

## Effects of oxygen on the upper critical fields of lead and tin molybdenum sulfide Chevrel phases

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The upper critical fields,  $H_{c2}$ , of  $\text{SnMo}_6\text{S}_{8-x}\text{O}_x$  and  $\text{PbMo}_6\text{S}_{8-x}\text{O}_x$  Chevrel-phase materials with controlled oxygen content were measured with dc and pulsed magnetic fields. The present results and those of many earlier investigations are explained by the presence of oxygen. Observations of increases in  $T_c$  and the variation of  $H_{c2}$  obtained by additions of Gd or Al are explained by the getting of oxygen by these additives. The highest  $T_c$  materials, which have the lowest oxygen content, do not have the highest  $H_{c2}(0)$ .

Recently the effects of oxygen on  $T_c$ , the pressure dependence of  $T_c$ , and the structure of the oxygen defect in well characterized Chevrel phase  $M\text{Mo}_6\text{S}_{8-x}\text{O}_x$  where  $M = \text{Pb}$ ,  $\text{Sn}$ , and  $\text{Eu}$  have been reported.<sup>1-5</sup> These studies demonstrated that much of the earlier research over the last decade must be reexamined because in general the presence and effects of oxygen were not considered. The strong dependence of  $T_c$  on oxygen content in the Chevrel-phase materials also must influence the upper critical field  $H_{c2}$ . In this Rapid Communication we report on measurements of  $H_{c2}(T)$  for  $\text{PbMo}_6\text{S}_{8-x}\text{O}_x$  and  $\text{SnMo}_6\text{S}_{8-x}\text{O}_x$  (hereafter referred to as  $\text{PbMoS}$  and  $\text{SnMoS}$ ). The results show systematic variations of  $H_{c2}(T)$  as a function of added oxygen and also indicate why earlier measurements of  $H_{c2}(T)$  for  $\text{PbMoS}$  varied over a wide range.<sup>6-8</sup> Increases in  $T_c$  for Gd additions<sup>8-11</sup> to  $\text{PbMoS}$  and Al additions<sup>6-8</sup> to  $\text{SnMoS}$  and their effects on  $H_{c2}(T)$  can be explained if we assume that Gd or Al act as getters and remove excess oxygen from these Chevrel-phase materials. Furthermore, *very pure*  $\text{PbMoS}$  and  $\text{SnMoS}$  materials will have a higher  $T_c$ , but may have a lower  $H_{c2}(0)$  and  $(dH_{c2}/dT)_{T=T_c}$ .

The materials with controlled oxygen content used for this work were synthesized as described previously<sup>3</sup> and are portions of the identical materials used for the investigations of the pressure dependence<sup>4</sup> of  $T_c$ . The starting compositions,  $T_c$  (measured using ac susceptibility), and lattice constants are given in Ref. 4. The actual oxygen content of the samples is not known; however, it will scale with oxygen added to the starting mixture ( $x$  values in Table I). The quantity  $x$  is used to identify the particular samples used in this study. For the Sn system, the total oxygen content  $x_T$  has been estimated at  $x + 0.07$ , i.e.,  $\text{SnMo}_6\text{S}_{8-x-0.07}\text{O}_{x+0.07}$ .<sup>5</sup> The 0.07 oxygen content is unintentionally incorporated during the synthesis and is assumed to be constant for all the  $\text{SnMoS}$  samples. The only exception is the  $x=0$   $\text{SnMoS}$  sample listed in Table I which has been gettered with  $\text{Gd}_2\text{S}_3$  as described in Ref. 3 and is oxygen free. This gettering procedure has not been successful for the  $x=0$   $\text{PbMoS}$  sample. Thus, this sample contains oxygen. The total oxygen content  $x_T$  shown in Table I for the  $\text{PbMoS}$  samples is assumed to contain 0.07 unintentionally incorporated oxy-

gen (the same as found for the  $\text{SnMoS}$  samples) in addition to the added oxygen. The absolute values for the oxygen content are still somewhat uncertain, but the relative values illustrate the important trends.

Measurements of  $H_{c2}(T)$  were made in dc fields with water-cooled Bitter magnets or the hybrid (30 T) magnet at the Francis Bitter National Magnet Laboratory using techniques discussed earlier.<sup>6</sup> Measurements above this dc field range were made in the pulsed field user facility at the laboratory. This facility uses multilayer copper coils reinforced by a hardened steel structure and cooled to liquid-nitrogen temperature. These magnets are identical to those used earlier.<sup>6</sup>

It should be noted that for both the  $\text{PbMoS}$  and  $\text{SnMoS}$  materials, the width of the  $H_{c2}(T)$  transition varies with field and at 20 T reaches approximately 3 T for  $\text{SnMoS}$  and approximately 5 T for  $\text{PbMoS}$ . Such broad temperature-dependent transitions limit the resolution of the data. As before<sup>13</sup> we define  $H_{c2}$  as the field at the knee where the material becomes nonsuperconducting. This definition of  $H_{c2}$  leads to a higher value of  $T_c$  (given in Table I) than found in Ref. 4.

The effects of added oxygen on  $H_{c2}(T)$  of  $\text{SnMoS}$  are illustrated in Fig. 1. Extrapolations of the dc results assuming a dirty type-II superconductor and no paramagnetic limiting (the dashed lines) are shown in Fig. 1 along with pulsed field data points at 4.2 K. For all the figures presented here, the solid lines are dc field data, the dashed lines are theory based on extrapolations of this data and the points at 4.2 K are pulsed field data. Agreement with the theory is within experimental error as previously observed.<sup>6,12</sup>

The  $\text{SnMoS}$  materials show rapid changes in  $T_c$  and  $(dH_{c2}/dT)_{T=T_c}$  with a small ( $x=0.10$ ) initial oxygen incorporation. Although the oxygen-containing samples show a  $(dH_{c2}/dT)_{T=T_c}$  which is independent of  $x$ , the  $x=0$  value is considerably lower (see Fig. 1 and Table I). The lowest oxygen content sample ( $x=0$ , gettered) has the highest  $T_c$ , but not the highest  $H_{c2}(0)$ . Pulsed field measurements for this sample showed a broad transition at 4.2 K which extended up to that shown for the  $x=0.05$  sample

TABLE I. Characteristics of oxygen containing  $\text{PbMo}_6\text{S}_8-x\text{O}_x$  and  $\text{SnMo}_6\text{S}_8-x\text{O}_x$  Chevrel-phase materials compared with some earlier materials (for which the oxygen content is not known).  $x$  and  $x_T$  are the added and total oxygen content, respectively.

	$x$	$x_T$	$T_c$ (K)	$(dH_{c2}/dT)_{T=T_c}$ (T/K)	Measured $H_{c2}(4.2\text{ K})$ (T)	Calculated $H_{c2}(0)$ (T)
SnMoS	0	0	14.5	3.0	28-31	30
	0.05	0.12	12.6	3.9	28	34
	0.10	0.17	10.9	3.9	23	30
	0.20	0.27	9.8	4.0	20	27
SnMoS (Refs. 6, 12)			13.4	3.7	29	34
SnAlMoS (Refs. 6, 12)			14.2	3.1	28	31
PbMoS	0.0	0.07	14.4	5.7	49 <sup>a</sup>	57
	0.05	0.12	13.1	5.6	42 <sup>a</sup>	51
	0.15	0.22	11.2	5.7	35	44
PbMoS (Refs. 6, 12)			14.4	6.0	51	60
$\text{Gd}_x\text{Pb}_{1.2}\text{MoS}$ (Ref. 10)	0.012		13.9	5.0	39-42	48
	0.24		14.8	4.9	42-45	51

<sup>a</sup>Calculated value.

suggesting that a portion of this sample contained some lower  $T_c$  material having higher  $H_{c2}$ .

The dc field measurements of  $H_{c2}(T)$  for PbMoS for nominally  $x=0, 0.05$ , and  $0.15$  oxygen are shown in Fig. 2. The highest  $T_c$  [and  $H_{c2}(T)$ ] is observed for the lowest  $x$ , and  $(dH_{c2}/dT)_{T=T_c}$  is large and independent of  $x$ . Such effects were also observed earlier by us for materials with various compositions.<sup>6,12</sup> The extrapolation of the dc results and the pulsed field result for the  $x=0.15$  PbMoS sample are shown in Fig. 3. The data from the earlier work for the

60-T PbMoS of Ref. 6 (labeled NML-3) are also shown for comparison. It is expected that if a pure (gettered  $x_T=0$  oxygen) PbMoS sample could be obtained it would show an increase in  $T_c$  and a decrease in  $(dH_{c2}/dT)_{T=T_c}$  and  $H_{c2}(0)$ .

Table I compares the results for the PbMoS and SnMoS material with controlled oxygen content with some previously reported results. The nominally pure PbMoS and SnMoS from Refs. 6 and 12 show values of  $(dH_{c2}/dT)_{T=T_c}$  and of

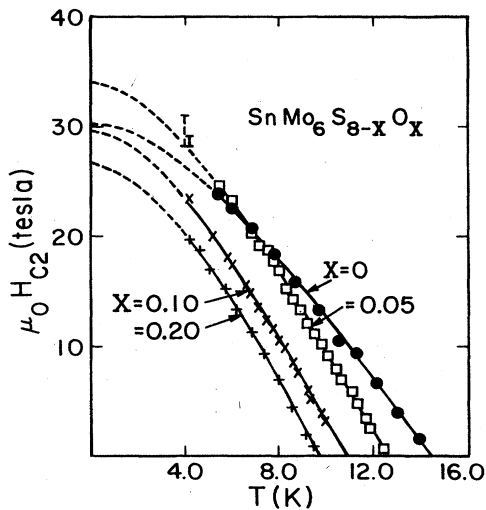


FIG. 1.  $H_{c2}$  vs  $T$  for  $\text{SnMo}_6\text{S}_8-x\text{O}_x$ . The solid lines are for dc data and the long dashes are theory for a dirty type-II superconductor with no Pauli paramagnetic limiting. The error bars at 4.2 K are for pulsed field measurements. The  $x$  is added oxygen (see Table I).

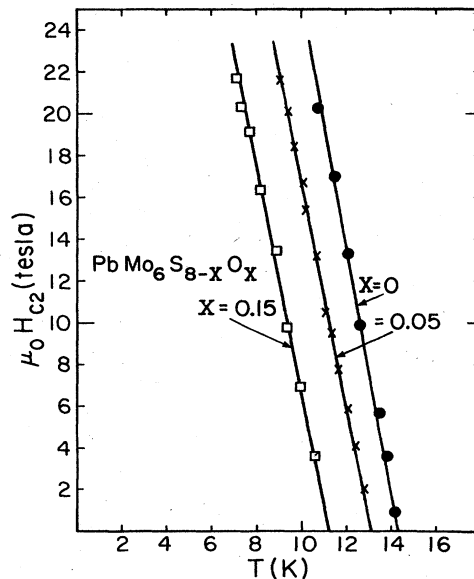


FIG. 2. High-temperature upper critical field,  $H_{c2}$ , vs temperature  $T$ , for nominally pure ( $x=0$ ) and oxygen containing  $\text{PbMo}_6\text{S}_8-x\text{O}_x$ . The  $x$  is added oxygen (see Table I).

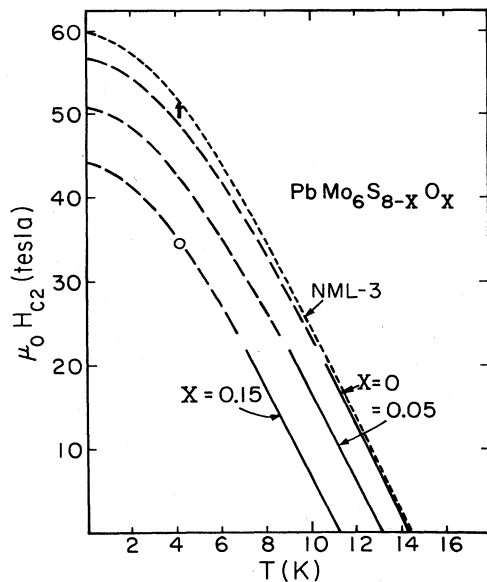


FIG. 3.  $H_{c2}$  vs  $T$  for  $\text{PbMo}_6\text{S}_{8-x}\text{O}_x$ . The solid and dashed curves are as in Fig. 1. The short dashed curve is PbMoS data of Ref. 6, shown as NML-3.

$H_{c2}(0)$  consistent with small oxygen content. The PbMoS sample is close to our  $x=0$  (ungettered sample) and the SnMoS sample is between our  $x=0$  ( $\text{Gd}_2\text{S}_3$  gettered) and  $x=0.5$  sample.

The Al addition to SnMoS gives a sample which is very similar to our  $x=0$  ( $\text{Gd}_2\text{S}_3$  gettered) sample. Similarly, the addition of Gd to PbMoS (Fig. 4 and Table I) shows an increase in  $T_c$  and a substantial decrease in  $(dH_{c2}/dT)_{T=T_c}$ . The interesting features of the PbMoS with Gd additions are (1) a slightly higher  $T_c$  (14.8 K) is observed for the highest Gd content, (2) both materials with Gd additions show values of  $(dH_{c2}/dT)_{T=T_c}$  well below that for all the PbMoS materials in Table I, and (3) as a result  $H_{c2}(0)$  is quite low for these materials despite the high values of  $T_c$ .

If we assume that Gd or Al acts as an oxygen getter in the Chevrel-phase materials, we obtain a consistent picture for various observations over the last decade. The data in Ref. 8 show that  $T_c=11.7$  K for SnMoS is raised to  $T_c=14.4$  K when Al is added. Similarly, data of Ref. 9 show a  $T_c$  from 11.0 to 12.6 K for PbMoS which increased to  $T_c=14.3$  K for additions of Gd. In general, for both PbMoS (Ref. 14) and SnMoS (Ref. 15) the addition of rare-earth ( $R$ ) metals leads to an increase in  $T_c$  up to  $\approx 20$  at. %  $R$  (i.e.,  $\text{SnR}_{0.2}\text{Mo}_6\text{S}_8$ ).

For SnMoS containing oxygen, small additions of reactive metals getter the oxygen and raise  $T_c$  and  $H_{c2}(T)$ . If the amount of reactive metal added is sufficient to remove all of the oxygen,  $(dH_{c2}/dT)_{T=T_c}$  and  $H_{c2}(0)$  are reduced despite the increased  $T_c$ . A parallel argument can be applied for reactive metal additions to PbMoS.

Additions of Eu to  $M\text{MoS}$  appear to be consistent with the above conclusions. Fischer, Treyvaud, Chevrel, and Sergent<sup>16</sup> found a relatively constant  $T_c \approx 11$  K for  $\text{Sn}_{1.2(1-x)}\text{Eu}_x\text{Mo}_{6.35}\text{S}_8$  for  $0 \leq x \leq 0.3$ . This is expected if Eu does not getter oxygen in the SnMoS system. The observation that oxygen can enter the EuMoS lattice and influence the pressure-dependent superconducting properties of

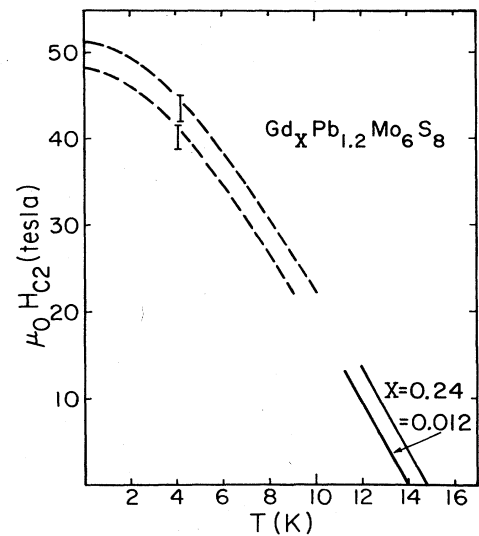


FIG. 4.  $H_{c2}$  vs  $T$  for  $\text{Gd}_x\text{Pb}_{1.2}\text{Mo}_6\text{S}_8$ .

the material indicates that Eu is not an efficient oxygen getter.<sup>1-4</sup> The maximum concentration of oxygen incorporated into the lattice will be determined by the oxygen activity of the oxygen-containing impurity phase. In the  $R\text{MoS}$  system this will be  $R_2\text{O}_2\text{S}$ .  $\text{Eu}_2\text{O}_2\text{S}$  has the least negative free energy of formation<sup>17</sup> (due to its stable divalent oxidation state) of the rare-earth metals; therefore, it will allow the largest concentration of oxygen defects because of the high oxygen partial pressure.

The present results and related research<sup>1-5</sup> on  $M\text{MoS}$  materials fabricated with controlled oxygen content demonstrate that the presence of oxygen strongly influences the superconducting properties of  $M\text{MoS}$  materials. The same behavior of  $T_c$ ,  $(dH_{c2}/dT)_{T=T_c}$ , and  $H_{c2}$  with increasing oxygen content is observed in both the Sn and PbMoS systems. In the SnMoS system, the first small addition of oxygen (up to  $x \approx 0.10$ ) increases the  $H_{c2}(0)$  and  $(dH_{c2}/dT)_{T=T_c}$  while decreasing  $T_c$ . Further additions of oxygen reduce  $T_c$  linearly<sup>3</sup> with oxygen content;  $(dH_{c2}/dT)_{T=T_c}$  remains approximately constant and  $H_{c2}$  is reduced. Similar effects of purity [i.e., increased  $T_c$  and reduced  $(dH_{c2}/dT)_{T=T_c}$  and  $H_{c2}(0)$  as purity increased] have been observed in other high  $T_c$  materials [such as  $\text{Nb}_3\text{Sn}$  (Ref. 18)].

Much of the data published over the last decade did not catalog the oxygen content. However, a consistent picture of the variation of  $T_c$  and  $H_{c2}(T)$  is obtained for all the literature on  $M\text{MoS}$  materials as a function of added Gd or Al if these additives are assumed to act as getters which remove oxygen from materials with substantial oxygen. The results also suggest that most of the SnMoS and PbMoS materials reported in the literature to date had substantial oxygen content resulting in low values of  $T_c$ . Thus, the oxygen content is an important ingredient in characterizing the Chevrel-phase materials.

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