

isotopes, we show in Fig. 2 Z^* values extrapolated to vanishing H or D concentrations (dashed lines).²⁰ For all metals, Z^* decreases with increasing concentration. The decrease reflects the hydrogen-induced variations of the electronic structure on the electron drag, and is caused by modifications in number and mobility of both electrons and holes. To study these effects more closely, we are presently extending the experiments to higher hydrogen concentrations.

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²⁰The dashed lines are fits according to Eq. (2), with values for K extrapolated linearly to $c=0$. For H in V and D in Ta with only one measured concentration, the concentration dependence of K was assumed to be equal to that of the other isotope. This seems a reasonable assumption since the concentration dependence of K was practically equal for H and D in Nb.

Phonon Spectra of Chevrel-Phase Lead and Tin Molybdenum Sulfides: A Molecular-Crystal Model and Its Implications for Superconductivity*

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Heat-capacity (2–400 K) and inelastic-neutron-scattering studies of the phonon spectra are reported for superconducting, high-critical-field, Chevrel-phase, lead and tin molybdenum sulfides ($T_c \sim 11$ –15 K). Nine phonon modes per unit cell are identified whose frequencies are in the immediate region Bergmann and Rainer indicate is necessary to optimize T_c . Acoustic-phonon softening on cooling is observed. A molecular-crystal model is proposed for the lattice dynamics of these materials.

Chevrel-phase ternary molybdenum sulfides were discovered¹ in 1971 and soon thereafter were found to possess superconducting transition

temperatures T_c as high as ~ 15 K (for PbMo_6S_8).² They also have the highest upper critical fields $H_{c2}(T=0)$ known: in the 500–700 kG range for

the Sn and Pb ternaries,³ and for $\text{Sn}_{1-x}\text{R}_x$ and $\text{Pb}_{1-x}\text{R}_x$ pseudoternaries, where R is a rare-earth element.⁴ The pressure derivatives⁵ of T_c are, in general, strongly positive or negative, can be nonmonotonic below 10 kbar, and initially can be larger even than those for α -U and La. Lattice instabilities⁶ and their precursors, lattice softening with decreasing temperature,⁷ have also been identified within the Chevrel-phase class of superconductors. In the present study we probe and identify, for the first time, the prominent features in the phonon density of states of these unusual materials to evaluate their influence on the striking superconducting properties.

The ideal formula for the superconducting ternary molybdenum sulfides is XMo_6S_8 , where, for instance, if X is Pb, Sn, Cu, Ag, or Yb, T_c is approximately 15, 14, 11, 9, or 8 K, respectively.⁸ Nonstoichiometric ternaries exist as defect structures with the approximate formula $\text{XMo}_n\text{S}_{n+1}$,¹ where $n \approx 5$ or 6, and have similar, but lower, T_c values. For example, our $\text{PbMo}_{5.1}\text{S}_6$ and SnMo_5S_6 samples have calorimetrically determined T_c values of 12.3 ± 0.2 and 11.4 ± 0.1 K, respectively. The crystal structure is rhombohedral, contains one XMo_6S_8 formula per unit cell, and is based on a distorted CsCl-type arrangement of individual X atoms and discrete Mo_6S_8 units, each of which consists of a Mo_6 octahedron within a tetragonally distorted S_8 cube that is tilted $\sim 15^\circ$ from the rhombohedral axes.⁸ Binary Mo_6Se_8 exists in the same crystal structure⁹ as these ternaries and has a T_c of 6 K.¹⁰ Also, Chevrel-phase paramagnetic rare-earth ternaries exist and are superconductors¹¹, i.e., NdMo_6S_8 has a T_c of 3.5 K. Hence, the valence and magnetic character or even the presence of the X atom may only be of secondary importance in understanding the occurrence of superconductivity in this class of materials. Furthermore, from the above types of observations it has been concluded that the Mo d electrons comprise the important Fermi-surface states that condense into Cooper pairs, and presumably such electrons do not have appreciable overlap onto the X sites.⁴ The stability of the Mo_6S_8 (or Mo_6Se_8) units suggests that these ternaries may be regarded as molecular crystals composed of X atoms bound to quasirigid Mo_6S_8 units. The lattice dynamics would then simplify since the 45 normal modes of the unit cell, derived from the 15 atoms of the formula unit, would group into 9 soft "external" modes, and 36 hard "internal"

modes which are associated with the Mo_6S_8 units. The external modes would contain 6 modes (3 acoustic plus 3 optic) associated with the translational motion of an X atom and a quasirigid Mo_6S_8 unit and 3 torsional modes of the Mo_6S_8 units.

The heat capacities of $\text{PbMo}_{5.1}\text{S}_6$ and SnMo_5S_6 were measured between 2 and 400 K, and are dominated by lattice contributions at all temperatures.¹² The effective Debye temperatures Θ^c and Θ^s , obtained respectively from the lattice heat capacities C_L and entropies for both materials, increase with temperature¹³ by a factor of ~ 2 . This variation is approximately an order of magnitude larger than that found for simple metals, but is one that is similar to that found for molecular crystals. Thus, we have evidence that a molecular-crystal approach is not unreasonable. To extract values of the characteristic internal- and external-mode frequencies from C_L we assume a simplified model for the phonon density of states:

$$F(\omega) = 3F_A(\omega) + 6F_E(\omega) + (3n - 9)F_I(\omega), \quad (1)$$

where n is the number of atoms in the unit cell; the acoustic contribution to $F(\omega)$, denoted F_A , is characterized by a Debye cutoff frequency ω_D ; the soft optic and torsional contributions F_E have been lumped together to reduce the number of parameters and are characterized by the Einstein frequency ω_E ; and the internal modes are characterized by an average frequency $\bar{\omega}_I$. In fitting to the data we found it necessary to use a broadened peak for F_I , rather than just a single hard Einstein frequency. We chose a Gaussian-broadening function $F_I = [(2\pi)^{1/2}\Gamma]^{-1} \exp[-(\omega - \bar{\omega}_I)^2/2\Gamma^2]$. For $\text{PbMo}_{5.1}\text{S}_6$, we find that $\omega_D = 70$ K (6.0 meV), $\omega_E = 140$ K (12.1 meV), $\omega_I = 465$ K (40.1 meV), and $\Gamma = 0.3\bar{\omega}_I$. For SnMo_5S_6 , $\omega_D = 74$ K (6.4 meV), $\omega_E = 155$ K (13.4 meV), and $\bar{\omega}_I$ and Γ are the same as above. Figure 1 demonstrates the quality of the fit for $\text{PbMo}_{5.1}\text{S}_6$. Note that the nine external mode frequencies are in the immediate region that Bergmann and Rainer¹⁴ indicate is necessary to optimize T_c (i.e., $\omega_{\text{opt}} \approx 2\pi T_c$). The major effect of the defect structure on C_L compared to a nondefect lattice that we have considered is that the value of n in Eq. (1) is lower than 12.

Inelastic-neutron-scattering studies were performed on polycrystalline PbMo_6S_8 ($T_c \sim 14$ K) at the Karlsruhe research reactor. The generalized phonon density of states $G(\omega)$ is obtained from the

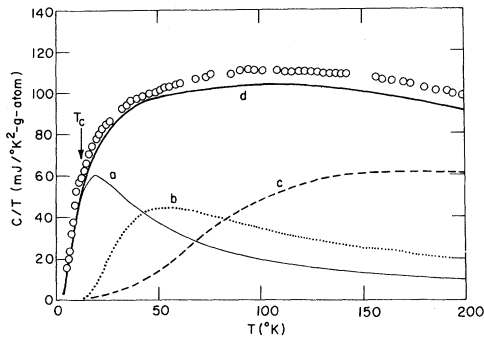


FIG. 1. The measured heat capacities (circles) and calculated lattice heat-capacity curves for PbMo_6S_8 . See text for details. Note that the F_A , F_E , and F_I contributions (denoted by curves a , b , and c) play important roles in influencing the shape of C_L/T in different temperature ranges. The experimental data rise above the total calculated curve d because they contain electronic and nonharmonic contributions, because the absolute accuracy is $\pm 2\%$, and because of obvious shortcomings of our simple model for $F(\omega)$.

scattering law measurements:

$$G(\omega) = \sum_i (\sigma/M)_i F_i(\omega) \times \exp[-2(W_i - \bar{W})] |\vec{Q} \cdot \vec{U}_i|^2, \quad (2)$$

where the index i is taken over the atomic sites of the unit cell; $(\sigma/M)_i$ is the ratio of the neutron-scattering cross section to the mass and is 0.033, 0.041, and 0.023 cm^2/g for Pb, Mo, and S, respectively; $F_i(\omega)$ is the phonon density of states due to site i ; $F(\omega) = \sum_i F_i(\omega)$; e^{-2W_i} is the appropriate Debye-Waller factor; $e^{-\bar{W}}$ is the average Debye-Waller factor which was used in the evaluation of the scattering-law data $S(\vec{q}, \omega)$; \vec{Q} is a momentum transfer; and \vec{U}_i is a polarization vector. To obtain an accurate $G(\omega)$ a weighted average over a region of scattering angles was calculated from the $S(\vec{q}, \omega)$ data using the method of Bredow *et al.*¹⁵ and corrections for multiphonon processes were applied iteratively. An average σ/M value had to be used in the data reduction which necessarily gives less weight to the highest frequencies which correspond mainly to vibrations of the sulfur atoms. Additionally, the eigenvector weighting and the Debye-Waller factors may exaggerate or suppress particular parts of the true phonon spectrum. Details of the time-of-flight spectrometer can be found in a paper by Gompf *et al.*¹⁶

Hence, the heat-capacity model $F(\omega)$ should only be qualitatively compared to $G(\omega)$. $G(\omega)$ for PbMo_6S_8 appears in Fig. 2, at 297 and 4.2 K. Note that within the rich structure of $G(\omega)$ the in-

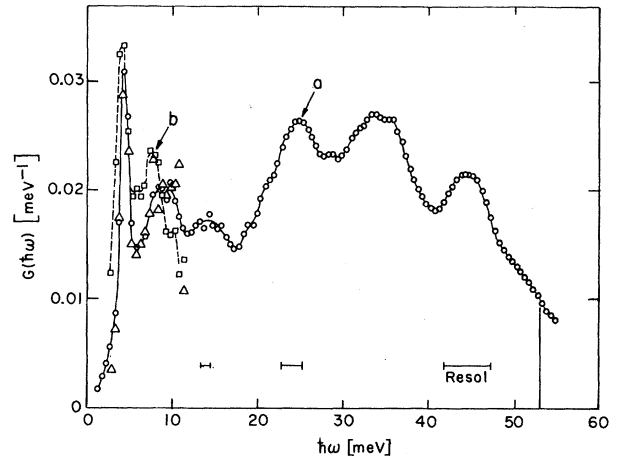


FIG. 2. The generalized phonon density of states $G(\omega)$ for PbMo_6S_8 . Curve a : room temperature results derived in energy gain with $E_0 = 5$ meV neutrons showing the whole spectrum with a pronounced Einstein mode at 4.3 meV (circles). This mode is attributed to the movement of lead atoms whereas the remaining region up to 18 meV contains the acoustical and the rocking modes of the Mo_6S_8 units, the optical vibrations of which are associated with the higher-energy part of the spectrum. The resolution broadening is significant at higher energies and the spectrum was cut off at 53 meV for normalization. Triangles belong to room temperature measurements in energy loss with $E_0 = 23.8$ meV. Curve b : low-temperature results at 4.2 K derived in energy loss with $E_0 = 23.8$ meV neutrons showing pronounced softening in the acoustical part of the phonon spectrum.

ternal modes appear as three bands at the highest frequencies. There is a trough in $G(\omega)$ centered at ~ 18 meV which, in the molecular-crystal model, corresponds to the gap between the internal and external modes. The external vibrations group into the sharp Einstein-like mode at 4.3 meV and a broad hump near 10 meV, which, in agreement with the heat-capacity model, may be identified as the translational modes and the torsional modes of the quasirigid Mo_6S_8 units, respectively. The Einstein-like mode is believed to be largely associated with motion of the Pb atom in the channels between the Mo_6S_8 units. Because of the large intramolecular distances in these compounds the overlap between the Pb orbitals and the nearest-neighbor S orbitals is rather small. Thus the Pb atoms can be thought to execute three-dimensional simple vibrations. The frequency must be very low because of the heavy mass and the small coupling force constants. Additional support of this picture comes from $G(\omega)$ measurements on the Mo_6Se_8 compound

where the only substantive difference is that a comparable sharp Einstein mode is absent in contrast to PbMo_6S_8 and PbMo_6Se_8 samples.¹⁷ Also, it is clear from Fig. 2 that the acoustical part hardens between 4.2 and 297 K. (We will discuss this feature later.) Measurements with an incident energy $E_0 = 65$ meV which are not shown in Fig. 2 also show the phonon hardening around 8 meV on heating. As a result of the better resolution at medium energies they show a more pronounced and temperature-independent gap around 18 meV. No hardening of the phonon frequencies is observed in the upper part of the $G(\omega)$ spectrum which is attributed to the internal modes.

The neutron-inelastic-scattering experiments on SnMo_6S_8 ($T_c = 12.4$ K) were performed at the Argonne CP-5 reactor at 300 and 90 K. The incident energy used was 4.83 meV and the measurements were performed with neutron-energy gain (see Fig. 3). The $G(\omega)$ were obtained from scattering-law measurements, except that no multiphonon corrections were made and $\bar{W} = 0$ was used in Eq. (2). The experimental apparatus is described elsewhere.¹⁹ The attenuation of the Einstein-like peak is believed, however, to be an experimental artifact.¹⁸

Mössbauer studies⁷ of SnMo_6S_8 indicate that the Debye-Waller factor is highly anharmonic due to the low-temperature softening of $F_{\text{Sn}}(\omega)$. The Sn (or Pb) atom undergoes large-amplitude displacements, since one Sn atom occupies essentially the same volume as a Mo_6 octahedron. Hence, the Sn atom may be expected to experience a highly anharmonic potential which would lead one to expect that the Einstein-like peak should be temperature dependent. Instead, the acoustic

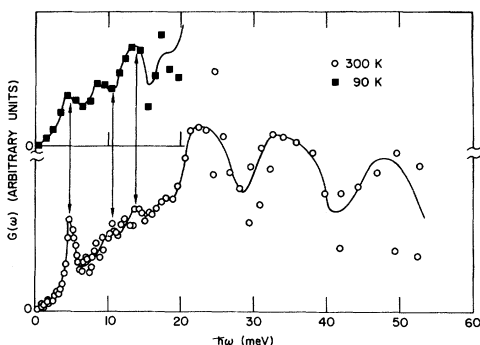


FIG. 3. $G(\omega)$ for SnMo_6S_8 at 300 and 90 K. The units for $G(\omega)$ are arbitrary and different at each temperature. Note the acoustic softening on cooling in the 8–10-meV region. The attenuation of the low-frequency peak at low temperature is believed to be an experimental artifact (Ref. 18).

peak softens considerably in both ternaries. Presumably the Einstein-like modes attributed to the X-atom motion are actually hybridized to the acoustic branches.

The molecular-crystal model has important implications for the superconductivity of these materials. The magnitude of T_c is expected to be largely governed by the coupling strengths of the conduction electrons to the *external* phonon modes. We speculate, since the conduction electrons are believed to be predominantly *d*-like states derived from Mo, that the torsional modes, which involve relative displacements of Mo_6 octahedra, will themselves be particularly important in determining the magnitude of T_c .

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Melting of Crystalline Suspensions of Polystyrene Spheres

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We have measured the melting temperatures of crystallized suspensions of polystyrene spheres as a function of concentration. By analyzing the data on the basis of a simple model we can estimate the heat of melting and the entropy change.

Charged spherical polymer particles in aqueous suspension¹ can form an ordered crystalline array.²⁻⁵ The particle size is nearly uniform and typically around $0.1 \mu\text{m}$. In the crystallized suspension the interparticle separation is typically around $0.5 \mu\text{m}$. Iridescence, due to strong Bragg scattering of visible light by the crystal lattice, gives visual evidence of long-range order. Well-defined individual crystallites, up to several millimeters in size, are visible. The crystal structure is bcc with some admixture of fcc at high particle concentrations.⁶ A remarkable feature of this system is that, by crystallizing suspensions of different concentrations, it is possible to vary the lattice constant systematically, by a factor of 3, without changing the crystal structure. This, together with the long range of the forces involved, has led us to propose⁶ that the crystal-ordering forces must be electrostatic, similar to those in the electron Wigner crystal. A similar crystalline order among large particles has been reported for some virus suspensions.⁷ In this Letter we report the first observation of the melting point in such a system as a function of the particle concentration. The melting temperature increases with increasing particle concentration. We interpret the data with an elementary model that gives an estimate of the heat of fusion and the corresponding entropy change.

Recently, Schaefer and Ackerson⁸ reported a melting transition in a crystalline suspension of polystyrene particles. We have investigated this transition further and find that the melting temperature can be strongly influenced by ionic impurities. By proper treatment with an ion-exchange resin, these can be removed, to give reproducible melting temperatures. The melting temperature then depends in a regular way on the concentration of polymer particles. For the concentration range over which we have worked, when care is taken to minimize ionic impurities, the crystals always grow to fill the entire volume of water. The phase separation reported by others³ does not appear under these conditions.

The behavior of the system indicates that the melting is a first-order transition. The crystallites have sharp boundaries and the melting of an individual crystallite takes place over a narrow temperature range of no more than 1 K. Thus, to analyze the concentration dependence of the melting point we will use a model with a finite energy and entropy of transition.

We used a suspension of uniform latex particles of polystyrene supplied by the Dow Chemical Co. The original suspension contained 1.4×10^{14} particles per cubic centimeter and the mean particle diameter was $0.109 \mu\text{m}$. It was a nearly monodisperse suspension. The standard deviation of the