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Ammonium Hydrogen Sulfate: A New Ferroelectric with Low Coercive Field

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$(NH_4)HSO_4$ is ferroelectric in the temperature range between −3°C and −119°C. The symmetry of the room-temperature phase is $P2_1/c$; the ferroelectric phase is also monoclinic, with space group Pc; and the lowest phase, which is piezoelectric, has triclinic symmetry $P1$. All three phases are pseudo-orthorhombic. The coercive field is very low: about 150 v/cm at −13°C. The spontaneous polarization P_s is about 0.4 μcoul/cm^2 at that temperature, and rises to a maximum of about 0.8 μcoul/cm^2 just above −119°C. P_s falls to zero abruptly at the lower transition point. The higher transition is of second order, and the lower of first order.

INTRODUCTION

The appearance of ferroelectricity in a good number of sulfates (and isomorphous selenates and fluoberyllates) renders advisable the dielectric examination of other sulfates. The chemically simplest ferroelectric sulfate to be found heretofore, by Matthias and Remeika,[1] was $(NH_4)_2SO_4$. We have recently discovered remarkable dielectric anomalies in a number of other simple inorganic sulfates, and several new ferroelectrics among these. The first and very simplest of these new ferroelectric compounds is reported here. It is monoammonium acid sulfate, $(NH_4)HSO_4$.

$(NH_4)HSO_4$ is ordinarily obtained by slow cooling of $(NH_4)_2SO_4$ dissolved in concentrated H_2SO_4.[2] Crystals so obtained show excessive electrical conductivity, which renders dielectric measurements difficult. We have found that excellent crystals of $(NH_4)HSO_4$ can be obtained by slow hydrolysis of chloroacetamide in dilute H_2SO_4, with 1 to 1 molar ratio of $ClCH_2CONH_2$ to H_2SO_4. These crystals are nonconducting at first, but must be stored in kerosene or silicone oil to prevent acquisition of atmospheric water. They should be thoroughly dried before dielectric testing, and maintained so. A 2 to 1 molar ratio of $ClCH_2CONH_2$ and H_2SO_4 produces excellent crystals of triammonium disulfate, $(NH_4)_3H(SO_4)_2$.

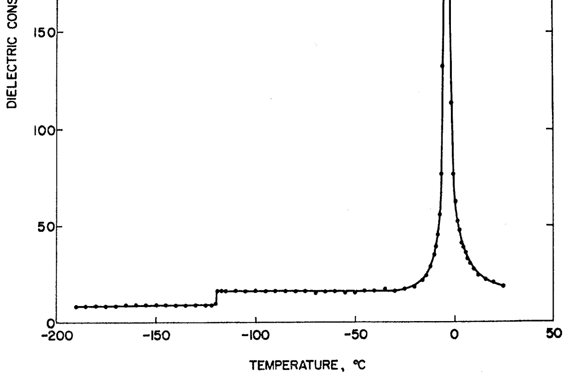

Fig. 1. $(NH_4)HSO_4$: Dielectric constant *vs* temperature.

We subsequently discovered that $(NH_4)HSO_4$ can also be grown from the melt, and is one of the few ammonium salts which can be so crystallized. The melting point is 146.9°C. This is the best method for preparation of large water-clear crystals. The boules show an excellent cleavage plane, and the important dielectric axis (see below) is perpendicular to this.

Both $(NH_4)HSO_4$ and $(NH_4)_3H(SO_4)_2$ show striking dielectric anomalies, and $(NH_4)HSO_4$ proves to be ferroelectric in the temperature range from −3°C to −119°C. As the temperature of $(NH_4)HSO_4$ is lowered to the point of the transition at −119°C, the spontaneous polarization drops sharply to zero and the dielectric constant shows a small but sharp drop. X-ray single-crystal diagrams show symmetry changes at −3°C and −119°C. Thus $(NH_4)HSO_4$ is the first pure material since Rochelle salt to show a ferroelectric phase sandwiched between two nonferroelectric phases.[3]

$(NH_4)_3H(SO_4)_2$ also shows similar dielectric anomalies at about −26°C and at −130°C. The intermediate phase is probably antiferroelectric. X-ray investigations to confirm the true behavior of this crystal in its various phases are in progress.

$(NH_4)HSO_4$ is also remarkable in that it shows an extremely low coercive field: E_c is about 150 v/cm at a point 10° below its Curie point; and this field rises slowly over a temperature range down to −119°C. The maximum value of E_c is 1100 v/cm, just above −119°C.

The specific heat *vs* temperature curve shows a fairly broad anomaly in the neighborhood of −5°C, and a double peak in the region near −115°C. In this latter

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[1] B. T. Matthias and J. P. Remeika, Phys. Rev. **103**, 262 (1956).

[2] P. von Groth, *Chemische Krystallographie* (W. Engelmann, Leipzig, 1908), Vol. 2, p. 314.

[3] See Shirane, Jona, and Pepinsky, Proc. Inst. Radio Engrs. **43**, 1738 (1955).

feature it resembles the double peak in the specific-heat curve of $(NH_4)_2SO_4$ near $-50°C$.[4]

CRYSTALLOGRAPHIC PROPERTIES AT ROOM TEMPERATURE

Groth[2] describes $(NH_4)HSO_4$ as orthorhombic, with axial ratios $a:b:c=0.6128:1:0.7436$. X-ray examination indicates the true symmetry at room temperature to be monoclinic, pseudo-orthorhombic. The symmetry of the pseudo-orthorhombic cell is $B2_1/a$, with $a=24.90_4$ A, $b=4.54_0$ A, $c=14.90_2$ A, $\beta=90°18'$, and $Z=16$. The conventional designation for this symmetry is $P2_1/c$, with $a=14.51_1$ A, $b=4.54_0$ A, $c=14.90_2$ A, $\beta=120°18'$, and $Z=8$. The c axis is the same for both cells.

DIELECTRIC BEHAVIOR

The behavior of the small-field dielectric constant of this crystal, with the electric field along the c axis, at a frequency of 10 kc/sec, is shown in Fig. 1. Two transitions are indicated by dielectric anomalies: one at $-3°C$, and another at $-119°C$. While the dielectric anomaly at the upper transition is very pronounced (the value of ϵ_c rises to a peak value of 1420), the anomaly at the lower transition is very weak, and appears merely as an abrupt decrease in the dielectric constant from a value of 16 to 9. The dielectric constants ϵ_a and ϵ_b do not exhibit any anomalies at these transitions, and their values remain practically constant.

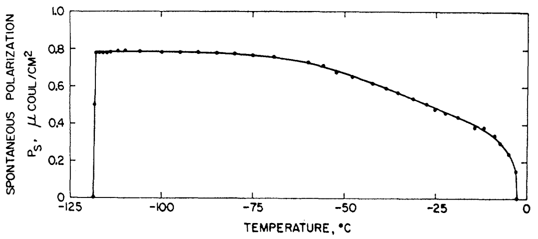

FIG. 2. $(NH_4)HSO_4$: Spontaneous polarization *vs* temperature.

When a c plate of the crystal is examined in a hysteresis bridge, the P *vs* E curve is linear at room temperature; and as the upper transition temperature is approached, the P *vs* E curve exhibits the familiar characteristics of a second-order transition. Below the upper transition temperature, and throughout the temperature region between the two transitions, well-saturated square hysteresis loops are obtained. The values of the spontaneous polarization and the coercive field are given in Figs. 2 and 3, respectively.

A quantitative comparison of the coercive field E_c of $(NH_4)HSO_4$ with that of other ferroelectrics cannot be made, since very few reliable data on the coercive field have been published for other crystals. This is not surprising, because the value of the coercive field is considerably affected by the previous history of the sample, inherent strain, method of mounting, etc., and possibly by defects and dislocations. It can be said that the coercive field observed in $(NH_4)HSO_4$ is one of the lowest so far recorded, and is considerably smaller than E_c for $(NH_4)_2SO_4$. The values of the coercive field given in Fig. 3 represent the lowest obtained in measurements of several crystals.

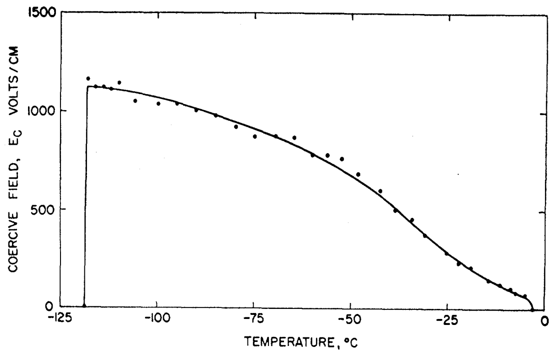

FIG. 3. $(NH_4)HSO_4$: Coercive field *vs* temperature.

At the low-temperature transition, the value of the spontaneous polarization decreases abruptly to zero, and below this transition temperature one obtains only a linear P *vs* E curve down to liquid nitrogen temperature. Examination of the crystal in a newly-constructed Giebe-Scheibe piezoelectric detector revealed piezoelectric properties at all temperatures from $-3°C$ to liquid nitrogen temperature.

Pronounced thermal hysteresis of about 7° was noticed at the low-temperature transition. A thermal hysteresis of 1° was observed at the upper transition, but this is within the error of temperature measurement. The strain involved at the lower transition appears to be rather large; in a few cases crystals cracked to bits as they were taken through this transition.

The extremely large value of the dielectric constant, the shape of the P *vs* E curve at temperatures slightly higher than the upper transition point, and the shape of the P_s *vs* T curve lead one to conclude that the upper transition is of second order. On the other hand, the abrupt discontinuities in the P_s *vs* T, ϵ_c *vs* T curves, the marked thermal hysteresis, and the occasional shattering of the crystals indicate that the lower transition is probably of first order.

THERMAL MEASUREMENTS

The variation of specific heat with temperature of $(NH_4)HSO_4$ is shown in Fig. 4. As already remarked, the double maxima in the neighborhood of $-115°C$ recall the thermal behavior of $(NH_4)_2SO_4$.[4] The lower transition is of first order, with $\Delta Q \simeq 0.34$ kcal/mole, and $\Delta S \simeq 2.1$ cal/mole deg. The transition at $-3°C$ is of second order, with $\Delta Q \simeq 0.12$ kcal/mole and $\Delta S \simeq 0.5$ cal/mole deg.

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[4] Hoshino, Vedam, Okaya, and Pepinsky, Phys. Rev. (to be published).

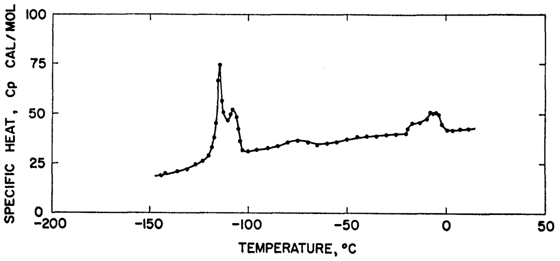

FIG. 4. $(NH_4)HSO_4$: Specific heat *vs* temperature.

FURTHER CRYSTALLOGRAPHIC OBSERVATIONS

It is interesting to note that at room temperature x-ray single-crystal diagrams of $(NH_4)HSO_4$ reveal marked one-dimensional disorder along the *c* axis, which is polar below the upper Curie point. Similar disorder is noted in $(\text{glycine})_3 \cdot H_2SO_4$ and $(\text{glycine})_3 \cdot H_2SeO_4$ slightly above their Curie points.[5]

The symmetry of the intermediate, ferroelectric phase is *Pc*, the twofold screw axis disappearing at the Curie point. Cell constants become $a=14.26$ A, $b=4.62$ A, $c=14.80$ A, $\beta=121°18'$ at -30°C. The pseudo-orthorhombic cell is described in terms of space group *Ba*, with $a=24.37$ A, $b=4.62$ A, $c=14.80$ A, $\beta\approx 90°$.

Below -119°C the symmetry is triclinic. Observations at -140°C show space group *P*1, with $a=14.24$ A, $b=4.56$ A, $c=15.15$ A, $\beta=123°24'$, $\alpha\approx 90°$, $\gamma\approx 90°$. The pseudo-orthorhombic cell with space group *B*1 has $a=24.43$ A, $b=4.56$ A, $c=15.15$ A, $\beta=91°12'$, $\alpha\approx 90°$, $\gamma\approx 90°$. The crystal exhibits marked twinning in this phase. The twin plane is (001).

The structures of the three phases of $(NH_4)HSO_4$ have been under examination in Osaka University by Ogawa and Nitta.[6]

ACKNOWLEDGMENTS

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[5] Hoshino, Okaya, and Pepinsky (to be published).

[6] K. Ogawa and I. Nitta (private communication).

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Theory of the Piezoelectric Effect in the Zincblende Structure

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A theory of the piezoelectric effect in the zincblende structure is developed on the basis of two assumptions: (1) that the Born theory of a homogeneous lattice deformation is applicable, and (2) that each chemical bond is characterized by a vector bond dipole moment. The theory leads to an equation relating the macroscopic piezoelectric constant to the static and dynamic effective charges (properties of the bond moment), and a lattice parameter γ_{14} which relates the internal strain (basis deformation) to the external strain. An x-ray method for measuring γ_{14} is discussed; it utilizes the failure of Friedel's rule in the anomalous dispersion region. An order-of-magnitude check of the theory is made on ZnS. Some remarks are made about the piezoelectric effect in wurtzite based on the same model.

1. INTRODUCTION

The zincblende structure (space group T_d^2 or $F\bar{4}3m$) is the simplest to show the piezoelectric effect.[1] In this structure there is only one piezoelectric constant, given by

$$P_x=e_{14}S_4,\quad P_y=e_{14}S_5,\quad P_z=e_{14}S_6, \tag{1}$$

where P_x, P_y, P_z are the components of the polarization along Cartesian axes, e_{14} is the piezoelectric constant, and S_4, S_5, S_6 are the components of the strain tensor.[2] Calculation of the sign and magnitude of this constant, and its relationship to the elastic and dielectric constants, has been the object of considerable effort since the early days of Born's dynamical lattice theory.[3,4] Unfortunately, neither the earlier work nor the more recent attempts [5–7] have been entirely satisfactory, owing to lack of precise *a priori* knowledge of the nature

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[1] W. Cady, *Piezoelectricity* (McGraw-Hill Book Company, Inc., New York, 1946).

[2] All notation in this paper follows that in M. Born and K. Huang *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954) except as indicated below. For definition of the strain tensor see p. 134.

[3] M. Born and E. Bormann, Ann. Physik **62**, 218 (1920).

[4] M. Born and M. G. Mayer, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), Vol. 24, Part 2, p. 635.

[5] K. Huang, Phil. Mag. **40**, 733 (1949).

[6] Y. LeCorre, thesis, Faculty of Sciences, University of Paris, Masson et Cie, Paris, 1955 (unpublished).

[7] B. D. Saksena, Phys. Rev. **81**, 1012 (1951). This theory is incorrect due to neglect of the "inner displacements"; this has been noted by LeCorre (reference 6, p. 1436) and J. L. Birman, Phys. Rev. **98**, 1567 (A) (1955).