Rapid Communications

Effect of pressure and oxygen defects in divalent Chevrel-phase superconductors

D. W. Capone II and R. P. Guertin*
Tufts University, Medford, Massachusetts 02155

S. Foner†
*Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139*

D. G. Hinks and H. C. Li‡
Argonne National Laboratory, Argonne, Illinois 60439
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The pressure dependence of the superconducting transition temperature T_c is measured for several samples each of the divalent Chevrel-phase systems $SnMo_6S_8$, $PbMo_6S_8$, and $EuMo_6S_8$. The pressure dependence of T_c scales with T_c and each system has the same scale factor. The data are discussed in terms of oxygen defects systematically introduced into each system and in terms of the lattice constants. Oxygen defects inadvertently introduced into Chevrel-phase superconducting systems may account for the wide variation of T_c quoted in the literature.

In this Rapid Communication we show that the divalent Chevrel-phase systems SnMoS, PbMoS, and EuMoS are sensitive to the systematic and controlled introduction of oxygen. In all of the compounds studied, as oxygen is added to the system, T_c decreases, the c-axis dimension and the unit-cell volume V decrease, and the pressure dependence of T_c becomes less negative. Research efforts in the past few years on the high-T_c Chevrel-phase superconductors, e.g., $PbMo_6S_8$ and $SnMo_6S_8$, here called "PbMoS" and "SnMoS," were largely directed towards optimizing the superconducting properties of these materials, i.e., T_c, H_{c2}, and j_c.[1] Pb and Sn are both divalent in their respective Chevrel-phase compounds,[2] and divalency of the metal ion appears to be correlated with high T_c. Two other examples of divalent metal ion Chevrel phases are YbMoS and EuMoS. The former has $T_c = 9$ K (Ref. 3) at ambient pressure, whereas the latter exhibits pressure-induced superconductivity[4] and requires an applied pressure of about 12 kbar before it becomes superconducting ($T_c \simeq 12$ K). However, once superconducting, the properties of EuMoS are similar to other divalent Chevrel-phase superconductors.[5] The results presented here and from other recent work[5-7] account for the wide variation in T_c and other superconducting properties reported for these systems.

The samples were prepared as described in Ref. 7 for the PbMoS and SnMoS systems and in Ref. 5 for the EuMoS system. In Table I we list the starting compositions and the lattice constants for the samples prepared by us. The compositions have been normalized to a value of 8.00 for the S atoms. The amount of oxygen unintentionally introduced during synthesis is unknown, and it will shift the quoted ox-

ygen content by a constant amount. The best estimate for this amount is 0.05. Since T_{c0} (the $P = 0$ transition temperature) is a linear function of oxygen content,[5-7] we show the pressure-dependent T_c data as a function of T_{c0} (which is an extrapolated value for EuMoS). For those cases where we have used data from other sources, the oxygen content is unknown; however, these samples can be characterized by T_{c0}, which is directly proportional to the amount of oxygen in the samples.[5-7]

The samples were placed in small beryllium copper pressure clamp devices with the use of a 1:1 mixture of n-pentane and isoamyl alcohol as the pressure-transmitting medium. Care was taken to assure that strains were not introduced in handling the samples, as these were found to broaden T_c appreciably. The experimental methods used to obtain the data are described in Ref. 5.

Figure 1 shows typical ac susceptibility data for two SnMoS samples. A transition is shown in the inset. The transition widths varied from 0.1 to 1 K for all the samples. No broadening of T_c with increased pressure was noted, indicating that the pressures were hydrostatic. In all cases, the order in which the pressure data were taken was changed frequently, and no hysteresis was observed. An interesting feature was observed for all the PbMoS samples including that of Ref. 8: the zero-pressure transition widths were about 1 K, but narrowed to about 0.5 K upon application of a small amount of pressure.

Figure 2 shows dT_c/dP vs T_{c0} for three $MMoS$ systems ($M = $ Pb, Sn, and Eu). T_c vs P for one of the PbMoS samples from Ref. 3 was nonmonotonic so that the value extrapolated from the high-pressure slope of T_c vs P was used in

TABLE I. Starting compositions and lattice constants for the samples prepared by us. The compositions are normalized to a value of 8.00 for S. The compositions should be read $M_a Mo_b S_c O_x$.

| | Starting composition | | | | | Lattice constants | |
| | | | | | | a (Å) | c (Å) |
	a	b	c	x	T_{c0} (K)	±0.002	±0.005
$M = $ Sn	1.00	6.00	8.00	0.00	14.40	9.177	11.397
	1.00	6.10	8.00	0.05	12.50	9.175	11.377
	0.97	6.18	8.00	0.10	10.80	9.169	11.359
	0.97	6.28	8.00	0.20	9.45	9.175	11.331
$M = $ Pb	1.00	6.05	8.00	0.00	14.00	9.199	11.483
	1.00	6.10	8.00	0.05	12.60	9.199	11.468
	1.00	6.20	8.00	0.15	10.90	9.195	11.431
$M = $ Eu	1.00	6.00	8.00	0.00	15.05	9.182	11.560
	0.99	6.07	8.00	0.03	12.50	9.180	11.535
	0.97	6.15	8.00	0.08	10.48	9.184	11.514
	0.96	6.23	8.00	0.13	9.06	9.184	11.481

that case. T_{c0} for EuMoS was also extrapolated from the high-pressure slope.[5] Two features of Fig. 2 should be noted: First, dT_c/dP decreases linearly as T_{c0} decreases. Secondly, the slope of dT_c/dP vs T_{c0} for all three systems is *constant* to better than 8%, the only difference between them being the initial superconducting transition tempera-

ture for each system. The lines drawn on the figure are least-mean-square fits to the data points for each system, and they have slopes of −0.032, −0.033, and −0.035 $kbar^{-1}$ for the Pb, Sn, and Eu systems, respectively.

The data presented here clearly show that the pressure dependence of T_c scales with T_{c0} and that the scale factor is essentially the same for all three divalent Chevrel-phase su-
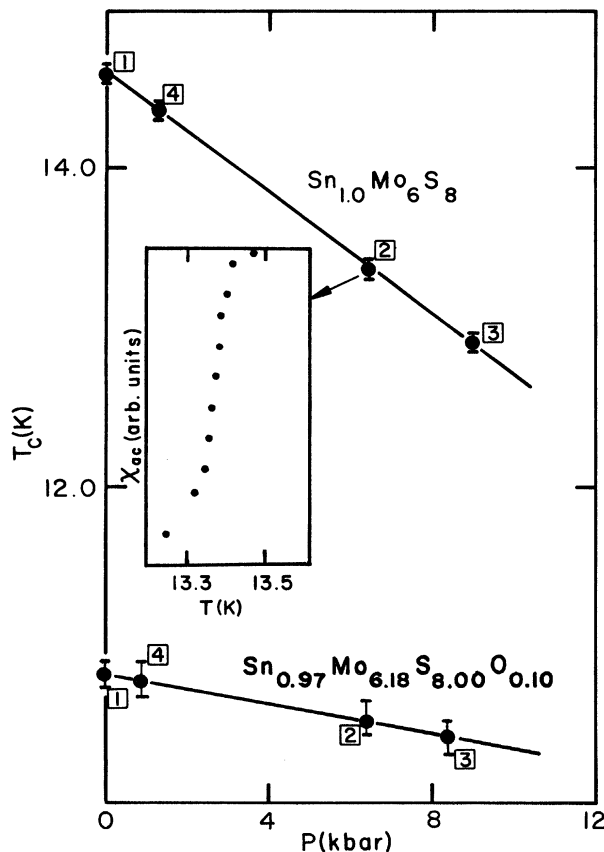

FIG. 1. Variation of superconducting transition temperature T_c with hydrostatic pressure for two $SnMo_6S_8$ samples. The upper data are for an oxygen-gettered sample, and the lower data are for a deliberately oxygenated sample. The numerals indicate the order in which the data were taken.
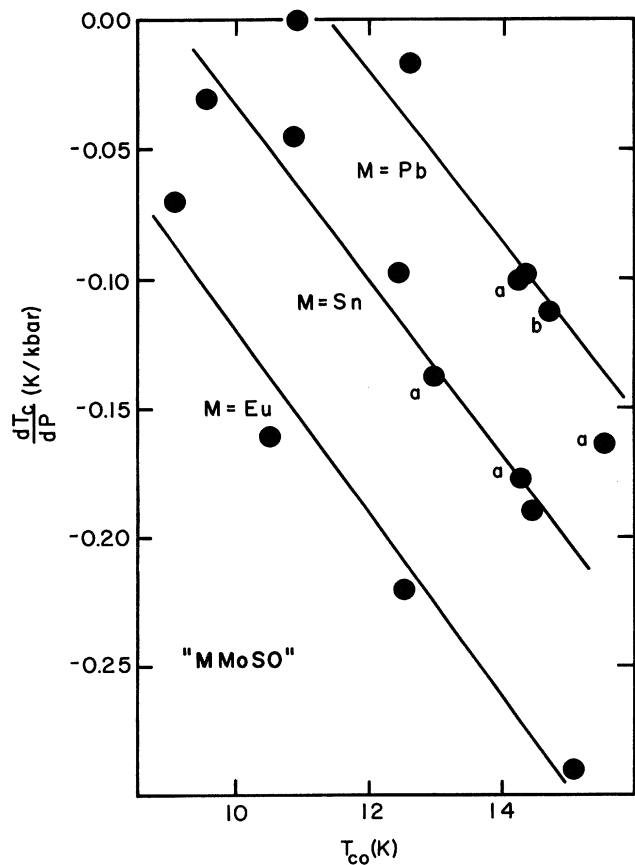

FIG. 2. Variation of the pressure dependence of T_c with T_c itself for three divalent Chevrel-phase systems. The data labeled a are from Ref. 3, and the data labeled b are from Ref. 8.

perconducting systems. In addition, the data show that T_c is reduced by both oxygen defects as well as by hydrostatic pressure, but that oxygen defects are much more effective in reducing T_c than hydrostatic pressure. For example, in the SnMoS system, the substitution of 0.20 oxygen atoms for sulfur reduces the unit-cell volume by only 0.6% but reduces T_c by 30%, whereas 10-kbar hydrostatic pressure reduces T_c by 10% with about a 2% volume reduction.[9] We believe that this difference results from the defects being more effective at reducing the c-axis dimension than pressure. The c axis is reduced in Chevrel phases when oxygen atoms are introduced in the lattice because they substitute for the sulfur atoms in the S_2 positions along the rhombehedral axis and bond covalently with the metal ions. This was determined from neutron scattering studies in SnMoS (Ref. 6) and PbMoS (Ref. 6) which show that the affected metal ions move about 0.8 Å closer to the oxygen atoms along the rhombehedral axis, producing an apparent defect at the cell center. We note in Table I that for all three Chevrel-phase systems, as the oxygen content increases, the c-axis dimension (and T_{c0}) decreases, whereas the a-axis dimension remains fairly constant. Furthermore, Spain et al.[10] carried out structural studies under hydrostatic pressure for MMoS systems and found that pressure tends to be more effective at reducing the a-axis dimension than the c axis. Thus application of pressure would not be as effective at reducing T_c, if T_c is correlated with the c-axis dimension. The strong reduction of $|dT_c/dP|$ with increasing oxygenation might be linked with a stiffening of the lattice as the c axis is reduced. Measurements of the compressibility of samples with controlled oxygenation would elucidate this point.

The microscopic origin of the large T_c reduction in oxygen containing samples still requires explanation. Moss-bauer studies of EuMoS (Ref. 11) and SnMoS (Ref. 12) indicate that little if any charge transfer takes place from the metal ion to the Mo-S clusters in cells where an oxygen atom resides in an S_2 sulfur site. In addition, high-field–high-pressure magnetization studies[13] indicate that little if any additional charge transfer takes place upon the application of high pressure. This is consistent with neutron-diffraction results,[6] which show that the oxygen defect does not reduce the Mo-Mo (intra- or intercluster) distances. Thus transfer of electrons from the metal ion to the Mo d bands does not occur. [This could directly affect the density of states at the Fermi surface, $N(E_F)$, and hence T_c.] However, the observed anisotropic contraction of the lattice could change the intercluster Mo-Mo bonding, and this could change the Mo d bands, leading to a reduction in $N(E_F)$ (and T_c) with no change in the total number of electrons. Another possible explanation is that oxygen defects, which affect the local symmetry, may alter those intra- or intercluster vibrational modes important for superconductivity in the Chevrel phases.

The divalent Chevrel-phase superconductors, in particular $PbMo_6S_8$ and $SnMo_6S_8$, are an important class of high-T_c, high-field superconductors. Consequently, proper characterization of starting materials is important for future developments in this area. The characterization and reduction of the amount of oxygen incorporated into the compounds during and after synthesis is important for maximizing T_c.

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*Visiting scientist at the Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139.

†Also at Physics Department, Massachusetts Institute of Technology, Cambridge, MA 02139.

‡Permanent address: Institute of Physics, Chinese Academy of Sciences, Beijing, People's Republic of China.

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