

Ferroelectric Transition in Rubidium Bisulfate

R. PEPINSKY AND K. VEDAM

Crystal Research Laboratory, Department of Physics, The Pennsylvania State University, University Park, Pennsylvania

(Received October 12, 1959)

RbHSO₄ is ferroelectric below -15°C . The room-temperature phase is monoclinic, with space group $P2_1/c$, $a=14.35_6$ Å, $b=4.62_2$ Å, $c=14.80_7$ Å, $\beta=121.0^{\circ}$ and $Z=8$. The symmetry of the ferroelectric phase is Pc , as established by systematic x-ray absences and the fact that spontaneous polarization appears along the c axis below -15°C . Both the high- and low-temperature phases are pseudo-orthorhombic. The dielectric constant ϵ_c at 10 kc/sec and for a field of 5 v/cm is 10 at room temperature; as the temperature is lowered, ϵ_c rises to a sharp peak of ~ 240 at -15°C and falls to ~ 5 at -196°C . The transition appears to be of second order. No second transition, as in the case of isomorphous NH₄HSO₄, could be detected in the temperature range -15°C to -196°C .

I. INTRODUCTION

AMMONIUM acid sulfate, NH₄HSO₄, is ferroelectric between -118°C and -3°C .¹ It is believed that N—H···O bonds play an important role in the dielectric behavior of this crystal, as they do in other ammonium and substituted ammonium ferroelectrics and antiferroelectrics. It was surprising, therefore, to discover that rubidium acid sulfate, RbHSO₄, which is isomorphous with NH₄HSO₄ at room temperature, is ferroelectric below -15°C .

Some crystallographic, dielectric, and thermal measurements of RbHSO₄ are reported here. A complete x-ray structural study of the paraelectric and ferroelectric phases is in progress.

II. PREPARATION AND PROPERTIES OF RbHSO₄

RbHSO₄ can be grown by slow evaporation of an aqueous solution of Rb₂SO₄ containing excess H₂SO₄. However, large water-clear crystals are most easily obtained from molten RbHSO₄ (Rb₂SO₄+H₂SO₄ in equi-molar ratio), by any of the standard melt techniques. The melting point is 208°C . Crystals so grown are not hygroscopic. The boules show an excellent

cleavage plane, and the important dielectric axis is perpendicular to this plane. It should be recalled that NH₄HSO₄ is also best grown from the melt.¹

X-ray examination reveals, as in the case of NH₄HSO₄, that rubidium bisulfate exhibits pseudo-orthorhombic symmetry at room temperature, with the space group $B2_1/a$ and cell dimensions $a'=24.61_2$ Å, $b'=4.62_2$ Å, $c'=14.80_7$ Å, $\beta=90^{\circ}3'$; the number of molecules per unit cell is $Z=16$. The conventional designation for this symmetry is $P2_1/c$, with $a=14.35_6$ Å, $b=4.62_2$ Å, $c=14.80_7$ Å, $\beta=120^{\circ}59'$, and 8 molecules per cell. The b and c axes are the same in both notations. The cleavage plane is perpendicular to the c axis.

The crystal exhibits ferroelectric properties below -15°C , with c becoming the polar axis. Therefore the two-fold screw axis should disappear below the Curie point, and the low-temperature phase must be either Pc or $P1$. X-ray observations at -170°C confirm the deduction from dielectric observation, that the twofold screw axis disappears below the transition point, and unequivocally establish the space group of the low-temperature phase as Pc .

The temperature dependence of the small-field di-

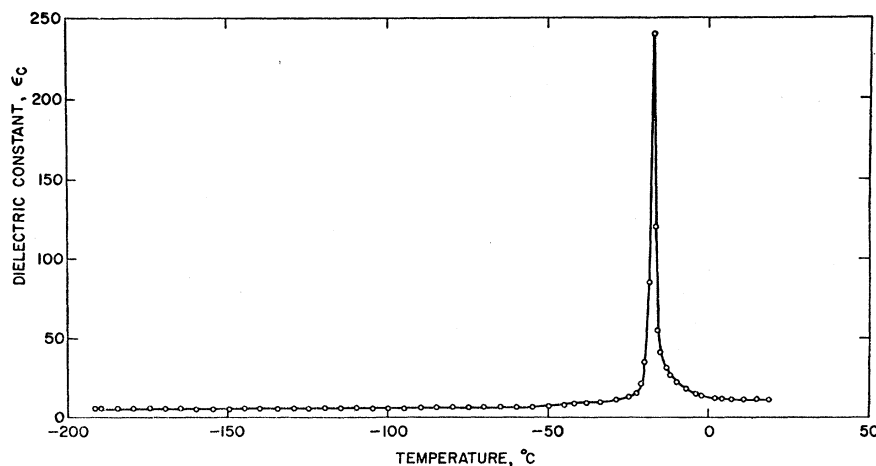


FIG. 1. RbHSO₄: dielectric constant vs temperature.

¹ Pepinsky, Vedam, Hosino, and Okaya, Phys. Rev. **111**, 1508 (1958).

electric constant, with the electric field of 5 v/cm at 10 kc/sec applied along the c axis, is represented in Fig. 1. ϵ_c has a value of 10 at room temperature; as the temperature is lowered it increases to a fairly sharp maximum value of ~ 240 at -15°C , below which temperature it drops rapidly and has a value of 5 at liquid nitrogen temperature. $\epsilon_{a'}$ and $\epsilon_{b'}$, on the other hand, decrease fairly uniformly from values of 7 and 8 at room temperature to 5 and 6 at liquid nitrogen temperature, respectively. Unlike NH_4HSO_4 , no second transition could be detected in this crystal in the temperature range -15°C to -196°C . If RbHSO_4 should exhibit an abrupt drop in the dielectric constant ϵ_c at lower temperatures, as does NH_4HSO_4 , the detection of such an anomaly will not be very easy because ϵ_c is already low (~ 5) at -196°C . No noticeable thermal hysteresis could be detected at the transition temperature; if such hysteresis exists at all, it does not exceed 0.5°C .

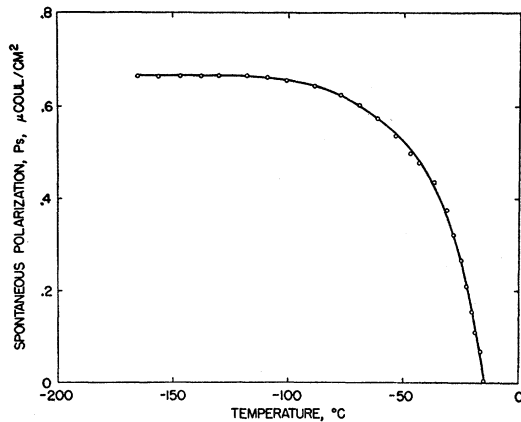


FIG. 2. RbHSO_4 : spontaneous polarization vs temperature.

When a c plate is examined in a hysteresis bridge, the P vs E curve is linear at room temperature. As the temperature is lowered the P vs E curve exhibits the familiar characteristics of a second-order transition just above the Curie point. Below this temperature and down to about -170°C one can observe well-saturated hysteresis loops. The values of the spontaneous polarization and the coercive field are given as a function of

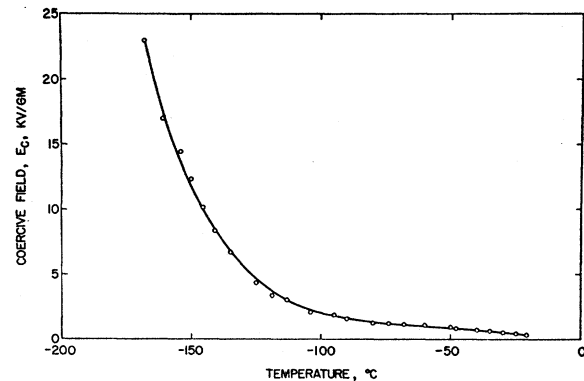


FIG. 3. RbHSO_4 : coercive field vs temperature.

temperature in Figs. 2 and 3, respectively. Below -170°C the coercive field is much higher than the breakdown field of the crystal.

A careful examination of this crystal with a modified Sykes' type^{2,3} calorimeter failed to reveal any noticeable specific heat anomaly at the transition temperature. Thus it can only be said that the heat of transition in this case is less than 25 cal/mole.

The extremely large value of the dielectric constant at the transition temperature, the shape of the P vs E curve at temperatures slightly above the transition point, and also the variation of P_s with temperature, lead one to conclude that the phase transition in this case is possibly of second order.

III. ACKNOWLEDGMENTS

The authors express their sincere thanks to Professor Yoshiharu Okaya for assistance in the x-ray measurements and for numerous stimulating discussions during the course of the investigation. This study was supported by the Air Force Office of Scientific Research, Directorate of Physical Sciences, Air Research Development Command, and the U. S. Atomic Energy Commission.

² S. Nagasaki and Y. Takagi, J. Appl. Phys. Japan **17**, 104 (1948).

³ Hoshino, Vedam, Okaya, and Pepinsky, Phys. Rev. **112**, 405 (1958).