Effects of Oxygen Content on Pressure-Induced Superconductivity in $EuMo_6S_8$

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Pressure-induced superconductivity in $EuMo_6S_8$ is sensitive to the systematic addition of oxygen. As oxygen content increases, the critical pressure above which the sample is superconducting ($P \simeq 11$ kbar) decreases, the onset is less abrupt, the maximum T_c (11.8 K) decreases, and dT_c/dP at high pressures (−0.29 K/kbar) is less negative. The c/a ratio and the unit cell volume vary linearly with the extrapolated zero pressure T_c. The results are discussed in terms of an oxygen-induced defect at the Eu site.

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Recently the Chevrel-phase compound $EuMo_6S_8$ (EuMoS) was reported to show superconductivity at high pressures.[1,2] However, in other reports pressure-induced superconductivity was not observed.[3,4] Futhermore, the pressure-temperature superconducting-normal phase boundaries that were reported differed from sample to sample.[1,2,5] No convincing evidence has been presented to explain these differing observations. In this Letter we report that pressure-induced superconductivity in EuMoS is sensitive to the systematic addition of oxygen. For example, as the oxygen content increases, the threshold pressure for superconductivity decreases. The oxygen content is also directly related to the hexagonal-lattice parameter ratio, c/a. As oxygen content increases, c/a and the unit cell volume decrease. An oxygen-induced defect at the Eu site is discussed in connection with the results.

EuMoS and CeMoS are the only rare-earth Chevrel-phase sulfides (RMoS) which are not superconducting at ambient pressure.[6-8] The rare-earth–conduction-electron exchange interaction is very small in the RMoS systems. If a straight line is drawn between the T_c's of the rare-earth series end members, R = La and Lu (both of which are nonmagnetic), then the other RMoS T_c's are depressed from this line by an amount roughly commensurate with the de Gennes factor of the particular R ion.[9] Gd and Eu (Eu is divalent in EuMoS)[10] have $J = S = \frac{7}{2}$ in their respective Chevrel phases, but $T_c = 1.3$ K for GdMoS whereas EuMoS is not superconducting at ambient pressure.[11] Thus the absence of superconductivity is not directly related to the magnetic moment of the rare-earth ion. Furthermore, divalent metal ions in Chevrel-phase superconductors generally have high T_c values, e.g., $T_c = 14.4$ K for $PbMo_6S_8$ and $T_c = 9$ K for $YbMo_6S_8$. The absence of superconductivity in EuMoS has been linked to an apparent metal-insulator transition near 100 K; the electrical resistivity at ambient pressure increases strongly below 100 K.[1,2] This is consistent with the appearance of a structural phase transformation (rhombohedral to triclinic lattice) occurring at 105 K.[12] Recently it was shown that the alkaline-earth Chevral phases undergo a similar phase transition and they are not superconducting.[13] For EuMoS, the application of pressure reduces the resistivity and at sufficiently high pressure superconductivity is induced.

The samples were prepared as described previously in the Sn-Mo-S-O system[14] except that three firings at 1250°C (with a thorough grinding of the material after each firing) were required to obtain homogeneous samples. At the time the samples for this study were synthesized, the structure of the oxygen-containing defect was not known. Thus the oxygen-containing samples were made at a nonideal composition. The starting compositions for the three samples were $Eu_aMo_bS_cO_x$ where x is the oxygen content *added* and a, b, c, and x are respectively 0.99, 6.07, 8.00, 0.03; 0.97, 6.15, 8.00, 0.08; and 0.96, 6.23, 8.00, 0.13. Thus it is difficult to know the actual oxygen content. X-ray diffraction data for the samples showed no impurity bands. This indicates that the oxygen composition is accurate to about 5%. In this Letter the samples will be designated by the added oxygen content. The nominally pure sample was made with a 1.00, 6.00, 8.00 composition. The amount of spurious oxygen that enters the lattice during synthesis is unknown. This will shift the quoted oxygen content by a constant amount. For SnMoS this amount was estimated to be 0.05.[14] The best estimate for the amount of oxygen present in the nominally pure EuMoS sample is 0.02. Therefore, the values given for the oxygen content are not absolute.

The samples were placed in small beryllium-copper pressure-clamp devices. Care was taken to assure that strains were not introduced in handling the samples because strains broaden T_c appreciably. Typically, T_c transition widths were about 0.5 K. Two methods were used to determine T_c as a function of pressure: dc magnetization using a vibrating-sample magnetometer in low fields[15] and ac susceptibility ($f \sim 80$ Hz). The two methods gave T_c results which were in agreement to better than 0.1 K. The dc method was particularly useful in searching for the presence of small quantities of EuS (which becomes ferromagnetic at $\simeq 20$ K). Such ferromagnetic components were detected in earlier work,[16] but were not detected in any of the samples reported here.

Figure 1 shows T_c versus hydrostatic pressure for the four EuMoS samples. Several trends with increasing oxygen content should be noted: (1) The pressure threshold for the appearance of superconductivity decreases and becomes less abrupt; (2) The maximum value of T_c decreases; (3) The maximum T_c occurs at approximately 12 kbar; (4) above the maximum in T_c, the transition temperature decreases less rapidly for higher oxygen content; and (5) the pressure dependence of the nominally pure sample (solid circles) indicates that $T_c = 0$ K for $P \gtrsim 50$ kbar. This is in agreement with the observations of Wu *et al.* in Ref. 1 which show that T_c vanishes above about 50 kbar. These observations would account for the results of Ref. 3 which failed to observe superconductivity for $90 < P < 130$ kbar in EuMoS. The onset of superconductivity is extremely sharp for the nominally pure sample. T_c increases from below 1.5 K to 11 K over a very small pressure range $10 \leq P \leq 11.3$ kbar. The data for this sample agree very well with that of Decroux *et al.* reported for a melted $EuMo_6S_8$ sample.[17] The diamagnetic ac susceptibility for each sample appeared to increase as T_c rose to its maximum value. However, for pressures above those giving the maximum T_c, there was no further increase in the diamagnetic signal.[18] The order in which the data of Fig. 1 were taken was changed frequently from increasing to decreasing pressure and no hysteresis was noted.

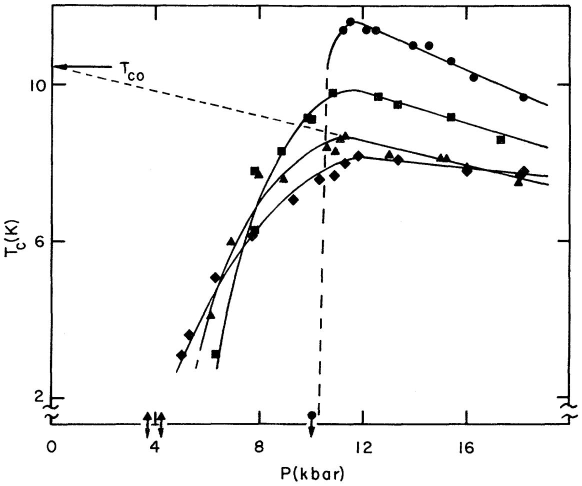

FIG. 1. Superconducting transition temperature T_c vs hydrostatic pressure P for EuMoS + O samples. The oxygen added to the system (see text) is as follows: circles, 0.00; squares, 0.03; triangles, 0.08; and lozenges, 0.13. T_{c0} is obtained by extrapolating the high-pressure slope, dT_c/dP, to $P = 0$. Points with arrows indicate that T_c was less than 1.5 K.

Figure 2 shows dT_c/dP at high pressures versus $T_c(P=0) = T_{c0}$, the extrapolated zero-pressure transition temperature for the four samples. T_{c0} may be taken as the expected transition temperature for EuMoS samples if they were superconducting at $P=0$. These values are comparable to those expected for divalent Chevrel superconductors. dT_c/dP varies linearly with T_{c0}. Also, c/a and the unit cell volume, V, vary linearly with T_{c0} as shown in the inset in Fig. 2. Similar relationships are found for SnMoS and PbMoS samples, which will be discussed in a forthcoming publication.[19]

In Table I we list data for several samples including data from other sources.[20] Extrapolation of these data suggests that for $x \geq 0.35$, EuMoS should be superconducting at ambient pressure. However, the maximum oxygen content that can be incorporated into the lattice is about 0.20. The results of Table I suggest that oxygen content can be estimated from a measure of c/a, as has been shown previously for the Sn and Pb Chevrel-

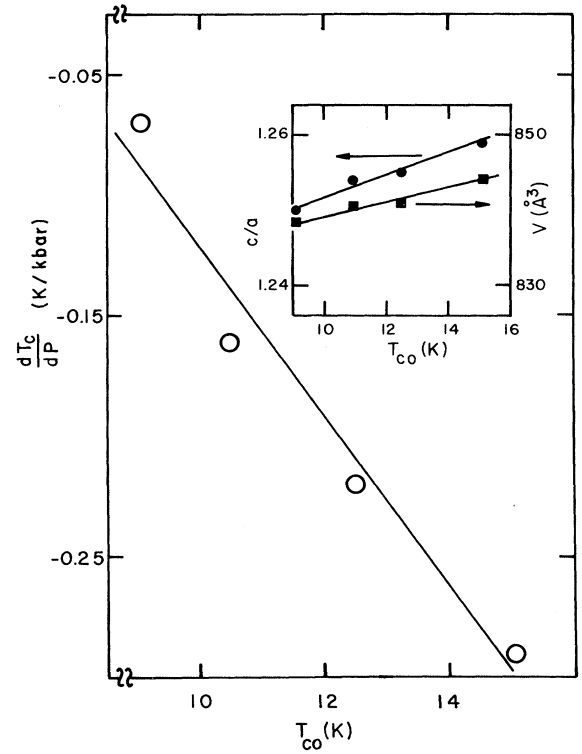

FIG. 2. High-pressure slope dT_c/dP vs transition temperature T_{c0} for four EuMoS samples with different oxygen content. Inset: the linear variation of c/a and the unit-cell volume V with T_{c0}.

phase systems.[14]

The experimental results presented here demonstrate that P_c, T_{c0}, and dT_c/dP ($P > P_c$) are correlated with oxygen content. This implies that many of the properties already reported for EuMoS and, perhaps more importantly, for other high-T_c Chevrel-phase systems may be governed by oxygen which is inadvertently introduced into the lattice. The oxygen is taken into the system substitutionally for the S atom at the S_2 sites on the Mo-S clusters. This is inferred from recent neutron-scattering[14] and Mössbauer-effect studies in oxygenated $SnMo_6S_8$.[21] For $SnMo_6S_{8-x}O_x$, the Sn atoms bond covalently to the oxygen atom, causing the Sn to move about 0.8 Å along the c axis toward the oxygen atom. This gives rise to an apparent defect at the Sn site and accounts for the shortened c axis, and the decreased c/a ratio.

The presence of oxygen-induced defects in the Chevrel phases may influence the density of electron states and the lattice vibrational structure, both of which directly affect the superconducting properties. Preliminary Mössbauer studies in

TABLE I. Threshold pressure for the onset of superconductivity, extrapolated (to $P = 0$) transition temperature, pressure dependence of T_c, and crystallographic data for EuMoS samples. x is the oxygen added to the starting mixture.

	P_c (kbar)	T_{c0} (K)	dT_c/dP (K/kbar)	c/a	V (Å^3)
$x = 0.00$	11	15.0	-0.29	1.2591(5)	844.0
$x \simeq 0$[a]	11	~ 16.0	$\simeq -0.3$		843.3
$x = 0.03$	6	12.5	-0.22	1.2565(5)	841.9
$x = 0.08$	5	10.5	-0.16	1.2535(5)	840.6
$x = 0.13$	4	9.1	-0.07	1.2501(5)	838.6

[a] Ref. 17.

EuMoS at high pressures[10] as well as our own high-field, high-pressure magnetization studies on EuMoS indicate that little if any charge transfer takes place in materials with oxygen defects. The magnetization would be expected to decrease under pressure if there were an appreciable magnetic [Eu^{2+}] to nonmagnetic [Eu^{3+}] valence transition. The difference in the superconducting properties between oxygenated EuMoS samples (e.g., lower dT_c/dP with increasing defect concentration) may thus be associated with changes in the phonon spectrum, possibly through the loss of a soft mode. A concomitant stiffening of the lattice may then account for the smaller pressure-induced reduction of T_c.

The Chevrel-phase sulfides form an important class of superconductors, which show pressure-induced superconductivity, the highest upper critical fields, and coexistence of magnetism and superconductivity. Consequently, proper sample characterization is important for future developments. Our present results on the effects of oxygen on T_c and dT_c/dP suggest that a careful reexamination of oxygen content is required of Chevrel-phase materials.

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[1] C. W. Chu, S. Z. Huang, C. H. Lin, R. L. Meng, M. K. Wu, and P. H. Schmidt, Phys. Rev. Lett. 46, 276 (1981); M. K. Wu, P. H. Hoo, R. L. Meng, T. H. Lin, V. Diatshenko, X. Y. Shao, X. C. Jin, and C. W. Chu, Phys. Rev. B 26, 5230 (1982).

[2] D. W. Harrison, K. C. Lim, J. D. Thompson, C. Y. Huang, P. D. Hambourger, and H. L. Luo, Phys. Rev. Lett. 46, 280 (1981); C. Y. Huang, D. W. Harrison, S. A. Wolf, W. W. Fuller, H. L. Luo, and S. Maekawa, Phys. Rev. B 26, 1442 (1982).

[3] R. N. Shelton and A. R. Moodenbaugh, Phys. Rev. B 24, 2863 (1981).

[4] R. W. McCallum, W. A. Kalsbach, T. S. Radhakrishnan, F. Pobell, R. N. Shelton, and P. Klavins, Solid State Commun. 42, 819 (1982).

[5] M. S. Torikachvili, M. B. Maple, R. P. Guertin, and S. Foner, J. Appl. Phys. 53, 2619 (1982).

[6] For a review of Chevrel-phase materials see Ø. Fischer, Appl. Phys. 16, 1 (1978).

[7] For extensive reviews of ternary superconducting systems, see *Superconductivity in Ternary Compounds I*, edited by Ø. Fischer and M. B. Maple, and *Superconductivity in Ternary Compounds, II*, edited by M. B. Maple and Ø. Fischer (Springer-Verlag, New York, 1982).

[8] R. W. McCallum, R. N. Shelton, M. B. Maple, and H. Adrian, Bull. Am. Phys. Soc. 21, 338 (1976).

[9] M. B. Maple, L. E. De Long, W. A. Fertig, D. C. Johnston, R. W. McCallum, and R. N. Shelton, in *Valence Instabilities and Related Narrow Band Phenomena*, edited by R. D. Parks (Plenum, New York, 1977), p. 17.

[10] M. M. Abd-Elmequid and H. Micklitz, J. Phys. C 15, L479 (1982).

[11] Ø. Fischer, A. Treyvaud, R. Chevrel, and M. Sergent, Solid State Commun. 17, 721 (1975).

[12] R. Baillif, A. Dunand, J. Muller, and K. Yvon, Phys. Rev. Lett. 47, 672 (1981).

[13] B. Lachal, R. Baillif, A. Junod, and J. Muller, Solid State Commun. 45, 849 (1983).

[14] D. G. Hinks, J. Jorgensen, and H. C. Li, to be published.

[15] R. P. Guertin and S. Foner, Rev. Sci. Instrum. 45, 863 (1974); R. P. Guertin, in *High Pressure and Low Temperature Physics*, edited by C. W. Chu and J. W. Woollam (Plenum, New York, 1978), p. 97.

[16] M. S. Torikachvili, M. B. Maple, R. P. Guertin, and S. Foner, J. Low Temp. Phys. 49, 573 (1982).

[17] M. Decroux, M. S. Torikachvili, M. B. Maple, R. Baillif, and J. Muller, Bull. Am. Phys. Soc. 28, 301 (1983), and private communication.

[18] The question of whether or not pressure-induced superconductivity in EuMoS is a *bulk* effect has been raised. [See Ref. 4 and R. L. Meng, T. H. Lin, M. K. Wu, C. W. Chu, and S. Z. Huang, J. Low Temp. Phys. 48, 383 (1982).] In order to address this problem, we performed several zero-field–cooled and low-field–cooled dc magnetization experiments on EuMoS at high pressure, similar to those done by F. Steglich, J. Appl. Phys. 53, 2111 (1982). The data were compared with data taken under identical conditions on SnMoS, which is a bulk superconductor, and no qualitative differences between the results on the two systems could be discerned. This suggests that the pressure-induced superconductivity in EuMoS is a bulk effect, at least for pressures well above the critical pressure.

[19] D. W. Capone, R. P. Guertin, S. Foner, D. G. Hinks, and H.-L. Li, to be published.

[20] Data of Ref. 1 give $P_c \simeq 7$ kbar and $V = 837$ Å^3. According to Table I we expect $V \simeq 842$ Å^3 and $x \simeq 0.05$ for this threshold pressure.

[21] G. Shenoy, private communication.