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 $\mu C/cm^2$ for HCl and 4.2 $\mu C/cm^2$ 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 NH_4Cl

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Observations of harmonic scattering (second-harmonic generation) by fluctuations in angular orientation are reported for polycrystalline NH_4Cl 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 $2\times10^{-4} \leq \epsilon < 2\times10^{-2}$, 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 (second-harmonic generation) by fluctuations in a system in the immediate vicinity of a critical point.[1] The substance we have studied is NH_4Cl, 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 critical-point behavior.

NH_4Cl undergoes a second-order phase transition[3] 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 $\bar{4}3m$, 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 NH_4^+ ions; these are related by a rotation of the NH_4^+ ion through $\frac{1}{2}\pi$ about a fourfold axis of the cube. In the low-temperature phase, neighboring NH_4^+ ions have parallel orientations; in the high-temperature phase, the NH_4^+ ions are distributed randomly in one or the other of these two orientations. The system is thus apparently as Ising lattice. The disordered phase has an effective macroscopic center of symmetry and does not exhibit second-harmonic generation. (The sign of the local nonlinear polarization is reversed by the reorientation of NH_4^+ ions.) In the neighborhood of the critical temperature ($T > T_C$), fluctuations in angular orientation away from complete randomness permit the observation of second-harmonic generation—a process we call critical harmonic scattering. We have measured the intensity of this scattering from polycrystalline samples over approximately three decades of intensity, and for values of the critical parameter $\epsilon = T/T_C - 1$, for $T > T_C$, of $1\times10^{-5} \leq \epsilon \leq 2\times10^{-2}$.

The sample, reagent-grade powdered NH_4Cl, of mean particle size ~0.2-0.5 mm, was contained in a fused quartz cell. This cell was housed in a gold-plated copper assembly consisting of a relatively massive block enclosed in an outer can which was filled with liquid 4-methylpentene-1, the liquid being in intimate contact with the powder. This arrangement proved important in maintaining adequate temperature uniformity at the sample. The assembly was housed in a conventional cold-finger Dewar; temperatures were regulated with a proportional controller, and measured with a calibrated copper-Constantan thermocouple located at the sample. A Q-switched Nd:glass laser and conventional associated equipment were employed. Variations in laser power and mode structure were compensated for by simultaneous monitoring of the second harmonic produced in a crystalline quartz wedge.[4] The laser power density at the sample was a few megawatts per square centimeter. Because of the low refractive index of the 4-methylpentene-1, 1.38, as compared to that of NH_4Cl, 1.63, extensive multiple scattering of both the laser and second harmonic occurred. The harmonic radiation was emitted essentially isotropically from the sample and was collected in the forward direction by a $f/2$ lens. Heating of the sample by the laser beam was demonstrated to be negligible by the constancy of the ratio σ of the sample signal to monitor signal under variations in laser power in the immediate region of the critical point, where σ varies at a rate given by $(1/\sigma)(d\sigma/dT) \geq 50/°K$.

The experimental second-harmonic intensities are plotted in Fig. 1 as a function of ϵ. In agreement with other workers, we locate the transition temperature (upon warming) in the region of the very sharp decrease[5] of σ at 242.35_3°K.[6] The exponential decay of σ for $2\times10^{-4} \leq \epsilon$ ($T > T_C$) over more than three orders of magnitude variation in intensity is quite striking. The lower limit of σ presented is the point at which the ratio of signal to background noise was approximately unity, and could certainly be extended by one or more orders of magnitude. For the region $T > T_C$ the data may be represented by $\sigma = \text{const} \times \exp(-577\epsilon)$, with an uncertainty of ~5 % in the exponent.

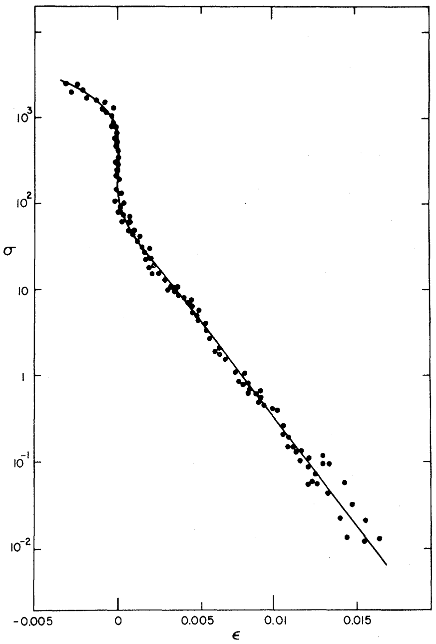

FIG. 1. Relative second-harmonic intensity σ vs $\epsilon = T/T_C - 1$.

For $T > T_C$ we may directly relate σ to the mean square amplitude of fluctuations in the nonlinear susceptibility β by

$$\sigma \propto \langle(\beta - \langle\beta\rangle)^2\rangle, \tag{1}$$

where the brackets denote a time average, and where we have made the assumption that above T_C, $\langle\beta\rangle = 0$. Fluctuations in β are directly related to fluctuations in angular orientation. We use a time-independent formulation even though the decay times of the fluctuations may be comparable with the laser pulse widths. This is justified because of the presumed lack of both spatial and temporal correlation between widely separated crystallites in the sample. As discussed by Bersohn, Pao, and Frisch,[7] the mean square structure factor for harmonic scattering is the Fourier transform of the two-particle angular correlation function describing the medium, $G(r, \Omega_1, \Omega_2)$, averaged over all angles available to the system. Their theory is written for an isotropic spatial distribution of point scatterers in which the range of angular correlations is much less than the sample dimensions. These are reasonable approximations to our material. Because of the multiple scattering discussed earlier, σ is proportional to the integral of the mean square structure factor over all scattering angles.

It is of interest to try to obtain an initial estimate of the variation in the range of angular correlations as a function of ϵ. To do this, we assume as an approximate solution to the Ising lattice problem the venerable Ornstein-Zernike[8] form for $G(r)$ adapted to our problem. Denoting the two orientations available to the NH_4^+ ions by subscripts + and −, we write

$$G(r, \Omega_1, \Omega_2) = \frac{5}{2\pi\rho l^2}\,\frac{1}{2}\,\frac{e^{-\kappa r}}{r}\left[\delta(\Omega_+ - \Omega_1)\delta(\Omega_1 - \Omega_2) + \delta(\Omega_- - \Omega_1)\delta(\Omega_1 - \Omega_2)\right], \quad (2)$$

where ρ denotes the density, κ^{-1} is a measure of long-range angular correlations, and l is the so-called short-range correlation length. In writing (2) we neglect fluctuations in density.

If we estimate a limiting value for σ as ϵ approaches zero, and assume $\kappa \approx 0$ at this point, we may readily calculate κ as a function of ϵ. In doing this we neglect the presumed slow variation of l with ϵ. The results are plotted as the circles in Fig. 2. The apparent exponential fit to σ vs ϵ is not physically untenable for any value of ϵ. We cannot directly test this fit for very small ϵ, but it is of interest to examine the consequences of assuming that it is valid through $\epsilon = 0$. With this assumption we obtain the relationship between κ^{-1} and ϵ shown by the solid curve in Fig. 2. For (surprisingly) small ϵ we recover the classical result that $\kappa^{-1} \sim \text{const} \times \epsilon^{-1/2}$. Modern theories[9] predict important, but nontheless relatively weak, deviations of both the correlation function and the ϵ dependence of κ from simple Ornstein-Zernike theory. Over most of the experimentally accessible range, however, we find that κ deviates far too strongly from a simple power-law function of ϵ, with exponent between $\frac{1}{2}$ and $\frac{2}{3}$, to permit agreement with present theories. This circumstance arises, of course, because of the very large coefficient of ϵ in the approximately exponential relationship between σ and ϵ. A fairly good fit to the data of Fig. 1 for $\epsilon > 0$ may, however, be obtained from a relationship between κ^{-1} and ϵ of the form $\kappa^{-1} \sim \text{const} \times \epsilon^{-\nu}$, with $\nu \approx 9/4$, but such a value for ν appears to have no grounding in theory. We note that we can never expect an experiment such as ours to yield reliable information on correlations over distances larger than the coherence length $l_c = \frac{1}{2}\lambda_1(n_2 - n_1)$, which in this instance is $\sim 27\ \mu$.[10] (This very long value for l_c is the primary reason for our use of a Nd laser; for ruby, $l_c \sim 6\ \mu$.)

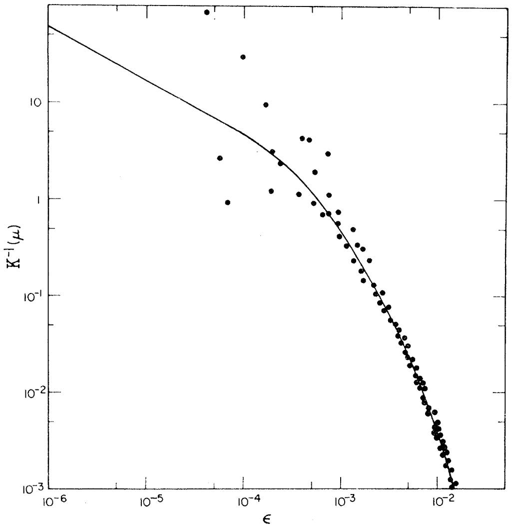

FIG. 2. Long-range correlation parameter κ^{-1} vs $\epsilon = T/T_c - 1$ for an assumed Ornstein-Zernike-type correlation function. The solid line is calculated from the exponential fit to the data discussed in the text. The circles are calculated directly from the measured values of σ.

The true form for $G(r, \Omega_1, \Omega_2)$ can be obtained from measurements on single crystals of the angular dependence of the scattered harmonic intensity. Such experiments are in progress and should permit further, detailed comparison with recent, sophisticated calculations.[9] Of equal interest, but experimentally more difficult, are measurements of the spectral broadening accompanying critical harmonic scattering, since these yield the relaxation times of the fluctuations considered here.[11]

I am pleased to acknowledge several interesting discussions with S. Kurtz, who has also generously made available to me the results of his recent theoretical and experimental studies prior to publication. I am grateful to D. A. Kleinman and J. A. Giordmaine for informative conversations, to E. Helfand for a critical reading of the manuscript and for important suggestions, and to L. Kopf for technical assistance.

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TIME VARIATION OF THE CHARGE OF THE PROTON

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From the terrestrial occurrence of the nuclei Re^{187} and Os^{187}, it is deduced that the elementary unit of charge e cannot have varied by as much as one part in 1600 during the history of the earth.

Gamow[1] has recently proposed the hypothesis that the elementary unit e of charge should increase with time according to the law

$$e^2 \sim t, \tag{1}$$

where t is the time elapsed since the beginning of the universe. This proposal was made in order to revive the old idea of Dirac[2] according to which the two dimensionless numbers

$$e^2/Gm^2, \quad tmc^2/\hbar, \tag{2}$$

which are presently both of the order 10^{38}, should increase proportionally as the universe evolves. Here G is the constant of gravitation and m is proton mass. Dirac supposed that e^2/Gm^2 would increase through a decrease of the strength of gravitational forces according to

$$G \sim t^{-1}. \tag{3}$$

However, various geophysical and astrophysical considerations[3] argue against (3), and so Gamow suggested (1) as a substitute. Independently, but impelled by the same desire for economy of large dimensionless ratios in the laws of physics, Teller[4] has suggested that e might decrease with time according to the law

$$(\hbar c/e^2) \sim \ln(tmc^2/\hbar), \tag{4}$$

so that "137" would be roughly equal to the logarithm of the big numbers (2). I present here a simple argument from nuclear systematics which excludes both possibilities (1) and (4).

On the earth there exist[5] substantial quantities of the stable isotope Os^{187} and of the β-active isotope Re^{187}, which decays to Os^{187} with a half-life of 4×10^{10} y and a decay energy $\Delta = 2.6$ keV. According to the semiempirical mass formula,[6] the energies of the two atoms contain