS_2, SnS_2, and MoS_2. Then, the sensitivity factors of these elements were assumed to be the same in the Chevrel phases as in the disulfides. The results of the measurements are listed in Table II. Also, listed are the compositions for the sum of the Pb and the Sn contents in each specimen. These decreased significantly from the stoichiometric

Table I. Preparation Conditions and Properties of (Pb,Sn)Mo_6S_8

Specimen	Start. Comp.(g)		Lattice Parameters (Å)			T_c(ac) Mid.
I.D.	Pb	Sn	c	a	c/a	(K)
1004	0.5	—	11.496	9.196	1.250	14.8
S107	0.5	0.05	—	—	—	14.7
S108	0.5	0.2	—	—	—	14.4
S109	0.5	0.5	11.460	9.188	1.247	14.1
S111	0.2	0.5	11.434	9.183	1.245	13.9
S112	0.1	0.5	—	—	—	—
S113	—	0.5	11.394	9.176	1.242	14.76

Table II. Compositions of (Pb,Sn)Mo_6S_8(a)

Specimen	Start. Comp.(g)		Measured Compositions (at.%)				
I.D.	Pb	Sn	Pb	Sn	Mo	S	(Pb+Sn)
1004	0.5	—	6.9±1.3	0.3±0.1	48.1±2.9	44.7±1.9	6.9
S107	0.5	0.05	5.2±0.5	0.9±0.2	42.4±2.9	51.6±2.3	6.1
S108	0.5	0.2	(3.3)(b)	(1.3)	—	—	(4.6)
S109	0.5	0.5	2.3±0.6	1.7±0.2	44.4±1.9	51.5±1.6	4.1
S111	0.2	0.5	1.7±0.5	4.3±0.6	41.7±4.7	52.3±4.5	6.1
				(2.3)			(3.9)
S112	0.1	0.5	1.3±0.5	3.0±0.8	42.1±2.5	53.6±1.4	4.3
S113	—	0.5	0.9±0.2	6.8±1.7	39.1±2	53.2±1.1	6.8
—	Stoichiometric		—	—	40.0	53.3	6.7

(a) All compositions are measured with an Auger electron microprobe and are normalized after subtracting measured counts for O and C.

(b) The values within parenthesis are interpolated values.

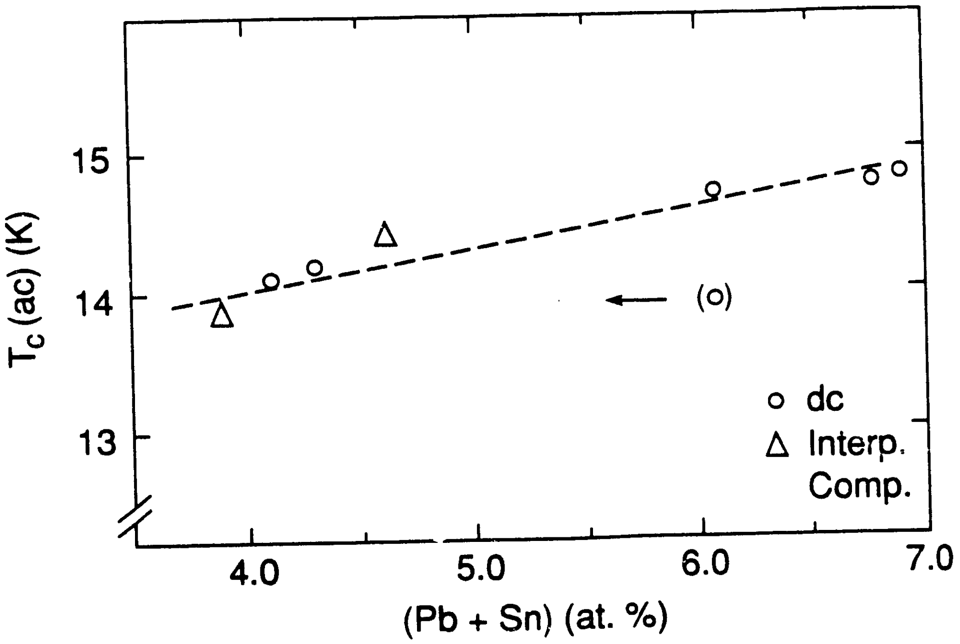

Fig. 1. Critical temperatures for (Pb, Sn)Mo_6S_8 are plotted as a function of the (Pb + Sn) content.

composition of 6.7 at.% as the Sn content increased even though both of the pure compounds contained approximately the stoichiometric value. In Fig. 2 the inductively measured T_c is plotted as a function of the total (Pb + Sn) content. It is shown that the values of T_c depend linearly on the (Pb + Sn) content, and the suppression in T_c for the alloys is likely to be due to their compositions becoming off-stoichiometric. However, what causes the off-stoichiometric compositions in the pseudo-ternaries is not clear at this point when the similarly processed Pb- and $SnMo_6S_8$ are shown to be stoichiometric.

The upper critical magnetic fields, H_{c2}, for the above specimens were measured as a function of temperature by a resistive 4-probe method in dc magnetic fields up to 23 kG. $H_{c2}(T)$ was defined as the midpoint of the resistive transitions as the magnetic field was swept slowly through the transition. For selected samples, a noncontacting rf technique, measuring the onset of the transition was used to define $H_{c2}(T)$. In general, the rf technique gave values of $H_{c2}(T)$ somewhat above those measured by the dc technique.

Several features of these alloyed Chevrel phase materials are summarized in Fig. 2. First, the values of T_c measured by our dc and rf measurements in Fig. 2 are lower than those in Fig. 1, measured by ac techniques. This reflects the fact that the ac method favors the onset of the fraction of the superconductor which has the highest T_c whereas the T_c values given for the other methods is obtained by extrapolation of the $H_{c2}(T)$ data on $H_{c2} = 0$.

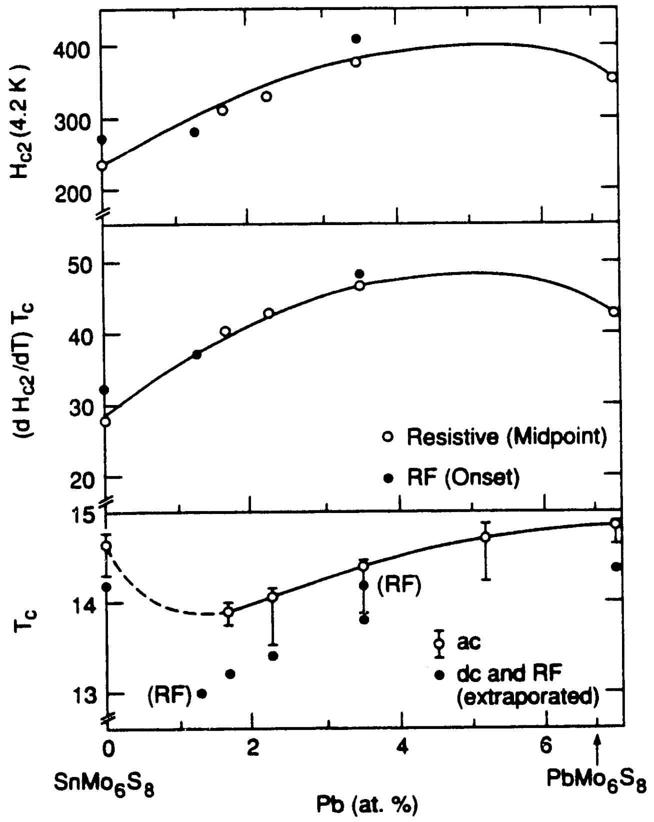

Fig. 2. Critical temperatures, magnetic fields and the slopes (dH_{c2}/dT) are plotted as a function of the Pb content.

The values of $H_{c2}(T)$ at (4.2 K) are extrapolated from the dc data based on a fit of the data to the predictions of a dirty type II superconductor (WHHM). Our previous work has shown that such fits are well satisfied for various Chevrel phase systems [1]. Because $(dH_{c2}/dT)_{T=T_c}$ increased more rapidly than the decrease in T_c as Pb is added to $SnMo_6S_8$, there is an increase in H_{c2}(4.2 K) with increasing Pb. However, the data for the pure $PbMo_6S_8$ are unexpected; the value of $(dH_{c2}/dT)_{T=T_c}$ is much lower than that reported [1] earlier (60 kG/K). If the earlier values are used then there would be a nearly-linear variation of $(dH_{c2}/dT)_{T=T_c}$ and H_{c2}(4.2 K) versus Pb additions.

As shown in the various results of Ref. [1], small changes in stoichiometry from the pure Chevrel phase first increases $(dH_{c2}/dT)_{T=T_c}$ slightly. Further changes in stoichiometry do not affect this slope but do depress T_c, resulting in lower $H_{c2}(T)$ values. In our work it is clear that the addition of Pb strongly affects the slope. However, the pure $PbMo_6S_8$ slope is anomalously low. The reason is not clear but we suspect that this may reflect the effect of the large thermal expansion mismatch between the Mo substrate and the pure $PbMo_6S_8$. Apparently this is not serious for $SnMo_6S_8$ and the alloys. This may be related to the observations, which were made by Meingast et al., of the low temperature anomaly in the thermal expansivity for $PbMo_6S_8$ but not for $SnMo_6S_8$ [12].

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