

not rule out the possibility that the present system may yet undergo a spin-glass-like transition at temperatures below those studied here.

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¹⁰A fit of the model described to higher-temperature measurements gives $a \sim -0.01$ deg/G \cdot mm. We adopt this value tentatively for the sake of Fig. 1, where it gives a correction $<3\%$. We also note that a has the opposite sign from the value stated in Ref. 8. Further experiments are necessary before we come to a firm conclusion about the sign and magnitude of a .

¹¹In Ref. 8, data on a similar sample for $1.6 \text{ K} \leq T \leq 2.3 \text{ K}$ led to an estimate $\langle \Theta \rangle \sim 0.3 \text{ K}$. Subsequent data at higher temperatures showed this to be an underestimate. For similar reasons, $\langle \sigma_x \rangle$ was overestimated by a factor ~ 2 at 1.6 K and the spin-flip cross section was underestimated by a factor ~ 4 .

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Self-Polarization at the Order-Disorder Phase Transition in NH_4Cl and NH_4Br

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Spontaneous or self-polarization current peaks were observed in NH_4Cl and NH_4Br , when the samples were thermally cycled through their order-disorder phase transition. In NH_4Cl , but not NH_4Br , these peaks can be modulated by an externally applied electric field. It is expected that this difference is due to the ferromagneticlike order in NH_4Cl and the antiferromagneticlike order in NH_4Br .

In this paper we report our observations on the spontaneous or self-polarization current peaks in NH_4Cl and NH_4Br , when the samples are thermally cycled through their low-temperature phase transition. The words "spontaneous" and "self" are used here to mean that the currents are the result of the rearrangement of charges in the sample that occurs during the phase transition and not due to an externally applied electric field. An earlier observation of this effect in NH_4Cl has been reported by Kessler.¹ Our results confirm his, but we have studied additional features of this self-polarization and have observed a signifi-

cant difference in the behavior of NH_4Cl as compared to NH_4Br .

NH_4Cl and NH_4Br show low-temperature phase transitions at 243 and 235 K, respectively. In the low-temperature phase, the NH_4 tetrahedra order ferromagnetically for NH_4Cl and antiferromagnetically for NH_4Br . In the ordered state, NH_4Cl is piezoelectric while NH_4Br is not.² Since the transition is associated with the preferred orientation of the NH_4 ions and our results show a self-polarization peak at the transition temperature, it is expected that this peak is related to the orientation or disorientation of the NH_4 ions

as the sample is taken through the transition.

The apparatus used for the results reported here is one designed to make ionic thermocurrent measurements. The electrometer is capable of measuring about 10^{-16} A, and the insulation of the wire from the top of the sample is by sapphire bushings so as to preserve this capability. The heating and cooling rates are constant in the range of 0.5 to 5 K/min. Mechanical stress to the crystal was minimized by using a very thin wire silver painted at one point to the silver-paint top electrode of the sample.

The measurements were made by bringing the sample to a steady temperature a few degrees above or below the transition and allowing the temperature controller to drive the temperature through the transition temperature. In some cases, the sample was polarized before making measurements. This was done by applying a polarizing voltage across the sample (electrometer removed) just above the transition temperature, and allowing the sample to cool to a temperature below the transition temperature. The externally applied voltage was then removed, the electrometer was reconnected, and the measurement proceeded as before.

A typical self-polarization peak for NH_4Cl is shown in Fig. 1. The delay in the onset of the polarization after going through the transition temperature is believed to be due to the fact that there exists a temperature gradient in the sample, such that the actual temperature of the sample is higher than the thermocouple on cooling

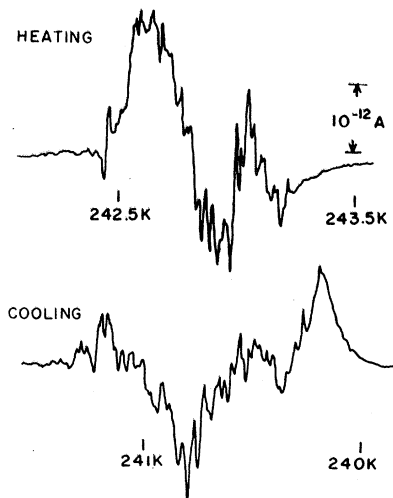


FIG. 1. Self-polarization data for NH_4Cl (I vs T). Heating and cooling rate is approximately 1.5 K/min.

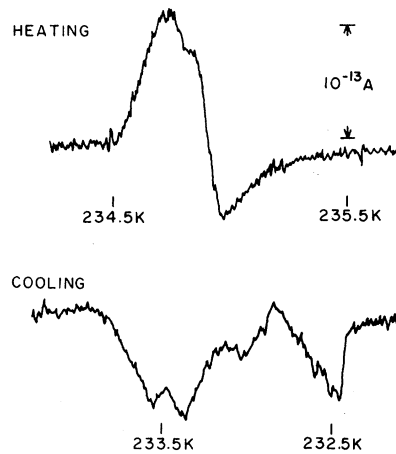


FIG. 2. Self-polarization data for NH_4Br (I vs T). Heating rate is approximately 1.5 K/min and cooling rate is approximately 2 K/min.

and lower than the thermocouple on heating. As can be seen in Fig. 2 similar curves were obtained for NH_4Br , but the peak height was typically smaller by a factor of 3–10 than that of a similarly sized sample of NH_4Cl .

To test whether the signal was associated with the temperature gradient, measurements of the gradient were made by inserting a thermocouple into a hole drilled about midway between the top and bottom of a 7-mm-thick sample. Figure 3

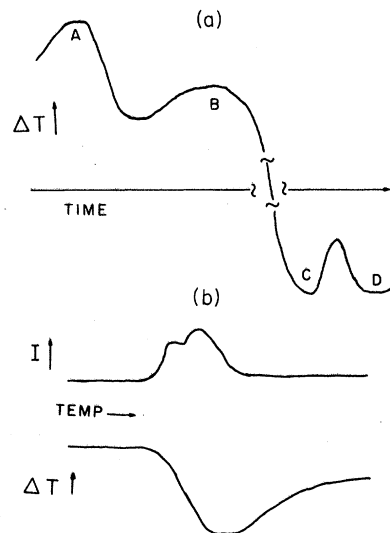


FIG. 3. Temperature gradient (ΔT) and I vs time for 7-mm-thick NH_4Cl sample. (a) ΔT vs time; onset of transition is at A and C. (b) I and ΔT vs time. The dip of ΔT is concurrent with the onset of the self-polarization current.

shows the difference in temperature (ΔT) between the center of the sample and the bottom electrode along with the self-polarization current as a function of time. The decrease of ΔT and its subsequent increase as the temperature decreases through the transition is probably due to a latent heat during the transition. In an attempt to modify the existing temperature gradient, one sample was mounted in a small aluminum planchet and measurements were performed with the planchet empty and filled with silicone pump oil. It was hoped that this would alter the gradient and show the gradient's effect on the signal. However, there was no perceptible difference in the two cases.

The effect of applying a polarizing field to NH_4Cl is shown in Fig. 4, curves A and B. The amplitude of the signal could be increased, decreased, or even reversed by the application of an appropriate external electric field. In NH_4Br the effect of an external electric field is either nonexistent or very small as shown in Fig. 4, curves C and D. The maximum electric field applied was about 2000 V/cm.

One further observation is interesting. The structure in the self-polarization data is more pronounced for lower heating and cooling rates. This structure was observed repeatedly and was found to be reproducible if the temperature of the sample did not vary appreciably from the transi-

tion temperature. The structure was not always reproducible if the sample was allowed to stand at room temperature for some time between runs.

At this stage we do not know the origin of this phenomenon of self-polarization in NH_4Cl and NH_4Br . It is obvious that it is associated with the phase transition temperature. Two candidates immediately suggest themselves: permanent dipoles and the piezoelectric effect.

It is known that NH_4Cl is piezoelectric in its ordered phase. Therefore, if the sample becomes strained as it goes through the transition, one would expect to see a signal due to this effect. The sample could become strained as a result of existing temperature gradients (Fig. 3). A self-polarization signal is seen between A and B and between C and D. However, a gradient which changes from positive to negative exists between B and C where the crystal is in the ordered phase and no signal was seen. One would expect this to be the region where the strain is greatest.

The difference between NH_4Cl and NH_4Br when subjected to an external electric field is noteworthy. However, at the moment we simply do not have an explanation for this, except to postulate that it is associated with the fact that NH_4Cl exhibits ferromagnetic order and is piezoelectric while NH_4Br orders antiferromagnetically and is not piezoelectric in the ordered state. Another study has shown there exist piezoelectric domains in NH_4Cl , and further that the domain structure can be modified by the application of suitable external fields.³ This is just the type of behavior observed in NH_4Cl . Since NH_4Br is not piezoelectric in the ordered phase, one would not expect a field effect to occur, as is the case.

The NH_4 ions do not have a dipole moment, but dipoles may be present in the crystal as a result of any of the following: (1) molecular defects such as NH_3 or HCl due to the possibility of a proton transfer in ammonium salts⁴; (2) dipole moments of anions due to octopolar interaction of NH_4 tetrahedra⁵; and (3) impurity-vacancy dipoles. Given that dipoles do exist in the crystal it is easy to see how the self-polarization signal comes about. Our research suggests that the dipoles become aligned as the crystal changes from the disordered state to the ordered state, thereby producing a current in the external circuit. A reverse signal is produced as the crystal is brought from the ordered state to the disordered state, thus reducing the net polarization to zero.

The normal ionic thermocurrent analysis cannot be applied to the self-polarization signals,

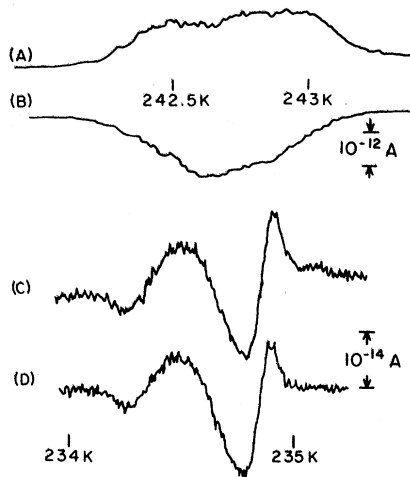


FIG. 4. Field effect for NH_4Cl and NH_4Br : Curve A, field of approximately +2000 V/cm applied to NH_4Cl . Curve B, field of approximately -2000 V/cm applied to NH_4Cl . Curve C, field of approximately +2000 V/cm applied to NH_4Br . Curve D, field of approximately -2000 V/cm applied to NH_4Br .

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 ex-

perimental evidence to give an explanation except in very tentative terms.

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

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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 ($\beta_{\text{Mo}} = 0.27 \pm 0.04$, $\beta_{\text{Se}} = 0.27 \pm 0.05$). 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 superconductivity¹ in Chevrel-phase² molybdenum chalcogenides has stimulated research on these compounds. The extraordinarily large upper critical fields,³ and the occurrence of short-range⁴ and long-range⁵ 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 method⁶),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