since it is obvious (Figs. 1 and 2) that this is not an ordinary thermally activated process. It seems possible that the signal is due to dipoles snapping into or out of alignment as the temperatures in different parts of the crystal pass through the transition temperature. Thus, the structure in the data may be attributed to the fact that dipoles may line up differently in different domains.

We can determine if impurities play a role by doing the experiment on crystals doped with impurities. We are now in the process of growing the crystals to do this.

In this paper we have reported experiments on self-polarization in NH_4Cl and NH_4Br. The effect is very interesting but we do not have enough experimental evidence to give an explanation except in very tentative terms.

We wish to express our appreciation to Dr. H. Hobgood and Mr. W. Mealing, who were responsible for the design and construction of the apparatus.

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Isotope Effect of the Superconducting Transition Temperature in Binary Chevrel-Phase Mo_6Se_8

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(Received 9 March 1978)

Isotope-effect measurements on the binary Chevrel superconductor Mo_6Se_8 are reported with either Mo or Se replaced by their isotopes. Within our uncertainty the isotope-effect exponent of $T_c \propto M^{-\beta}$ is equal in both cases ($\beta_{Mo} = 0.27 \pm 0.04$, $\beta_{Se} = 0.27 \pm 0.05$). We concluded that only modes to which the six Mo and the eight Se atoms contribute about equally are determining T_c: These are acoustic translational modes of the Mo_6Se_8 cluster and its internal optical modes, whereas torsional modes of the cluster must be of minor importance.

The discovery of superconductivity[1] in Chevrel-phase[2] molybdenum chalcogenides has stimulated research on these compounds. The extraordinarily large upper critical fields,[3] and the occurrence of short-range[4] and long-range[5] magnetic order are among the prominent features of these superconductors. To understand their superconducting behavior, and to see which of the various phonon modes of these compounds are important for superconductivity, measurements of the Eliashberg electron-phonon coupling $\alpha^2F(\omega)$ by tunneling spectroscopy should be performed. These experiments are very difficult because of the high pressure sensitivity of the compounds (using a point-contact method[6]),[7] and problems in making coherent and reliable barriers (for sandwich investigations). We have applied another method to answer—at least partially—questions concerning $\alpha^2F(\omega)$, and the influence of the various modes by using the superconducting isotope effect.

The quasirigid Mo_6Se_8 clusters are building blocks for the ternary Chevrel-phase molybdenum selenides and are believed to be essential for their properties.[3,8] This binary system whose crystal structure is hexagonal-rhombohedral, space group $R\bar{3}$, with one Mo_6Se_8 per unit cell,[9] is well suited for measurements of the isotope effect because both atoms have a substantial number of stable isotopes. It is possible to vary the mass of Mo and Se independently by about 8%. The resulting variation of the transition temperature, T_c, to the superconducting state gives information which modes of the atoms contribute most to superconductivity in this system.

The main experimental problem in this investigation has been the synthesis of compounds with a reproducible and sharp transition temperature. Usually the transition width of Chevrel-phase superconductors and the T_c scattering of nominally identical samples are at least a few tenths of a degree.[3,10]

The optimal preparation conditions to obtain single-phase samples with reproducible and sharp transitions have been found empirically using natural Mo and Se powder as starting materials.[11] The understoichiometric initial composition $Mo_6Se_{7.6}$ has been taken because the composition Mo_6Se_8 leads to $MoSe_2$ contamination of the binary Chevrel phase.[10] Following the standard preparation methods, the powders (100 mg total) have been thoroughly mixed in an agate mortar under spectroscopically pure acetone and sealed in dried transparent quartz tubes at 10^{-5} Torr. For the reaction a long tube furnace stuffed with high-temperature insulation material on both ends was used to keep temperature gradients as small as possible. In each reaction cycle, up to twelve samples have been heated simultaneously from 400°C to 1200°C at a rate of 2.4°C/min, reacted for 13 h at 1200°C, and quenched in air afterwards.

These prereacted identical samples have been powdered and compressed to pellets (3 mm diam, 2 mm length) at 400 kPa. For annealing, the pellets have been placed again in quartz tubes and sealed under 10^{-5} Torr. The samples have then been heated continuously from room temperature to 1200°C at a rate of 20°C/min and annealed at 1200°C fro 17 hours. Finally they have been cooled down slowly inside the furnace. The resulting samples of $Mo_6Se_{7.6}$, containing natural Mo and Se, have been used to study the T_c scattering of identical pellets from the same production cycle. The maximum T_c scattering of these samples is $\Delta T_c = \pm 0.015$ K; this value has been used to calculate the standard deviation for the isotope-effect exponents (see below). The transition temperatures of nominally identical samples produced in separate runs differ by a few hundredths of a degree.

For the preparation of the isotope samples, following the above mentioned procedure, $^{92,94,96,98,100}Mo$ or $^{76,78,80,82}Se$ have been used.[12] In order to remove oxygen we have reduced the Mo-isotope powders simultaneously for 3 h at 900°C in high-purity hydrogen atmosphere. The obtained powders are of metallic gray luster equivalent to Mo powder of 2-μm grain size.

The lattice parameters of the hexagonal cell for the nine isotope samples evaluated from x-ray diffraction diagrams (Cu Kα, $\lambda = 1.5418$ Å), are constant to within ±0.005 Å ($\bar{a} = 9.56$ Å, $\bar{c} = 11.17$ Å). The samples were single phase except for $^{100}Mo_6Se_{7.6}$ which contained a barely detectable amount of an unidentified second phase. Samples prepared from oxygen-contaminated Mo powder showed a significally broadened superconducting transition. No such broadening has been detected for $^{100}Mo_6Se_{7.6}$ (see Fig. 1).

The superconducting transitions have been measured using a mutual-induction technique. For each cooldown, five isotope samples and a Pb reference sample were placed in a copper chamber containing the pickup coils in a circular arrangement inside an ac field coil (0.2 Oe at 117 Hz). The temperature has been measured by a calibrated germanium resistor. T_c has been defined as the midpoint of the inductive transition, and the width ΔT_c is taken between 10% and 90% of this transition.

Figure 1 shows the transition curves of the series $Mo_6{}^{76,78,80,82}Se_{7.6}$ and of $^{92,94,96,98,100}Mo_6Se_{7.6}$. A very similar dependence of T_c on isotopic mass is clearly visible in both cases. Figure 2 shows plots of $\log T_c$ versus $\log M$ where M is the Mo or Se mass. The experimental data are fitted with the relation $T_c = \mathrm{const}M^{-\beta}$ using a least-squares-fit procedure. Using the above mentioned value for the T_c scatter of identical samples ($\Delta T_c = \pm 0.015$ K) to calculate the standard deviation of β, we obtain for the isotope-effect exponents

$$\begin{aligned} \beta(M = M_{\mathrm{Mo}}) &= 0.27 \pm 0.04, \\ \beta(M = M_{\mathrm{Se}}) &= 0.27 \pm 0.05. \end{aligned} \tag{1}$$

The same exponents are found for other definitions of T_c.

Besides the direct change $\partial \ln T_c / \partial \ln M$ of the

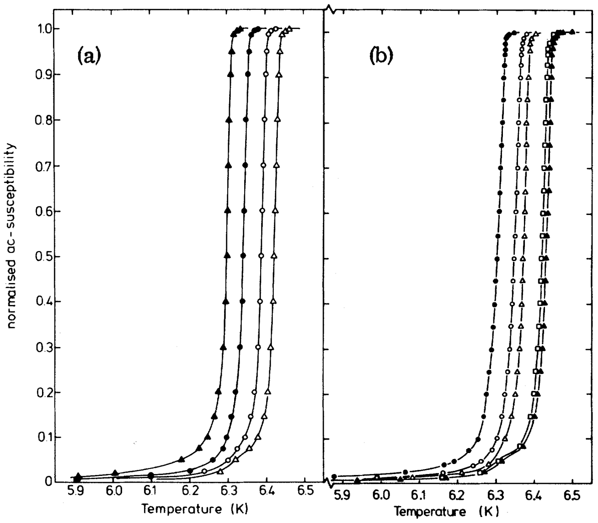

FIG. 1. Inductively measured superconductive transitions of (a) $Mo_6{}^mSe_{7.6}$ and (b) $^nMo_6Se_{7.6}$. The nominal isotopic masses are $m = 82, 80, 78, 76$ in (a) and $n = 100, 98, 96, 94, 92$ in (b), from left to right (Ref. 12).

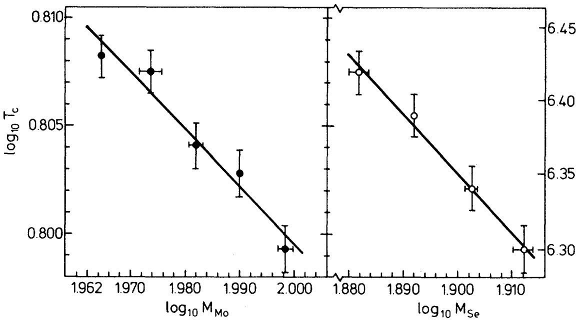

FIG. 2. Logarithmic plot of T_c vs isotopic mass M of Mo and Se. The lines have slopes of -0.27.

superconducting transition temperature T_c by the variation of the isotopic mass (via the variation of the phonon structure by changing the kinetic energy of the ions) there exist indirect contributions from the mass dependence of the unit-cell volume due to zero-point lattice vibrations,[13] T_c being volume dependent. The experimentally found isotope-effect exponent, β_{expt}, is therefore

$$\beta_{\text{expt}} = -\frac{d\ln T_c}{d\ln M} = -\frac{\partial \ln T_c}{\partial \ln M} - \frac{\partial \ln T_c}{\partial \ln V}\frac{d\ln V}{d\ln M}$$

$$= \beta_M + \beta_V. \tag{2}$$

Using the pressure dependence of T_c and the compressibility, κ, the exponent β_V can be written as $\beta_V = (\partial T_c/\partial P)_0 (d\ln V/d\ln M)/T_c\kappa$. Unfortunately, $d\ln V/d\ln M$ is not known for Chevrel-phase superconductors but from the sign of $(\partial T_c/\partial P)_0$ for Mo_6Se_8,[7] we can conclude that β_V is positive. This could well account for the fact that we observe $\beta_{Mo} + \beta_{Se} \gtrsim 0.5$.

For a discussion of our results we use the molecular crystal model proposed by Bader *et al.*[14] which allows the separation of the 42 phonon modes per unit cell of Mo_6Se_8 into three groups: three acoustic translational plus three torsional modes of the Mo_6Se_8 cluster (external modes), and its 36 internal modes. With use of this simplified model for the phonon density of states,

$$F(\omega) = 3F_{\text{trans}}(\omega) + 3F_{\text{tors}}(\omega) + 36F_{\text{int}}(\omega), \tag{3}$$

the total Eliashberg electron-phonon coupling function $\alpha^2F(\omega)$ is

$$\alpha^2F(\omega) = 3\alpha_{\text{trans}}^2 F_{\text{trans}}(\omega) + 3\alpha_{\text{tors}}^2 F_{\text{tors}}(\omega) + 36\alpha_{\text{int}}^2 F_{\text{int}}(\omega), \tag{4}$$

where the α's are electron-phonon coupling constants for the various groups of lattice modes. Each of the three phonon modes is connected with an effective mass $M_{\text{eff}}(\omega_i)$, $i = 1, 2, 3$; the mass dependence of the phonon frequencies is then given by

$$d\ln\omega_i = -\tfrac{1}{2} d\ln M_{\text{eff}}(\omega_i).$$

The frequency change $\delta\omega$ gives rise to a change in $\alpha^2F(\omega)$; the resulting $\delta\alpha^2F(\omega)$ varies T_c by δT_c. According to this reasoning the contribution of the direct isotope-effect exponent β_M to the experimentally observed isotope-effect exponent β_{expt} has been calculated by Rainer[15] by solving the linearized Eliashberg equations, and is

$$d\ln T_c = -\int_0^\infty d\omega\, R(\omega)\, \alpha^2F(\omega) d\ln M_{\text{eff}}(\omega), \tag{5}$$

with

$$R(\omega) = \frac{d}{d\omega}\left(\frac{\omega}{2T_c}\frac{\delta T_c}{\delta\alpha^2F(\omega)}\right),$$

where $\delta T_c/\delta\alpha^2F(\omega)$ is the functional derivative introduced by Bergmann and Rainer.[16] The weighting function $R(\omega)$ shows how much a phonon mode of frequency ω contributes to the isotope effect; it puts maximum weight to phonons in the range of $2\pi kT_c$. To distinguish between the Mo and Se isotope effects we need the coefficients c_{Mo} and c_{Se}, defined by $d\ln M_{\text{eff}} = c_{Mo} d\ln M_{Mo} + c_{Se} d\ln M_{Se}$. These coefficients describe how much the six Mo or the eight Se atoms contribute to a particular mode. They can be calculated from the effective masses for the three modes, and are given with those masses in Table I.

Assuming discrete phonon frequencies for the various modes as an approximation, the above expression equation (5) simplifies to

$$d\ln T_c = -\sum_{\omega=\omega_{\text{trans}},\omega_{\text{tors}},\omega_{\text{int}}} R(\omega)\alpha^2(\omega)F(\omega)[c_{Mo}(\omega) d\ln M_{Mo} + c_{Se}(\omega) d\ln M_{Se}]. \tag{6}$$

For the calculation of numerical values of the coefficients c_{Mo} and c_{Se}, mean masses of the Mo and Se isotopes ($\bar{M}_{Mo} = 95.91$, $\bar{M}_{Se} = 78.92$) of our samples have been used. Neglect of slight cluster distortions and of changes of the cluster mass due to the understoichiometirc composition $Mo_6Se_{7.6}$ is justi-

TABLE I. The coefficient c_{Mo} and c_{Se} as calculated from the effective masses M_{eff} for the three phonon modes.

	$\mathrm{Mo_6Se_8}$ cluster translation mode	Libration around a symmetry axis of the idealized $\mathrm{Mo_6Se_8}$ cluster [a]	Typical internal optical mode
M_{eff}	$6M_{\mathrm{Mo}} + 8M_{\mathrm{Se}}$	$a^2(M_{\mathrm{Mo}} + 4M_{\mathrm{Se}})$	$\frac{M_{\mathrm{Mo}}M_{\mathrm{Se}}}{M_{\mathrm{Mo}} + M_{\mathrm{Se}}}$
$6_{\mathrm{Mo}}(\omega)$	$\frac{6M_{\mathrm{Mo}}}{6M_{\mathrm{Mo}} + 8M_{\mathrm{Se}}} = 0.48$	$\frac{M_{\mathrm{Mo}}}{M_{\mathrm{Mo}} + 4M_{\mathrm{Se}}} = 0.23$	$\frac{M_{\mathrm{Se}}}{M_{\mathrm{Mo}} + M_{\mathrm{Se}}} = 0.45$
$c_{\mathrm{Se}}(\omega)$	$\frac{8M_{\mathrm{Se}}}{6M_{\mathrm{Mo}} + 8M_{\mathrm{Se}}} = 0.52$	$\frac{4M_{\mathrm{Se}}}{M_{\mathrm{Mo}} + 4M_{\mathrm{Se}}} = 0.77$	$\frac{M_{\mathrm{Mo}}}{M_{\mathrm{Mo}} + M_{\mathrm{Se}}} = 0.55$

[a] Cluster distortions have been neglected; the eight Se atoms form a cube of length a.

fied in this crude model, and the idealized coefficients may well be used for further argumentation.

Within the molecular crystal model, Bader *et al.*[14] except the magnitude of T_c to be governed largely by the coupling strength of the conduction electrons to the external (translational and torsional) phonon modes, which lie near the frequency range known to optimize T_c.[16] They suggest that torsional modes involving relative displacements of the $\mathrm{Mo_6}$ octahedra will be particularly important in determining the magnitude of T_c. As can be seen from Table I, the torsional modes have the tendency to increase β_{Se} at the expense of β_{Mo}. If only torsional modes had a nonzero coupling α^2 to the conduction-electron system, the ratio of the isotope-effect exponents $\beta_{\mathrm{Se}}/\beta_{\mathrm{Mo}}$ should be ~ 3.3. Equal nonzero coupling for translational and torsional modes gives a ratio of ~ 1.6. These values contradict the experimentally found ratio of 1.0. Therefore an equal coupling of translational and torsional modes when they are largely governing T_c can be excluded; torsional modes do not contribute substantially to β and T_c. For translational or internal modes $\beta_{\mathrm{Se}}/\beta_{\mathrm{Mo}}$ are ~ 1.1 or 1.2, respectively —both close to the measured value. Unfortunately, we are therefore unable to tell whether the translational modes or the internal modes of the cluster are of more importance in determining T_c and β. Furthermore, it is too crude an approximation to take only one effective mass for the 36 internal modes; so more detailed calculations are necessary to answer the latter question.

We are very grateful to Dr. D. Rainer for many discussions and calculations related to this work and we thank Professor H. Kirchmayr for his interest.

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Phase Diagrams of Pseudo One-Dimensional Heisenberg Systems

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(Received 13 January 1978)

We present the first theoretical results on the anomalous field dependence of the Néel temperature for a system of loosely coupled classical Heisenberg chains with orthorhombic anisotropy for different directions of the applied magnetic field. The results compare favorably with the experimental phase diagrams of a series of selected $S=\frac{5}{2}$ compounds with varying degrees of one dimensionality and anisotropy.

The ordering temperature $T_N(H)$ of a pseudo one-dimensional Heisenberg antiferromagnet may increase drastically when an external magnetic field is applied. This initially surprising effect has been documented recently by a number of experimental results.[1-5] It seems that the theoretical approach suggested by Villain and Loveluck,[6] which is based on the behavior of the correlation length within the individual chains in the classical spin model,[7-10] gives at least the right order of magnitude. However, as we will show, the drastic influence of some anisotropy resulting in essentially different phase boundaries with the field applied along different directions (including the introduction of a spin-flop phase) cannot be reproduced by this isotropic theory. Therefore a conclusion about the validity of the description of this effect is precluded so far.

In this Letter we will present the first results of a transfer-matrix approach for the classical Heisenberg chain with small orthorhombic anisotropy. We will show that this approach is capable of reproducing the field dependence of the Néel temperature in a series of real pseudo one-dimensional Heisenberg $S=\frac{5}{2}$ systems with the field along each of the three principal axes.

In Figs. 1–3 our data on the phase diagrams are presented for a selected, representative series of pseudo one-dimensional systems. Some characteristic parameter values of this series are tabulated in Table I. The data were obtained from a continuous heating method, thus identifying the transitions by the maxima in the specific heat. From inspection of these results it is obvious that in a general sense the rise in $T_N(H)$ strongly depends on the degree of one dimensionality, characterized by the entities in Table I. This indicates that basically the understanding of this anomalous behavior must be sought in the properties of the individual chains. Therefore, we will treat the system as consisting of loosely coupled chains.

For such a system T_N is implicity given in the mean-field approach by[5]

$$2zJ'\chi(T_N(H),H)=1, \quad (1)$$

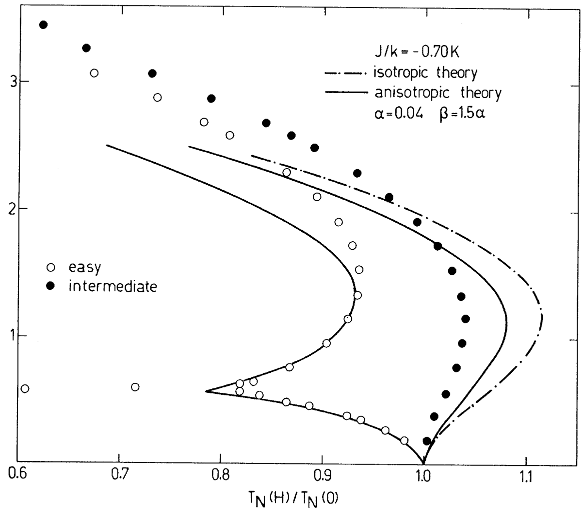

FIG. 1. Experimental phase diagram of $(NC_5H_6)MnCl_3\cdot H_2O$ (PMC), together with the theoretical predictions. Data for the hard axis are not shown since they reveal a more complicated phase diagram which is most likely due to a small canting of the magnetic moments.