

Clogston, and J. E. Kunzler for helpful discussion.

¹B. W. Batterman and C. S. Barrett, *Phys. Rev. Letters* **13**, 390 (1964).

²E. S. Greiner and H. Mason, Jr., *J. Appl. Phys.* **35**, 3058 (1964), give details of crystal preparation.

³H. J. McSkimin, *J. Acoust. Soc. Am.* **33**, 12 (1961).

⁴W. P. Mason, *Physical Acoustics and the Properties of Solids* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1958), pp. 370-71.

⁵ $(c_{11}-c_{12})/2c_{44}$ is the reciprocal of the elastic anisotropy factor. (See reference 4, p. 357.) The value of unity for this factor near room temperature indicates glasslike elastic isotropy. In the superconducting

state the anisotropy is probably the largest reported for any crystal.

⁶W. P. Mason and H. E. Bommel, *J. Acoust. Soc. Am.* **28**, 930 (1956).

⁷The anomalous attenuation was not observed in a crystal in which no structural transformation was found from x-ray studies.

⁸B. W. Batterman has recently found that on cooling through T_c the growing deformation of the transformed lattice is arrested. From specific-heat data J. E. Kunzler and coworkers have arrived at similar conclusions (private communications). However, sluggish transformations, occurring continuously between 4 and 30°K, are occasionally observed.

⁹Reference 4, p. 325.

¹⁰Reference 4, p. 346.

ANTIFERROELECTRIC PHASE TRANSITION IN COPPER-FORMATE TETRAHYDRATE*

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Copper formate tetrahydrate $\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$ has been found by Kiriya, Ibamata, and Matsuo¹ to have a layer structure in which layers of H_2O are sandwiched between layers of copper formate in the (001) plane. The symmetry is $P2_1/a$, $a = 8.18$, $b = 8.15$, $c = 6.35$ Å. Several investigators²⁻⁴ published descriptions of the antiferromagnetic transition at about 17°K in this crystal. While attempting to determine hydrogen positions by neutron diffraction at room temperature, preliminary to investigating the magnetic structure, some water hydrogens were found to be disordered.⁵ This stimulated us to measure the dielectric properties as a function of temperature. A preliminary check showed an anomalous dielectric constant as high as 400 at room temperature in an (010) plate. This publication reports that the crystal appears to be antiferroelectric due to hydrogen motion. It has a typical antiferroelectric behavior comparable to perovskite-type antiferroelectrics. In addition, unlike previously discovered antiferroelectrics, large single crystals can easily be grown and detailed experiments carried out. Antiferroelectric antiferromagnetism can be expected in this crystal below 17°K.

Single crystals were grown from aqueous solution by slow evaporation of water. (100) and (010) plates were cut from the single-crystal ingot by the wet-thread method and polished by fine emery paper. Thin "as-grown" (001)

plates were obtained in a certain condition of crystal growth. The plates were about 0.4 mm thick. Electrodes were air-drying conductive silver coatings painted on the crystal surfaces to eliminate any gap between the crystal surface and the electrode. Moreover, crystals were coated by an insulating spray coating to avoid contact with air which would cause rapid dehydration.

Figure 1 shows the dielectric constant at low ac amplitude and 1000 cps versus temperature. As the temperature is decreased, the dielectric constant of the (010) plate rises to a peak of 1500 at -38.9°C and a large discontinuous decrease occurs at this temperature. Above this transition point, T_c , the Curie-Weiss law, $\epsilon = C/(T - T_0)$, is satisfied, and a plot of the reciprocal dielectric constant versus temperature is a straight line, as seen in the figure, with $T_0 = -58^\circ\text{C}$ and $C = 3.2 \times 10^4$ °C. The (001) plate has a low dielectric constant varying gradually from 20 at room temperature to 5 at liquid-nitrogen temperature without any anomaly. The (100) plate gave a small discontinuity at T_c as shown in Fig. 1. This might be attributed to a small component of the large anomaly in the [010] direction owing to the cutting error of the crystal plate, in contrast to the perfect orientation of the (001), "as-grown" crystal plate. This high anisotropy can be expected from the predominantly layer structure of this crystal. After most of this work was

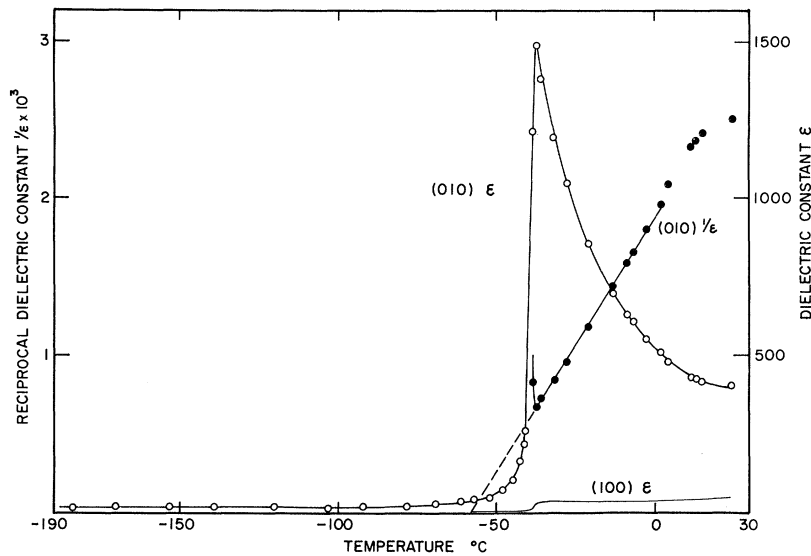


FIG. 1. Dielectric constant versus temperature in copper-formate tetrahydrate at 1000 cps.

done, we found a paper published by Kiriyama⁶ on the phase transition of this crystal. However, her value of the dielectric constant at the transition point is 1/50 of that reported in this paper.

A clear double E - D hysteresis loop was observed within a certain temperature region below the transition point with the ordinary Sawyer-Tower hysteresis-loop circuit with a high ac amplitude of 19 kV/cm and 60 cps as shown in Fig. 2. At low temperature the E - D relation is a straight line. With rising temperature, nonlinearities appear at the ends of the straight

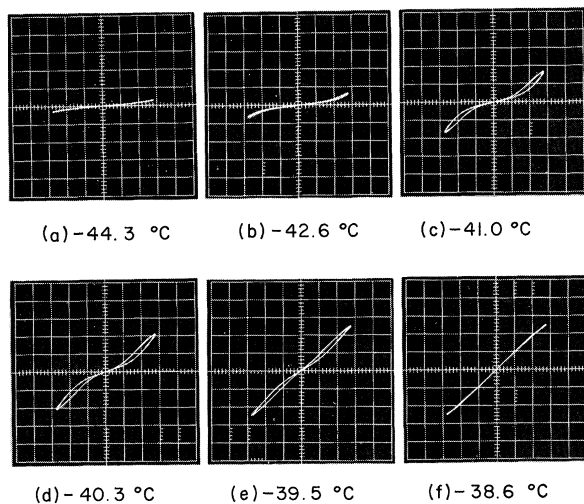


FIG. 2. Double hysteresis loops of (010) copper-formate tetrahydrate plate at various temperatures below T_c at 60 cps. Sweeping amplitude: 19 kV/cm.

line as seen in (a). A double hysteresis loop comes out with further warming as in (b) through (e). On passing through the transition point, the loop disappears. The double hysteresis loop was observed only in a narrow temperature region from -42.6°C to the transition point. This range seemed to depend upon the applied ac amplitude.

A small thermal hysteresis in dielectric constant was observed at the transition point by careful temperature control. Additionally, an external dc bias field shifted the transition point to a lower temperature. The phenomena mentioned above are quite parallel to those of the typical antiferroelectric crystals, PbZrO_3 ^{7,8} and $\text{PbCo}_{1/2}\text{W}_{1/2}\text{O}_3$,^{9,10} discovered very recently. The behavior of the dielectric constant and the double hysteresis loop below the transition point, together with the thermal hysteresis and dc bias effect on the transition point, strongly suggest that copper-formate tetrahydrate may have a first-order transition at -38.9°C and that it appears to be antiferroelectric below this temperature.

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ANISOTROPIC ENERGY LOSSES IN A FACE-CENTERED-CUBIC CRYSTAL FOR HIGH-ENERGY ⁷⁹Br AND ¹²⁷I IONS*

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Multicomponent beams of Br and I ions from the Oak Ridge tandem accelerator,¹ with energies up to 80 MeV have been used to study crystal orientation effects on energy losses in thin gold single crystals. Channel effects were predicted theoretically by Robinson and Oen²; they have been observed with 75-keV protons transmitted through gold,³ and by range measurements with low-energy heavy ions.^{4,5} Evidence has been found for channeling effects with (p, γ) and (p, n) reactions and in studies of yields of x rays induced by proton bombardment.⁶⁻⁸ Other observations with fast light particles in Si have been reported by Dearnaldy,⁹ Erginsoy, Wegner, and Gibson,¹⁰ and Shiffer and Holland.¹¹

For the experiments reported here, Au single crystals were prepared by evaporation and epitaxial growth upon cleaved rock-salt faces. The crystals were formed with a (100) face parallel to their surfaces and were 1.1 mg/cm² (0.57 μ) thick, as determined by α -particle energy-loss measurements and by weighing. Following removal from their rock-salt substrates, they were mounted for rotation about a fixed axis in the surface plane. Two rotations, one about a [100] axis and the other about a [110] axis, were studied. The angular position error was $\pm 0.1^\circ$. The [100] axis rotation allowed alignment of the [001] and the [110] directions with the incident beam, while the [110] axis rotation permitted alignment with the [001], [112], and the [111] crystal directions. It should be noted that in both rotations low-index crystal planes were parallel to the beam at all goniometer settings. As in earlier work,¹ Br

and I negative ions were accelerated in the first stage of the tandem accelerator, stripped of some of their electrons, and stripped further during acceleration in the second stage. The resulting high-energy continuous spectrum of particles was passed through a 90° magnetic analyzer which gave a beam consisting of a series of accurately known energies. Incidence of this beam onto a Si surface-barrier detector produced the pulse-height spectra shown in Figs. 1(a) and 2(a). The procedure was to measure the effects upon each peak in these spectra produced by the insertion of a crystal in various orientations. The collimator arrangement consisted of the target, 3 mm in diameter followed by a 1-cm diameter aperture at a distance of 10 cm, followed by the 2-cm-diameter detector at a distance of 5 cm from the aperture. In earlier experiments with polycrystalline absorbers, the only effects observed were simple peak shifts without appreciable shape distortions. Earlier dE/dx measurements on polycrystalline samples¹² have been employed to calculate estimated normal energy losses corresponding to the thickness of the specimens used in the present experiments, and these are shown in the figures.

The spectrum of Fig. 1(c) illustrates the effects produced when the [001] crystal direction was aligned to a ⁷⁹Br beam. The energy losses for the various groups are characterized by single peaks. The losses are less than corresponding normal (polycrystalline) losses for a foil of this thickness. Although the peaks are asymmetric, the fraction of particles with normal energy loss was less than 0.1. Almost

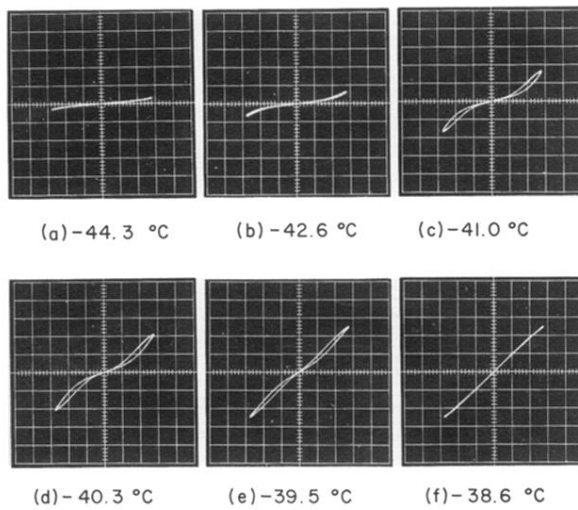


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