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Room-Temperature Ferroelectricity in Lithium Hydrazinium Sulfate, $Li(N_2H_5)SO_4$

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$Li(N_2H_5)SO_4$ is ferroelectric over the temperature range from below −15°C to above 80°C, and shows no dielectric peaks between −196°C and 140°C. No thermal anomalies are observed. The crystals are orthorhombic, space group $Pbn2_1$, with $a=8.96_9$ A, $b=9.91_3$ A, $c=5.17_8$ A, and the ferroelectric axis is, of course, along c; $\rho=1.966$ g/cc, and there are 4 molecules per cell. The coercive field is about 320 volts/cm at room temperature, and the spontaneous polarization is 0.30 microcoulomb/cm^2. Beautiful large crystals can be grown from water by a variety of methods. After electroding, the crystal plates should be protected by silicone oil. Without such protection, reaction with normal atmosphere for prolonged time results in excessive conductivity.

INTRODUCTION

A NUMBER of hydrazine compounds show crystal transitions. Hydrazonium sulfate, $(N_2H_6)SO_4$, and the hydrazinium alums such as $(N_2H_5)Al(SO_4)_2\cdot 12H_2O$, for example, both shatter at about −50°C.[1]

Lithium ammonium sulfate, $LiNH_4SO_4$, exists in two forms.[2] The β form, which is the stable phase at room temperature, shows a very pronounced dielectric anomaly at about 10°C. The low-temperature phase is apparently antiferroelectric. Crystallographic, dielectric, and thermal studies of this material will be separately reported.[3]

Ammonium hydrogen sulfate, $(NH_4)HSO_4$, has recently been found to be ferroelectric in the temperature range between −3°C and −118°C.[4] This behavior of course recalls the ferroelectric character of $(NH_4)_2SO_4$ below −49.5°C, as discovered by Matthias and Remeika.[5]

It thus appeared wise to examine lithium hydrazinium sulfate, $Li(N_2H_5)SO_4$, dielectrically. The abbreviation LHzS is used for this compound hereafter. The compound was first prepared by Sommer and Weise,[6] and grows in beautifully clear, large crystals by slow evaporation of an aqueous solution. Dielectric observations immediately revealed ferroelectric behavior at room temperature, and indeed over a range of temperatures from below −15°C to above 80°C. Above the latter point conductivity becomes excessive. The crystals are fairly stable in air, and decompose with mild explosiveness at about 285°C. Complete stability in the range of ferroelectric behavior is achieved by coating with silicone oil.

The first crystals examined were prepared from Li_2SO_4 and $(N_2H_5)_2SO_4$, and showed a rectifying behavior which resulted in collapse of the ferroelectric loops. This property apparently resulted from impurities in the hydrazine hydrate used for preparation of the hydrazinium sulfate. Preparation from reagent-grade Li_2CO_3 and fairly pure (but not reagent-grade) $(N_2H_6)SO_4$ resulted in elimination of the conductivity. Storage in silicone, and dielectric examination without removal of the oil from the side surfaces, eliminates increase in conductivity with time.

CRYSTALLOGRAPHIC DATA

LHzS is orthorhombic, with space group $Pbn2_1$, $a=8.96_9$ A, $b=9.91_3$ A, $c=5.17_8$ A, $\rho=1.966$ g/cc, $Z=4$ molecular units/cell. The ferroelectric axis is of course along c. The compound had not been examined crystallographically, heretofore. A structure analysis is in progress.

DIELECTRIC PROPERTIES

LHzS shows no dielectric peak between −196°C and 140°C. In the neighborhood of the latter temperature, conductivity becomes excessive. Examination on the ferroelectric hysteresis bridge reveals a good hysteresis loop from about −15°C to 80°C. Below −15°C the loops become unsymmetric and difficult to saturate. Above 80°C the conductivity interferes with the hysteresis test.

The value of the dielectric constant ϵ_c is about 14 at room temperature; the coercive field there is about 320 v/cm, and the spontaneous polarization is 0.30 microcoulomb/cm^2. ϵ_c drops fairly uniformly to 8.5 at −196°C. The coercive field E_c is practically constant from 70°C to 15°C; and as the temperature is lowered further, E_c begins to rise very rapidly. E_c is about 1000 v/cm at −15°C, below which point good loops are difficult to obtain. The spontaneous polarization is about 0.75 microcoulomb/cm^2 at 70°C, and about 0.05 microcoulomb/cm^2 at −10°C.

LHzS is possibly a ferroelectric of practical importance, despite its low spontaneous polarization. Its coercive field is advantageously low. Its spontaneous polarization is about equal to that of Rochelle salt; it is much lower than that of $(glycine)_3\cdot H_2SO_4$ and

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[1] R. Pepinsky and K. Vedam (unpublished).

[2] P. von Groth, *Chemische Krystallographie* (W. Engelmann, Leipzig, 1908), Vol. 2, p. 330.

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

[4] Pepinsky, Vedam, Hoshino, and Okaya, Phys. Rev. **111**, 1508 (1958), this issue.

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

[6] F. Sommer and K. Weise, Z. anorg. allgem. Chem. **94**, 51 (1916).

(glycine)$_3 \cdot H_2SeO_4$[7] and (glycine)$_3 \cdot H_2BeF_4$,[8] however; and nothing is known as yet about the switching time of LHzS. The ferroelectric loops are not as square as those of (glycine)$_3 \cdot H_2SO_4$ and isomorphs of the latter.

SPECIFIC-HEAT MEASUREMENTS

Specific-heat measurements were carried out in an adiabatic calorimeter, in the region from −120°C to 205°C. No anomaly was detected in this temperature range.

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[8] Pepinsky, Okaya, and Jona, Bull. Am. Phys. Soc. Ser. II, **2**, 220 (1957).

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V-Type Center Resonance of Neutron-Irradiated LiF at Room Temperature*

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A *V*-type center similar to one described by Känzig and co-workers has been found in LiF single crystals neutron-irradiated at room temperature. Analysis of the *s* and *p* admixture in the electron wave function, using the Hamiltonian of Woodruff and Känzig, is made from the angular dependence of the electron-spin resonance spectrum.

ELECTRON-SPIN paramagnetic resonance (ESPR) investigations at room temperature of neutron-irradiated LiF single crystals have yielded two different groups of hyperfine lines.

The rectangular samples, approximately 0.14 in. ×0.14 in.×0.75 in., were cleaved from large crystals obtained from the Harshaw Chemical Company. Neutron irradiation for periods ranging from 10 minutes to 72 hours was secured at room temperature with a flux of approximately 2.3×10^{12} $n/\text{cm}^2\text{sec}$. After irradiation, the samples were kept at dry-ice temperature until the ESPR experiments were performed with a Varian Associates Model No. 4500 ESPR spectrometer.

The samples were rotated about a [100]-type axis in a dc magnetic field (H_0) perpendicular to the axis of rotation. Two distinct hyperfine groups were observed. One group,[1] in the vicinity of $H_0 \simeq 3400$ gauss with a microwave frequency of 9500 Mc/sec, is very intense; the other is much less intense and is spread widely on both sides of the first (Fig. 1). The spacings of the resonances in both groups are dependent on the direction of H_0 and are conveniently analyzed in terms of the angle α between H_0 and either of the [100]-type axes perpendicular to the axis of rotation.

The observed resonance magnetic field for each of the weaker and widely spaced group of lines is indicated by a square in Fig. 2. Solid lines show the shift of each resonance as α ranges from 0° to 45°. The pattern is symmetric about $\alpha=45°$. The lines are distributed over a range of 2000 gauss with the outermost line on each side of the pattern being appreciably weaker than the others. Peak-to-peak widths of these lines are of the order of 50 gauss.

The pattern of the solid lines in Fig. 2 is strikingly similar to the R_1 and R_4 curves of Fig. 10 in the paper of Woodruff and Känzig.[2] A regraphing of the R_1 and R_4 curves of their θ *vs* H diagram into our α *vs* H_0 diagram yields the circles and dotted lines of Fig. 2. The R_2 and R_3 families are obscure in our spectrum because of the strong central resonance. A comparison of the two patterns of Fig. 2 suggests the interpretation that the observed weak and widely spaced lines arise from a *V*-type (F_2^- ion) center similar to the one proposed by Känzig and co-workers.[2,3]

The separation of the lines R_1 and R_4 for $\alpha=45°$ ($\theta=0°$) in our spectrum enabled us to determine $a+b=951$ gauss by means of the approximation formula Eq. (6) of Castner and Känzig[3] which gives $a+b=887$ gauss for $\theta=0°$ in their spectrum. Although a correct estimation of $|a|$ is very difficult in our case, it is estimated to be of the order of 100 gauss by fitting at various θ values. Such analysis indicates that the characteristic shift of our curve relative to Känzig's,

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[1] Kim, Kaplan, and Bray, Bull. Am. Phys. Soc. Ser. II, **3**, 178 (1958).

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[3] T. G. Castner and W. Känzig, J. Phys. Chem. Solids **3**, 178 (1957).