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Structural phase transition and structure refinement of triclinic $EuMo_6S_8$ at 14 K studied by x-ray powder diffraction

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Lattice-parameter measurements of $EuMo_6S_8$ as a function of temperature show an increase of the cell volume by 1.0 Å^3 as the rhombohedral high-temperature modification transforms at $T_l \sim 110$ K into the triclinic low-temperature modification. The triclinic structure at 14 K was refined from film data by using the x-ray Rietveld method. The results show a distortion of the Mo_6 octahedra by up to 0.07 Å compared to those in the rhombohedral high-temperature modification.

The absence of superconductivity in $EuMo_6S_8$ at ambient pressure was attributed to the occurrence of a structural phase transformation at 110 K from a rhombohedral high temperature to a triclinic low-temperature modification.[1,2] Superconductivity has been induced by application of hydrostatic pressure[3,4] which presumably suppressed the structural phase transition and yielded critical temperatures of up to 12.2 K at 13.2 kbar.[5] From the pressure dependence of the lattice-transformation temperature T_l, an increase of the cell volume for the triclinic modification of about $\Delta V = 0.5$ Å^3 at zero pressure was predicted[5] from the Clausius-Clapeyron equation $dT_l/dp = T\Delta V/L$ (L is the latent heat). Except for preliminary powder-diffraction data[1] of relatively low resolution, structure data of $EuMo_6S_8$ at low temperature have not been reported in the literature as yet. In particular the atomic coordinates of its triclinic low-temperature modification have not been published so far. These data are important for energy-band calculations. In this Brief Report we present the results of an x-ray powder-diffraction study of relatively high resolution as a function of temperature.

Lattice parameters were refined from film data taken in the temperature interval between 20 and 298 K by using a Guinier camera (Cu $K\alpha_1$) equipped with a low-temperature helium closed-cycle cryostat.[6] Bragg angles were measured for 13 (17) reflections of the rhombohedral (triclinic) modification and corrected against a Si standard by using tabulated values of its cell parameter as a function of temperature.[7] Results are shown in Fig. 1. The rhombohedral cell parameters a_{rh} and α_{rh} decrease as the temperature decreases until they split into triclinic cell parameters (a_{tr}, b_{tr}, c_{tr}, α_{tr}, β_{tr}, γ_{tr}) at the lattice transformation temperature $T_l = 110$ K. Below T_l the deformation of the triclinic lattice continues until about 90 K at which temperature it stays approximately constant. The

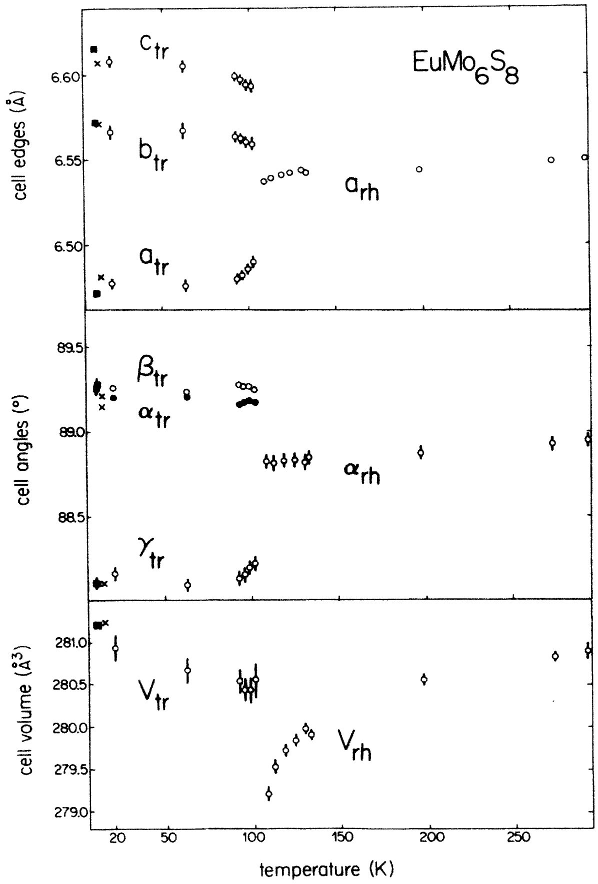

FIG. 1. Lattice parameters and cell volume of $EuMo_6S_8$ as a function of temperature. Crosses indicate data from present Rietveld refinement; filled squares indicate data from Ref. 1 (b,c and α,β interchanged); error bars indicate estimated standard deviations, errors of α and β (not drawn) are similar to those of γ.

data below 20 K are consistent with those reported[1] previously. The phase transition is of first order and the cell volume increases discontinuously at T_l by about 1.0 Å^3, i.e., by a factor of 2 greater than predicted.[5] The slight increase of cell volume below T_l is puzzling but may not be significant in view of possible systematic errors in the film data. By contrast, no significant volume discontinuity was found during a neutron-powder-diffraction study[8] of the analogous rhombohedral-to-triclinic phase transition in $BaMo_6S_8$. This could be due either to the scarcity of data points reported or to the smallness of the effect as expected from the presumably smaller pressure derivative of T_l for that compound.[8,9]

Atomic positions of the triclinic low-temperature modification were refined from transmission data at 14 K (optical densitometer,[10] scan step 0.01° in θ) by using a program package[11] containing an x-ray Rietveld code. Each intensity value was averaged over six neighboring values to avoid correlations.[12] The background was manually subtracted. The data points in the regions between $18.0° < 2\theta < 18.9°$ and $48.6° < 2\theta < 49.1°$ were excluded from the refinement because of intensity residuals which presumably resulted from film damage and/or the presence of an unknown impurity phase. Starting positions for atomic coordinates were taken from a preliminary structure refinement[1] on triclinic $BaMo_6S_8$ in space group $P\bar{1}$, with one Eu atom at (0,0,0), and three independent Mo and four independent S atoms in general positions $\pm(x,y,z)$. Altogether 35 parameters were refined [one scale factor, one zero point, six lattice parameters, three profile parameters, one asymmetry parameter, one overall, and one individual (Eu) temperature factor, 21 positional parameters] leading to consistency factors of $R(F)=7.8\%$ for 447 reflections and $R(WP)=10.6\%$, and a Durbin-Watson d value of 1.8. None of the correlation factors between the atomic positional parameters exceeded 0.5. The lattice parameters and atomic coordinates are summarized in Table I. The setting chosen corresponds to the standardized[13] structure description and has the pseudo-threefold axis parallel to [111]. The observed and calculated diffraction patterns and their difference are presented in Fig. 2. These patterns have a significantly better resolution than those reported previously (Fig. 1 in Ref. 1, Fig. 3 in Ref. 2). There is no indication for the simultaneous presence of a rhombohedral modification such as that found[14] at low temperature in $BaMo_6S_8$ samples.

Calculation of interatomic distances show that the Mo_6 cluster in the triclinic low-temperature modification (point group symmetry $\bar{1}$) is significantly distorted compared to that in the rhombohedral high-temperature modification (point symmetry $\bar{3}$). At 14 K the Mo-Mo distances within the octahedra faces approximately perpendicular to the pseudo-threefold axis are 2.599(17), 2.647(16), and 2.691(16), compared to 2.6659(2) Å (3 symmetry equivalent distances) in the rhombohedral modification[15] at 298 K, whereas those between these faces are 2.698(17), 2.765(17), and 2.792(18) compared to 2.7173(2) Å (3 symmetry equivalent distances) in the rhombohedral modification. The intercluster distances are 3.195(16), 3.275(18), and 3.317(17) compared to 3.2768(2) Å (3 symmetry equivalent distances) in the rhombohedral modification. Thus, the changes in the Mo—Mo bond lengths induced by the structural phase transition are surprisingly small (less than 0.08 Å) if one considers its drastic effect on the electronic properties. In fact $EuMo_6S_8$ (at ambient pressure) is known[16] to be metallic at room temperature and semiconducting at low temperature. This change in properties is consistent with theoretical calculations[17] which are based on atomic coordinates of triclinic $BaMo_6S_8$ and suggest the opening of an energy gap at E_F in Mo d-like conduction bands.

In conclusion, we have measured the increase of cell

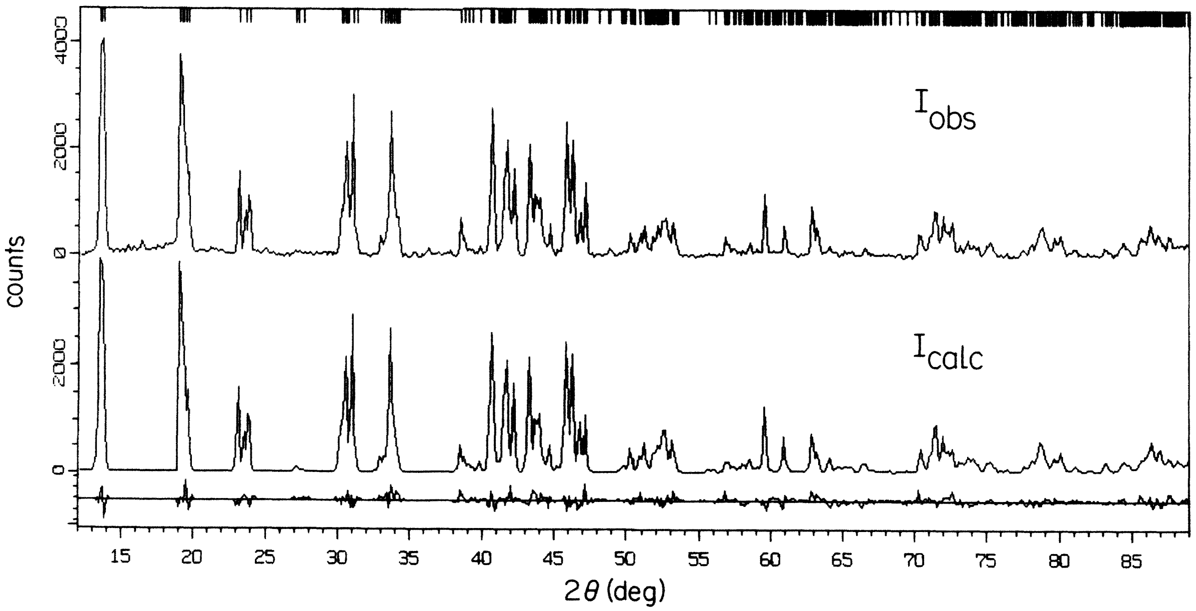

FIG. 2. Observed (I_{obs}) and calculated (I_{calc}) x-ray diffraction patterns and their difference ($I_{diff}=I_{obs}-I_{calc}$) for $EuMo_6S_8$ at 14 K (Cu $K\alpha_1$ radiation).

TABLE I. Structural parameters of $EuMo_6S_8$ at 14 K. Space group $P\bar{1}$.

Lattice constants

a:	6.4815(5) Å	α:	89.138(5)°
b:	6.5700(5) Å	β:	89.208(4)°
c:	6.6091(5) Å	γ:	88.106(4)°
V:	281.23(4) Å^3		

Atomic parameters

	x	y	z	B_{iso} (Å^2)
Eu:	0.0	0.0	0.0(−)	4.2(4)
Mo(1):	0.2333(18)	0.5611(16)	0.4184(20)	0.35(9)
Mo(2):	0.4164(17)	0.2305(20)	0.5562(18)	
Mo(3):	0.5615(16)	0.4145(19)	0.2193(17)	
S(1):	0.146(5)	0.398(5)	0.764(5)	
S(2):	0.248(5)	0.246(4)	0.235(4)	
S(3):	0.380(5)	0.738(5)	0.153(5)	
S(4):	0.740(4)	0.111(5)	0.377(5)	

Form of the temperature factor: $\exp\{-B_{iso}\sin^2\theta/\lambda^2\}$; values for B_{iso} may not be significant due to neglect of film absorption. Estimated standard deviations in parentheses; the sulfur atom closest to the pseudo-threefold inversion axis is S(2).

volume of $EuMo_6S_8$ at the rhombohedral-to-triclinic phase transition, and have characterized its triclinic low-temperature structure from x-ray powder diffraction data collected at ambient pressure. As a next step to understand the unusual properties of this compound we suggest diffraction studies on single crystals in order to increase the precision of the atomic coordinates, and diffraction studies under pressure in order to confirm the expected suppression of the structural phase transition by application of high pressure.

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