ta and a secular-equation-Fermi-surface fit, principally to the β -arm third-zone structure. A very similar set of band gaps has recently been obtained by O'Sullivan et al.¹⁰ from their studies of the de Haas-van Alphen effect in In as well as to pressure dependence. From an analysis of the lines of band contact and the occupation of the zones around the symmetry points,⁸ it follows that $V_{1,1,\alpha}$, as implied by these photoemission studies (which is consistent with the β -arm structure), will completely remove the α -arm structure. Experimental evidence for the presence of this system based on an interpretation of periods observed in the low-field de Haas-van Alphen effect has been reported¹¹: The areas attributed (in consequence) to the α system exceed the corresponding free-electron areas, an occurrence which is certainly anomalous for nearly-freeelectronlike metals. The other galvanomagnetic studies of In at low temperatures have generally failed to provide evidence supporting the existence of the α -arm structure.¹² Since the band-gap determination by photoemission supports the "theoretical absence" of the thirdzone, α -arm Fermi surface in In, it is now of considerable interest to conduct additional low-temperature galvanomagnetic measurements on strain-free single crystals of In metal to resolve this issue.

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[†]Summer visitor, Stanford University, 1967.

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FERROELECTRICITY IN SOLID HYDROGEN HALIDES

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It is widely known that solid hydrogen halides, HCl, HBr, and HI, show a phase transition at low temperature. The nature of the phase transition has been discussed phenomenologically by several authors¹⁻⁵ and associated with an orientational or a rotational behavior of linear dipolar molecules.

In this Letter we wish to report our recently discovered evidence for the ferroelectricity of HCl and HBr in their lowest temperature phases. According to the measurements of the temperature dependence of specific heat⁶ and dielectric constant,⁷ HCl exhibits a transition at 98.4°K and HBr has three transition points at 89.7, 113.6, and 116.9°K. Lattice types and dimensions for some phases of these substances have long been known by the early x-ray work.⁸ As for crystal symmetries and molecular orientations, discussions have been made by several authors from measurements of infrared, far-infrared, and Raman spectra,⁹ but the crystal structures have not been definitely established. Recently, Sandor and Farrow¹⁰ determined the crystal structure of the lowest phase of DCl using powder neutron-diffraction data. They found that the molecules formed a zig-zag chain along the orthorhombic b axis corresponding to the polar direction in the space group $C_{2v}^{12}-Bb2_1m$. The crystal lattice becomes fcc above the transition point and the statistical average of a disordered structure was concluded from the intensity distribution of the neutron powder pattern though the unambiguous disordered model was not obtained. If such structural features are realized in the crystal, a spontaneous polarization should appear below the transition temperature, and the polarization reversal by an ac electric field, that is, ferroelectricity, would be expected.

Special equipment for the observation of a D-E hysteresis loop was designed. Since the hydrogen halides are in gaseous state at room temperature, it was extremely difficult to make a single crystal in a vessel in which thin electrodes were inserted beforehand. After a number of improvements on the vessel were made, the growth of the single crystal which is in good contact with the Ni-foil electrodes was successfully attained by cooling the sample gradually from liquid state. The typical D-E hysteresis loop at 50 cps was observed for HCl and HBr below the lowest transition temperature. An example is shown in Fig. 1 where the loops at various temperatures are superimposed. In spite of the success for growing single crystals, the orientation of the crystal was not fully controlled. Therefore, values of the spontaneous polarization estimated from the loops for different measurements were scattered. After iterated crystal growths, the following spontaneous polarizations were obtained as a maximum value up to the present: 1.2 μ C/ cm² at 90°K for HCl and 0.4 μ C/cm² at 78°K for HBr. The values of the coercive field at these measurements were 3.3 and 4.3 kV/cm,



FIG. 1. *D-E* hysteresis loops for HBr.

respectively. Temperature dependences of the spontaneous polarization are shown in Fig. 2.

In the experiment for HCl, temperature hysteresis was clearly observed between the transition temperatures in the heating and the cooling measurements, which is in agreement with the suggestion given in the literature^{3,4,6} that the transition in HCl is of the first order. Nevertheless, no clear jump of the spontaneous polarization P_s at the transition point can be seen in Fig. 2. However, the present measurement was only the preliminary one, i.e., the rate of temperature variations of the sample was not sufficiently slow and some inhomogeneity of the temperature of the specimen might have occurred. Such experimental conditions may obscure the evidence for the first-order transition in the P_s -versus-temperature curve. On the other hand, the temperature hysteresis could not be detected in the measurements for HBr. According to the literature,^{3,6,7} the lowest transition of HBr has been assumed to be of second order. Our measurements seem to support this assumption. One must, however, be very cautious in concluding that a transition is not of the first order. The nature of the phase transition in HBr will be discussed after the crystal structures below and above the transition point are analyzed. At the present stage, it can be said that the structure of the lowest temperature phase of HBr is polar and therefore should have structure similar to that of HCl. The measurement for HI has not yet been carried out because of the temperature of its lowest transition, 70.1°K, and of experimental restrictions. However, it might be imagined from the close resemblance of the nature of the thermal and the dielectric properties to those of HBr that HI is also ferroelectric in the lowest phase.



FIG. 2. Spontaneous polarization versus reduced temperature.

If we assume the crystal structure based upon the zig-zag chain of molecules and the dipole moment for a gas molecule, the maximum values of the polarization can be estimated at 6.4 μ C/cm² for HCl and 4.2 μ C/cm² for HBr. The experimental values are several times smaller than these calculated ones, but this is not unreasonable if the experimental condition is taken into consideration. Though the detailed discussion should be suspended until the crystal structures and their changes with temperature are clarified, it seems worthwhile to promote further experimental as well as theoretical studies on the phase transitions in the solid hydrogen halides, which consist of very simple dipolar molecules and are the simplest ferroelectrics discovered so far.

More quantitative measurements of the dielectric properties and structural investigation by the neutron-diffraction method by use of single crystals are now in progress in our laboratory.

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CRITICAL HARMONIC SCATTERING IN NH₄Cl

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Observations of harmonic scattering (second-harmonic generation) by fluctuations in angular orientation are reported for polycrystalline NH₄Cl for temperatures in the immediate vicinity of the second-order phase transition at ~242.4°K. Harmonic intensities were found to decrease exponentially within the range $2 \times 10^{-4} \le \epsilon < 2 \times 10^{-2}$, where $\epsilon = T/T_c - 1$. The results, together with suitable assumptions, are used to obtain an estimate of the variation of the long-range correlation parameter κ^{-1} with ϵ , with results different from those expected.

We report here what we believe to be the first observations of harmonic scattering (secondharmonic generation) by fluctuations in a system in the immediate vicinity of a critical point.¹ The substance we have studied is NH₄Cl, initially chosen because the nature of the transition was apparently simple and well understood,² because the lattice has cubic symmetry both above and below the transition temperature, and because this and similar materials are not readily amenable to detailed study by conventional scattering techniques. We find that the harmonic intensity decreases exponentially with temperature for $T > T_c$ and that this result is not in accord with present ideas on criticalpoint behavior.

NH₄Cl undergoes a second-order phase transition³ at $T_c \approx 242.4$ °K, in which a reorientation of the tetrahedral NH_4^+ ions occurs. The low-temperature phase is ordered, of symmetry $\overline{4}3m$, and consists of a simple cubic lattice of Cl⁻ ions in which NH_4^+ ions reside at cube centers, oriented such that the H atoms lie along the 3-fold axes of the cube. There are two symmetrically equivalent orientations for the NH₄⁺ ions; these are related by a rotation of the NH⁺ ion through $\frac{1}{2}\pi$ about a fourfold axis of the cube. In the low-temperature phase, neighboring NH₄⁺ ions have parallel orientations; in the hightemperature phase, the NH_4^+ ions are distributed randomly in one or the other of these two orientations. The system is thus apparently

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FIG. 1. D-E hysteresis loops for HBr.