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Lattice instability and superconductivity in the Pb, Sn, and Ba Chevrel phases

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High-resolution neutron powder diffraction measurements show that sintered samples of $PbMo_6S_8$, $SnMo_6S_8$, and $BaMo_6S_8$ all transform from a high-temperature rhombohedral $R\bar{3}$ structure to a low-temperature triclinic $P\bar{1}$ structure, but with a broad temperature range over which both phases are present. The temperature of the structural transition, which may be varied with pressure or composition, is empirically correlated with the superconducting transition temperature T_c.

Over the past ten years numerous authors have reported evidence for a subtle phase transition occurring at temperatures near 100 K in $PbMo_6S_8$ and $SnMo_6S_8$. The experiments which have shown an anomaly in this temperature region include studies of the ^{119}Sn Mössbauer effect,[1-3] inelastic neutron scattering (Ref. 4), ^{119}Sn NMR relaxation,[5] elastic properties,[6] magnetic susceptibility,[7,8] resistivity,[8] specific heat,[8] x-ray powder diffraction,[8,9] and neutron powder diffraction.[10] Unfortunately, in every case the observed anomalies have been small and it has been impossible to determine the exact nature of the suspected transition. Evidence for lattice instability in $PbMo_6S_8$ and $SnMo_6S_8$ is of particular interest because these two compounds exhibit the highest superconducting transition temperatures $T_c > 14$ K observed in the Chevrel phases. Two recent authors presented models which show a relationship between electronic or structural instability and superconducting behavior in the Chevrel phases with divalent metal cations, $M^{2+}Mo_6S_8$ (M=Pb,Sn,Eu,Ba,Ca,Sr,Yb).[11,12] Johnson, Tarascon, and Sienko suggested a systematic relationsip between phase transition temperature (or pressure), superconducting transition temperature, and second ionization potential of the ternary cation.[11] However, they define as "phase transition temperature" the temperature of the well-known structural transition to the triclinic $P\bar{1}$ phase of some materials (i.e., M=Eu,Ba,Ca,Sr)[13-15] and the temperature of the above-mentioned anomaly in other cases (i.e., M=Pb,Sn,Yb). Conversely, Meul concludes that the experimental evidence supports the existence of two transitions in the $M^{2+}Mo_6S_8$ Chevrel phases, based on the fact that even in systems such as $BaMo_6S_8$, $EuMo_6S_8$, and $SrMo_6S_8$ anomalies in transport and other properties extend well above the triclinic phase transition temperature.[12,16] Such conclusions bring forth the proposal of an "intermediate" phase. The purpose of this Rapid Communication is to elucidate the nature of this intermediate region and to discuss the observed correlation between structural instability and superconducting behavior in these materials.

The powder samples for this study were synthesized by sintering the elements at high temperature in sealed, evacuated, fused-silica ampoules in quantities of about 15 g each. Neutron powder diffraction data were collected over a range of temperatures by the time-of-flight technique on the Special Environment Powder Diffractometer at the Intense Pulsed Neutron Source and the data were analyzed by the Rietveld technique.[17,18] For $BaMo_6S_8$, a triclinic $P\bar{1}$ phase as reported by Baillif, Dunand, Muller, and Yvon[13] was observed below 175 K. The results of our structural refinements in the $P\bar{1}$ phase have been published elsewhere.[19] Above 350 K, $BaMo_6S_8$ exhibits a rhombohedral $R\bar{3}$ structure, exactly as was previously seen in $PbMo_6S_8$ and $SnMo_6S_8$ above 100 K.[10] Between 350 and 175 K, new Bragg reflections develop as shoulders on many of the $R\bar{3}$ reflections with a pattern for $BaMo_6S_8$ identical to that previously reported below 100 K for $PbMo_6S_8$.[10]

In the case of $PbMo_6S_8$ and $SnMo_6S_8$, these new Bragg reflections were originally interpreted as evidence for a modulation of the $R\bar{3}$ structure.[10] (The $R\bar{3}$ peaks persist in the intermediate region, with intensity decreasing with the temperature.) However, a careful analysis of the q dependence of the new Bragg peaks reveals that they cannot be assigned to a modulated $R\bar{3}$ structure. Assuming for simplicity one modulation period $\mathbf{\Lambda}$ in an arbitrary direction, satellites should appear around a peak with lattice spacing $\mathbf{d}_i$ at the values of the scattering vector:

$$\mathbf{q} = \left(\frac{2\pi}{\mathbf{d}_i}\right) \pm \left(\frac{2\pi}{\mathbf{\Lambda}}\right) = \mathbf{q}_{R\bar{3}} \pm \mathbf{q}_M \ . \tag{1}$$

This relation has important consequences even for a powder pattern, which contains diffraction peaks due to all relative orientations of $\mathbf{q}_{R\bar{3}}$ and $\mathbf{q}_M$. Thus, around the peaks $|q_{h,k,l}|$ and $|q_{2h,2k,2l}|$ of the $R\bar{3}$ structure, one should be able to find satellites displaced with the same $|\Delta q|$. In the $PbMo_6S_8$ and $BaMo_6S_8$ data, this is not the case. Instead, all the "modulation" peaks exhibit $|\Delta q| \propto |q|$, which is the signature of a new structure with symmetry lower than $R\bar{3}$. A visual inspection of the diffraction patterns at different temperatures indicates that the modulation pattern is identical to the $P\bar{1}$ pattern at lower temperature.

The presence of two phases ($R\bar{3}$ and $P\bar{1}$) in the intermediate region has been extensively tested by analyzing both the $BaMo_6S_8$ and $PbMo_6S_8$ data with a two-phase Rietveld refinement code.[20] The refinements included approximately 700 $R\bar{3}$ reflections and 2100 $P\bar{1}$ reflections within the range 0.66 Å $< d <$ 3.1 Å. In all cases, the positions and intensities of the new peaks were correctly fit,

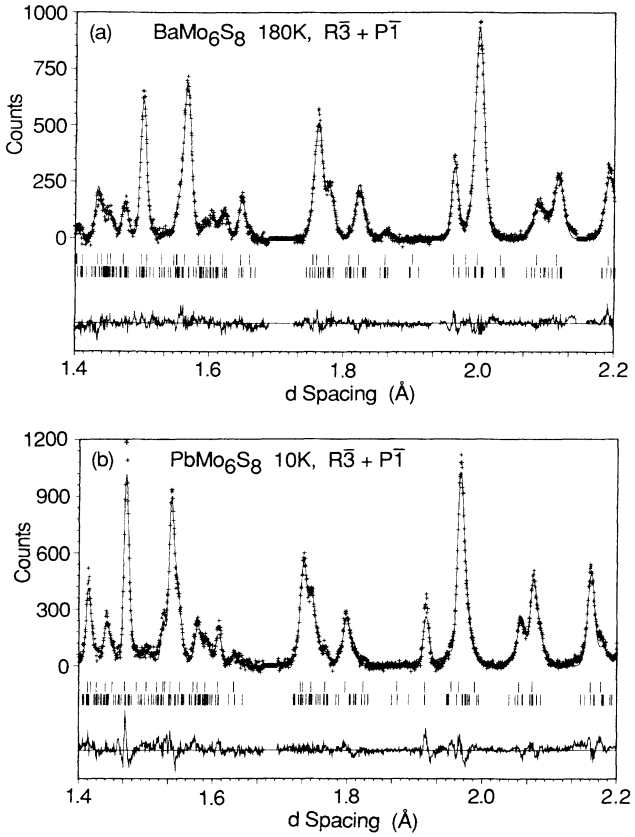

FIG. 1. Portion of the Rietveld refinement profiles based upon a two-phase ($R\bar{3}+P\bar{1}$) model for (a) $BaMo_6S_8$ at 180 K and (b) $PbMo_6S_8$ at 10 K. Plus signs (+) are raw data. The continuous line is the calculated profile. At the bottom of the curves, vertical tick marks (|) indicate positions of allowed $R\bar{3}$ (upper tick marks) and $P\bar{1}$ (lower tick marks) reflections.

as shown for small regions of refined data in Fig. 1. Two-phase refinements were not attempted for our $SnMo_6S_8$ data because the observed new reflections are considerably less pronounced in that case.

The refined $R\bar{3}$ and $P\bar{1}$ lattice constants in the two-phase region for $BaMo_6S_8$ at 180 K and $PbMo_6S_8$ at 10 K are given in Table I. In both cases, the triclinic cell volume is slightly (less than 0.5%) larger than the rhombohedral cell volume, consistent with the fact that the

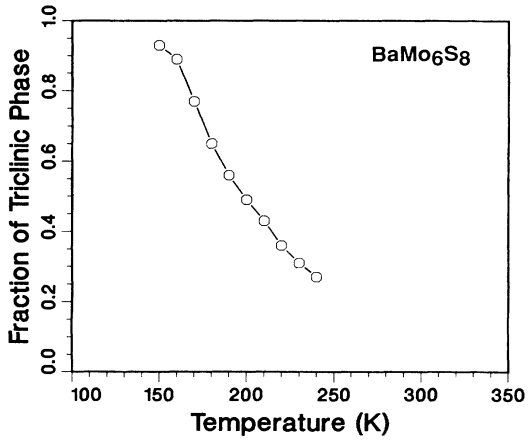

FIG. 2. Fraction of the sample which is in the triclinic phase vs temperature for $BaMo_6S_8$.

rhombohedral cell is favored at high pressure. The relative fraction of the $R\bar{3}$ and $P\bar{1}$ phases as a function of temperature for $BaMo_6S_8$ is shown in Fig. 2. The behavior is analogous for $PbMo_6S_8$, where at 10 K the sample studied in this experiment is about 70% triclinic.

The onset of the two-phase region corresponds to the "upper" transition proposed by Meul[12] and the experimental anomaly reported by numerous other authors. The onset temperature is observed in neutron diffraction as a change in the sign of the hexagonal c-axis thermal expansion when data are refined in an $R\bar{3}$ model. The results reported in Fig. 3 for $PbMo_6S_8$, $SnMo_6S_8$, and $BaMo_6S_8$ suggest approximate onset temperatures of about 110, 140, and 350 K, respectively. These onset temperatures are undoubtedly sample dependent, as is typical of two-phase behavior associated with first-order transitions.

Based on these observations, a generalized phase diagram which approximately describes the structural behavior of the $M^{2+}Mo_6S_8$ Chevrel phases is proposed in Fig. 4. The vertical lines, labeled for each compound, represent the zero pressure axes for the various compounds; i.e., for a given compound, pressure is zero at this point and increases to the right according to the scale shown in the figure. Figure 4 also illustrates the existence of a correlation between unit cell volumes (which scale with the ionic radius of the M^{2+} ion) and the positions of the zero pressure axes in the phase diagram.

TABLE I. Rhombohedral $R\bar{3}$ and triclinic $P\bar{1}$ lattice constants in the two-phase region for $BaMo_6S_8$ at 180 K and $PbMo_6S_8$ at 10 K.

	$BaMo_6S_8$ 180 K		$PbMo_6S_8$ 10 K	
	$R\bar{3}$	$P\bar{1}$	$R\bar{3}$	$P\bar{1}$
a (Å)	6.6446(3)	6.6795(15)	6.5273(2)	6.5759(9)
b (Å)		6.6551(15)		6.5383(9)
c (Å)		6.6067(12)		6.4948(8)
α(deg)	88.642(4)	88.254(18)	89.066(3)	88.516(12)
β(deg)		88.846(16)		89.604(11)
γ(deg)		88.878(17)		89.298(13)
V (Å^3)	293.12(3)	293.44(16)	277.99(2)	279.12(4)

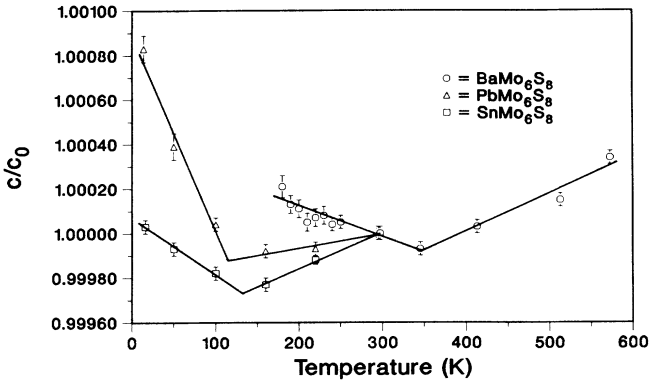

FIG. 3. Hexagonal c-axis lattice constants, based on Rietveld refinement in $R\bar{3}$ symmetry, vs temperature for $BaMo_6S_8$, $PbMo_6S_8$, and $SnMo_6S_8$. c_0 is the room temperature value [$c_0(BaMo_6S_8)=11.7765(4)$ Å, $c_0(PbMo_6S_8)=11.4896(3)$ Å, $c_0(SnMo_6S_8)=11.3918(2)$ Å].

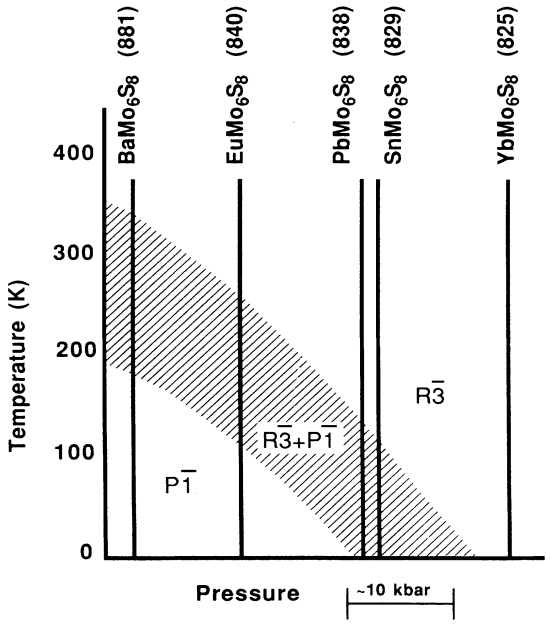

FIG. 4. Generalized structural phase diagram for Chevrel phases with divalent tenary metal cations. Vertical lines are the zero pressure axes for the compounds indicated. Numbers in parentheses are the hexagonal unit cell volumes (at room temperature and zero pressure) for the compounds indicated.

An empirical correlation exists between the superconducting properties of the $M^{2+}Mo_6S_8$ Chevrel phases where the metal cation occupies the origin position (e.g., M=Pb,Sn,Eu,Ba,Yb, etc.) and the proposed structural phase diagram. The compounds with a stable $P\bar{1}$ structure at atmospheric pressure (i.e., $EuMo_6S_8$ and $BaMo_6S_8$) are not superconducting. For the others, when superconductivity is not perturbed by impurity defects, the highest T_c's always occur in the two-phase region adjacent to the $P\bar{1}$ transition line. As one moves away from this line, for example, by applying pressure to $PbMo_6S_8$ or $SnMo_6S_8$, T_c decreases.[21,22] The effects of pressure on T_c are among the largest reported for any compounds. $YbMo_6S_8$, which shows no mixed-phase behavior at low temperature in our neutron diffraction experiments,[23] has a lower T_c—approximately 10 K. Analogous behvaior is observed in $EuMo_6S_8$: As pressure is increased, there is a sudden onset of superconductivity with $T_c=11.8$ K upon crossing the triclinic phase line, but a further increase in pressure decreases T_c.[24] The onset of pressure-induced superconductivity in $BaMo_6S_8$ was originally reported to be at 19 kbar.[25] The two-phase behavior could explain initial reports that superconductivity in $BaMo_6S_8$ (based on observations under nonhydrostatic conditions at 15 kbar) is nonbulk.[26] More recent data show an onset of superconductivity in $BaMo_6S_8$ at 25 kbar with a T_c of 14 K.[27] These observations, thus, show that high T_c's in the $M^{2+}Mo_6S_8$ Chevrel phases are related in a systematic way to the lattice instability which drives the triclinic phase transition.

These conclusions have several implications for understanding the observed superconductivity behavior in the Chevrel phases. Since $PbMo_6S_8$ and $SnMo_6S_8$ already lie directly adjacent to the triclinic phase line, attempts to achieve T_c's higher than 14 K (e.g., by alloying) may never succeed unless the transition to the triclinic phase can be suppressed. Furthermore, existing samples of $PbMo_6S_8$ and $SnMo_6S_8$ may contain large fractions of nonsuperconducting ($P\bar{1}$) material. Such a hypothesis could explain the failure to achieve the expected large critical current densities in wires and films of these materials.[28] In summary, many of the properties of these compounds hitherto observed are undoubtedly related to the presence of two coexisting phases. The next experimental challenge is to produce samples with sharp first-order transitions so that the intrinsic behavior can be studied.

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