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Higher-order critical phenomena in ND_4Cl†

Carl W. Garland and Douglas E. Bruins
Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Thomas J. Greytak
Department of Physics and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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The behavior of the length L and the piezoelectric constant d_{14} of ND_4Cl single crystals in the vicinity of the order-disorder transition has been investigated at 1 atm. In the absence of complications associated with changes in the domain structure, the value of d_{14} is directly proportional to the order parameter Ψ. A laser interferometric technique, capable of detecting piezoelectrically induced vibrations as small as 4×10^{-12} cm, made it possible to follow the variation in Ψ very close to the transition. The temperature variation of L and d_{14} in the ordered phase determines the critical exponents α' and β. Two ND_4Cl samples cut from the same 99.2% deuterated crystal gave the least-squares values $\alpha'=0.69\pm0.06$ and $\beta=0.126\pm0.006$ with $T_c=249.690\pm0.030$ K for sample A and $T_c=249.725\pm0.025$ K for sample B.

I. INTRODUCTION

The order-disorder phase transition in NH_4Cl involves changes in the relative orientations of the tetrahedral NH_4^+ ions in a CsCl-type lattice. In the ordered phase neighboring NH_4^+ ions are oriented parallel to each other ("ferromagnetic" ordering), while in the disordered phase they are distributed at random with respect to two equivalent orientations in the cubic unit cell. At 1 atm, part of the ordering process occurs discontinuously; i.e., a small first-order transition is superimposed on the over-all λ-like behavior and there is a hysteresis of ~0.3 K. The magnitude of the first-order discontinuity associated with the transition decreases as the pressure is increased. At about 1500 bar, the transition becomes continuous ("second" order) and remains so at higher pressures.[1] The point at which the transition changes from first order to second order is a special point qualitatively similar to the tricritical point observed in metamagnets and ^3He-^4He solutions.[2] Indeed, this special point has been referred to as a tricritical point in the literature,[3,4] but it has also been suggested that it could be a critical point of order 4 (tetracritical point).[5] Resolution of this question depends on establishing the values of appropriate critical exponents. For the present, we shall refer to this special point as a multicritical point (MCP).

Deuterated ammonium chloride undergoes the same cooperative ordering as NH_4Cl. Although most properties of these two salts (except the librational motions of the ammonium ions) are very similar,[6] the transition temperature depends on the extent of deuteration[7] and the first-order character of the transition is very sensitive to deuteration. According to a recent neutron-diffraction study,[3] a single crystal of $N(D_{0.93}H_{0.07})_4Cl$ exhibited a first-order discontinuity with a hysteresis of 0.035 K at 1 atm. This first-order character diminished with increasing pressure and disappeared at ~130 bar. However, an early but high-precision dilatometric investigation of a finely powdered ND_4Cl sample showed that the volume variation was continuous and free from hysteresis even at 1 atm.[8] Thus, one might expect that the MCP of a fully deuterated single crystal would be very close to 1 atm.

Critical exponents play a very important role in systems that display multicritical points. Theory predicts that the various critical exponents remain constant along a line of similar critical points. However, this notion of "smoothness" should break down when the nature of a transition changes, and different exponents are expected near a multicritical point.[9] Of special interest are the exponents α and β, which characterize the temperature dependence of the heat capacity and the order parameter, respectively, since these exponents have quite distinct values for second-, third-, and fourth-order critical points. Measurements of the neutron scattering intensity as a function of pressure and temperature for $N(D_{0.93}H_{0.07})_4$ Cl have confirmed some of the theoretical expectations for such a system, including crossover effects into a second-order region at higher pressures.[3] However, the reported values of β near the MCP are lower than those expected at a tricritical point, and it is desirable to carry out an independent determination of the β value.

The present paper describes the determination of the critical exponents α' and β from simultaneous measurements of the thermal expansion and piezoelectricity of ND_4Cl at 1 atm. The piezoelectric determination of β has some advantages over the neutron determination since the latter is complicated by considerable critical scattering near the transition (see Fig. 5 of Ref. 3). Thus we are able to observe details in the order-parameter behavior very close to the transition which are masked in the neutron work. Section II establishes the connection between the order parameter and the piezoelectric constant d_{14} and describes briefly a new interferometric method which has been developed for measuring very small piezoelectric responses. Section III presents results for two sample crystals which were cut from the same 99.2% deuterated single crystal. The detailed behavior of these two samples in the immediate vicinity of the transition was surprisingly different in spite of good agreement in their over-all behavior. Section IV provides a general discussion of the results, including the role of domains and the persistence of very weak piezoelectricity up to ~0.2 K above the transition. A detailed analysis of the data below T_c leads to values of the critical exponents α' and β, neither of which agree with the values predicted for a Gaussian tricritical point.

II. EXPERIMENTAL METHODS AND PROCEDURES

The piezoelectric constant d_{14} of ND$_4$Cl single crystals has been measured as a function of temperature in order to determine the behavior of the order parameter Ψ. Completely ordered ND$_4$Cl crystals belong to the $P\bar{4}3m$ symmetry class, for which $d_{14}=d_{25}=d_{36}$ and all other $d_{ij}=0$. Thus the piezoelectric coupling can be described by the single expression

$$x_4=d_{14}E_1\,, \qquad (1)$$

where E_1 is the electric field applied along any one of the cubic crystallographic axes and x_4 is the resulting shear strain developed about that axis. When a ND$_4$Cl crystal is heated through its order-disorder transition, the value of d_{14} should decrease and go to zero when the crystal becomes completely disordered.[10] To understand the origin of this behavior and the connection between d_{14} and Ψ, consider the distortion of a single ND$_4^+$ ion caused by applying an electric field along the x axis. As indicated by Fig. 1, the net effect is to increase the upper D–N–D bond angle while decreasing the lower one. The cube of eight Cl$^-$ ions surrounding this ND$_4^+$ ion in the crystal lattice responds to the change in the ND$_4^+$ structure by undergoing a distortion in which the faces perpendicular to the x axis grow along one face diagonal and shrink along the other. Hence on a unit-cell basis, a field along the x axis produces a shearing strain about the axis. It is obvious that rotating the ND$_4^+$ ion in Fig. 1 by 90° about the x axis exactly reverses the directions of the unit-cell distortion.

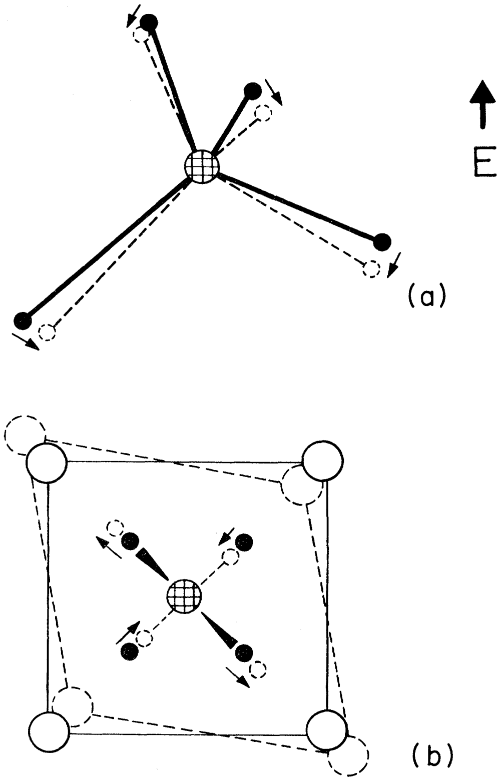

FIG. 1. (a) Distortion of a tetrahedral ND$_4^+$ ion due to the electric field E (based on an arbitrarily assumed polarity for the ND bond dipole); (b) the resulting distortion of the ND$_4$Cl unit cell viewed along the direction of the $\vec{E}$ vector.

In a completely ordered single-domain crystal, where all the ND$_4^+$ ions are oriented in the same way, all the unit cells undergo the same distortion and a macroscopic shear strain is produced. However, a completely disordered ND$_4$Cl crystal, having equal numbers of the two ND$_4^+$ orientations, is nonpiezoelectric since individual unit-cell distortions cancel each other out and there is no net expansion or contraction.

For any given configuration of a ND$_4$Cl crystal the magnitude and sign of the macroscopic piezoelectric coefficient d_{14} will depend directly on the relative number of ND$_4^+$ ions in the two orientations. If the two orientations are labeled plus and minus, then

$$d_{14}=\frac{N_+-N_-}{N_++N_-}\,d^0=\frac{N_+-N_-}{N}\,d^0\,, \qquad (2)$$

where N_+ is the number of ions in the plus orientation, N_- is the number in the minus orientation, and d^0 is the magnitude of the microscopic piezoelectric constant associated with a single unit cell. (Note that d^0 also corresponds to the macroscopic d_{14} value for a single-domain crystal at 0 K.) Although Eq. (2) is valid in all situations, the desired proportionality between d_{14} values and the long-range order parameter Ψ will depend on the stability of the domain pattern in the ordered phase. It will be shown experimentally that plus and minus antiphase domains do occur in ND_4Cl, and it is important to be aware of their effect on the observed values of d_{14}. Equation (2) can be rewritten in the form

$$d_{14}(T)=\sum_i \frac{N^i}{N}\,\Psi^i d^0=\left(\sum_i \frac{N^i}{N}(\mathrm{sgn}\Psi^i)\right) d^0\Psi(T)\,, \tag{3}$$

where N^i is the number of ND_4^+ ions in the ith domain with order parameter $\Psi^i=(N_+^i-N_-^i)/N^i$. The final expression is based on the reasonable assumption that at a given temperature the long-range-order parameters for various domains have the same magnitude and differ only in sign. Since the quantity $\sum(\mathrm{sgn}\Psi^i)N^i/N$ can have any value from + 1 to − 1 depending on the particular domain pattern, any change in domain structure during a run would cause an unpredictable change in the proportionality factor relating Ψ to d_{14}. Fortunately, the piezoelectric response in a given ND_4Cl sample was found to be quite stable except very close to the transition temperature. Thus $\sum(\mathrm{sgn}\Psi^i)N^i/N$ was assumed to be independent of temperature over a wide range, and the observed temperature variation in $d_{14}(T)$ was used to determine the critical exponent β.

When an ac potential is applied along the [100] axis of an ordered ND_4Cl crystal, the piezoelectric shear strain will cause the crystal to expand and contract in the [011] and $[0\bar{1}1]$ directions. (These oscillations are always out of phase with each other, but their phase relationship to the exciting voltage depends on the sign of d_{14}.) Thus ND_4Cl crystals which were thin in the [100] direction and relatively long in the [011] direction were used to maximize the amplitude of the length changes caused by a given applied voltage. Two sample crystals were cut carefully with a diamond saw from a large ND_4Cl single crystal.[11] Sample A was a rectangular parallelopiped with room-temperature dimensions of 0.200 cm along [100], 0.250 cm along $[0\bar{1}1]$, and 1.125 cm along [011]; sample B had corresponding dimensions of 0.180×0.282 ×1.012 cm. Although both samples were of very good quality, sample A had a small number of defects which were visible under a microscope while sample B was free of visible defects. The percent deuteration, as determined by a high-precision density measurement, was $(99.2\pm0.2)\%$.

Since the maximum value observed for d_{14} in the ordered phase of ND_4Cl is $\sim10^{-10}$ cm/V and we wish to follow the variation in d_{14} as it drops to zero above the transition, a very sensitive technique is needed to measure the subangstrom strains x_4 that can be generated by reasonable applied voltages (say 100 $\mathrm{V\,cm^{-1}}$). A laser interferometric technique, utilizing a spherical mirror Fabry-Perot interferometer and lock-in detection, was developed for this purpose. One mirror of the interferometer was rigidly mounted on a ND_4Cl sample which was piezoelectrically vibrated at a frequency $\omega/2\pi$. The amplitude of vibration Δl was determined by measuring the maximum intensity of the ω component of the output, $I(\omega)$, when the interferometer was swept through a transmission peak:

$$\Delta l=(\lambda/3\sqrt{3}\,F)\,I(\omega)/I_0\,, \tag{4}$$

where λ is the laser wavelength, F is the finesse, and I_0 is the intensity of the dc output at the center of a transmission peak. This new technique, a detailed description of which is given elsewhere,[12] is capable of detecting piezoelectrically induced modulations of the interferometer mirror spacing as small as 4×10^{-12} cm with very modest acoustic isolation. In view of its sensitivity, compactness, and ease of operation this technique represents a substantial improvement over other methods of measuring weak piezoelectric responses.

The temperature of the entire interferometer assembly was regulated by circulating cold methanol through a jacket around the interferometer. The temperature of the sample, as measured with a platinum resistance thermometer, could be maintained constant with a short-term (20-min) stability of ± 2 mK and a long-term stability of ± 10 mK. This temperature-control arrangement was not ideal since considerable mechanical noise was transmitted from the circulating pump when the connecting tubing became stiff (below 235 K). Thus, in spite of the advantages of lock-in detection, the operating sensitivity achieved at low temperatures was only 2×10^{-10} cm. Fortunately, this decrease in sensitivity was not a limiting factor in the measurements on ND_4Cl.

In addition to using the Fabry-Perot interferometer for measuring very small piezoelectrically induced oscillations, it is also easy to make simultaneous thermal-expansion measurements. The transmission peaks of the interferometer are separated by $\frac{1}{4}\lambda$, which is 1582 Å for our He-Ne laser. Therefore by simply counting the number of transmission peaks through which the interferometer passes in changing from one temperature to another, one can measure the thermal expansion of the interferometer in units of 1582 Å. Indeed, a resolution of ~100 Å can be achieved by interpolation, but a realistic estimate of the error in a ΔL value relative to the starting point of a run would be 500 Å.[13] It is important to remember that one is measuring the variation in the mirror spacing. This variation is due partly to the change in the length of the sample in the [011] direction and partly to dimensional changes in various pieces of the interferometer framework. Ideally the interferometer should have been constructed of Invar or some other low-expansion material, but since thermal-expansion measurements were not contemplated when the experimental cell was originally designed, this was not done. Therefore, the length variations reported in Sec. III have an appreciable contribution from the expansion of the interferometer framework. While this complicates direct comparison with other expansion data on ammonium halides, it does not prevent the determination of critical variations and the evaluation of the critical-point exponent α'. Furthermore, the simultaneous measurement of piezoelectricity and thermal expansion is of great value in clarifying the nature of the anomalous behavior observed very close to the transition temperature.

III. RESULTS

In spite of the presence of antiphase domains, it was possible to obtain a good characterization of the over-all temperature dependence of d_{14} in both the investigated samples. These piezoelectric results are shown in Fig. 2 in the form of a log-log plot of d_{14} versus $\Delta T = T_c - T$. The choice of the critical temperature T_c is discussed in Sec. IV. It will suffice here to point out that the T_c value for sample B is 35 mK higher than that for sample A, but this small change in T_c does not appreciably affect the linearity of the log-log plots. The most striking feature of Fig. 2 is the considerable difference in the magnitude of d_{14} for these two samples cut from the same single crystal. This can be explained by a difference in the domain structure which occurs in the ordered phase of these samples, with sample B (which was cut from a more perfect region) being closer to a single-domain crystal.

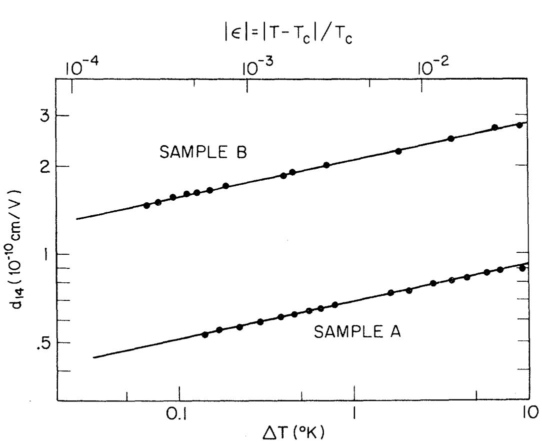

FIG. 2. Piezoelectric constant d_{14} as a function of $T_c - T$ for two single-crystal samples of ND_4Cl.

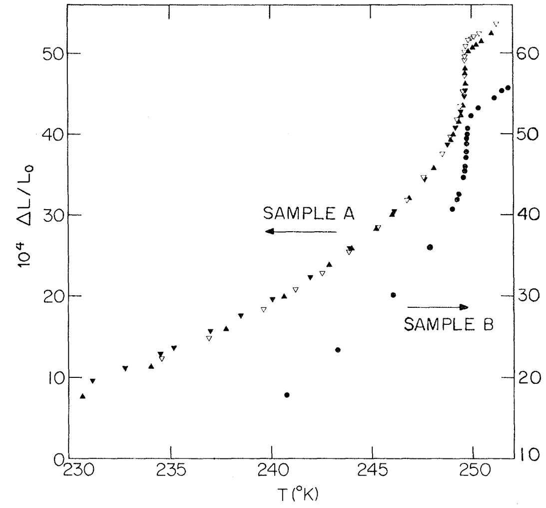

FIG. 3. Variation in the length L of ND_4Cl single crystals: Runs $A5$ warming (triangles), $A6$ warming (inverted solid triangles), $A6$ cooling (inverted open triangles), and $B2$ warming (dots). These data are uncorrected for expansion of the interferometer framework.

Indeed, it should be possible to obtain a single domain in the ordered phase by cooling the crystal while simultaneously applying a static uniaxial stress and a dc electric field. This has not been attempted in the present investigation, but it has been carried out successfully for NH_4Cl.[14] The resulting values of d_{14} for single-domain NH_4Cl are approximately three times those reported here for sample B. Fortunately, the piezoelectric response (and thus the domain pattern) was quite stable in ND_4Cl samples below the transition. Values of d_{14} measured at any given temperature differed from each other by less than 10% for the six runs that were made on sample A. Data obtained in a given run on cooling were in excellent agreement with the data subsequently obtained for that run on warming, indicating that the domain pattern did not change at all if the sample was not taken through the transition. Details of anomalous behavior in the immediate vicinity of the transition are given below.

The over-all thermal expansion observed in several runs is shown in Fig. 3. The quantity plotted is $\Delta L/L_0$, where ΔL is the directly measured change in mirror spacing uncorrected for expansion of the interferometer framework and L_0 is the room-temperature length of the ND_4Cl sample. Since different runs did not start from the same reference point, the zero on the $\Delta L/L_0$ scale was arbitrarily chosen for display purposes so that

$\Delta L/L_0 \equiv 30\times10^{-4}$ at 246 K for all runs. Although the interferometer-framework expansion is not negligible, it does not need to be known for a power-law analysis of the critical variation in L. The determination of the exponent α' in Sec. IV is based on the assumption that both the interferometer-framework expansion and the noncritical ND_4Cl expansion (due to anharmonic lattice contributions) are linear functions of temperature over the range studied and can be lumped together as a single background term. Measurements on several runs that extend up to room temperature support this assumption. However, the background slope is larger for sample *B* than for the runs on sample *A*. This is due to changes in the framework expansion that resulted from the disassembling and reassembling of the interferometer to change samples.

Simultaneous piezoelectric and thermal-expansion measurements in the immediate vicinity of the transition have revealed several unexpected features. These anomalies are highly reproducible for a given sample but surprisingly different for the two samples studied. Typical results for sample *A* are shown in Fig. 4. The complex behavior of both d_{14} and the length change was similar on warming and cooling, but the transition occurred at 249.595 K on cooling and at 249.630 K on warming. The observation of a small first-order transition with a hysteresis of 35 mK agrees with the results reported by Yelon *et al.*[3] for their single-crystal sample of $N(D_{0.93}H_{0.07})_4Cl$ but disagrees with the results of Smits *et al.*[8] on high-purity powdered ND_4Cl.

There are several features of the data in Fig. 4 which deserve special comment. First of all, the piezoelectricity did not vanish above the first-order break. Indeed, the d_{14} values oscillated in sign indicating major domain rearrangements and the persistence of some long-range order as much as 0.2 K above the transition. Second, the static length of the crystal underwent very complex changes. On approaching the transition from above, there was a gradual, almost linear contraction in the length until an anomalous expansion "hump" occurred at 249.67 K. Further cooling produced a substantial contraction down to the point marked 1 at 249.600 K. At this point another very small expansion hump (not shown) occurred before the sample continued to contract to the point marked 2 at 249.595 K. The time involved in lowering the temperature from 249.9 K to point 2 on the cooling curve was ~9 h. At point 2, the following events occurred isothermally in a time period of less than 10 min. The crystal first expanded rapidly to the point marked 3, where the expansion stopped abruptly and the length remained constant for a few seconds. Then a very rapid contraction occurred until point 4 was reached. After point 4, the crystal contracted smoothly as the temperature was lowered to 249.34 K over a time interval of ~4 h. After sitting at this temperature overnight, the sample was slowly warmed back through the transition. The warming and cooling data were in agreement up to 249.55 K, where the first evidence of hysteresis began to show up. All the anomalies observed in the cooling run also occurred on warming, but at higher temperatures. From point 1 on the warming run at 249.630 K, the crystal expanded rapidly and isothermally to point 2, where the expansion stopped abruptly. The crystal then contracted rapidly from point 2 to point 3 and subsequently went through another small expansion and contraction similar to the one near point 1 on the cooling

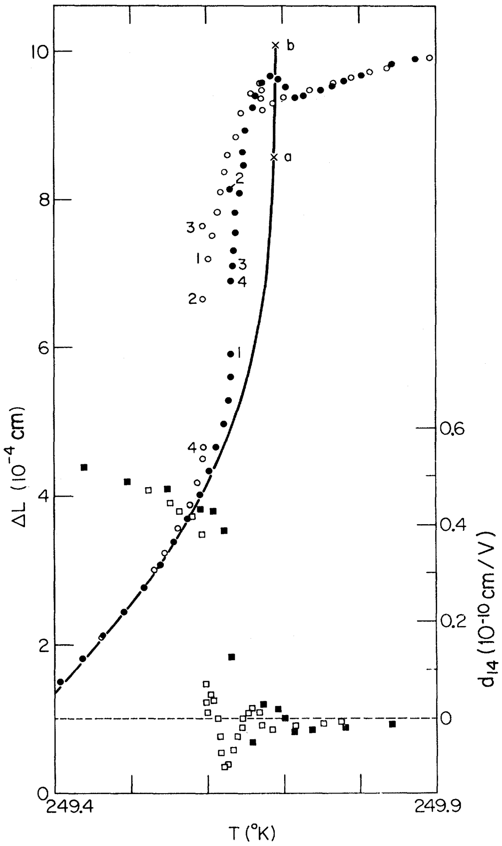

FIG. 4. Close-up of the transition region for ND_4Cl sample *A* (run *A*4). The solid and open squares show d_{14} on warming and cooling, respectively. The solid and open circles show the [011] length change on warming and cooling, uncorrected for background interferometer expansion. The smooth curve terminating at ×(*b*) represents the best fit to the experimental data over a wide temperature range; ×(*a*) is an alternate fitting point. The zero position on the ΔL scale is arbitrarily chosen for display purposes.

curve. This contraction ended at point 4, which was still at 249.630 K. The elapsed time from point 1 to point 4 was ~10 min. From point 4 the crystal expanded in a continuous fashion up to 249.690 K and then contracted until the temperature reached 249.715 K. Above this temperature the warming and cooling data superimposed.

The behavior of d_{14} and ΔL close to the transition was strikingly different for sample *B*, as shown in Fig. 5. Run *B*2 began at 240.8 K. The sample was slowly warmed through the transition up to a temperature of 251.8 K and then cooled back through the transition. The piezoelectric response showed no oscillations and no discontinuous jumps but rather a monotonic variation with a distinct "kink" at which the curvature changed sign. This kink occurred at 249.660 K on warming and at 249.645 K on subsequent cooling. Clearly defined changes in curvature were observed in the length variation at identical temperatures. It is doubtful that there is any significance in the apparent shift of the ΔL cooling data relative to the warming data, since there was a shift in the opposite sense for run *B*1. In both cases, the shifts were most likely caused by slight changes in the interferometer framework.

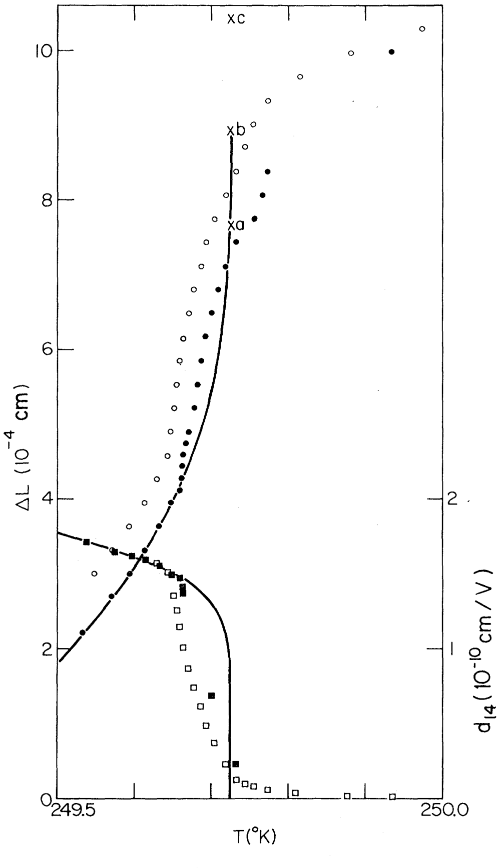

FIG. 5. Close-up of the transition region for ND_4Cl sample *B* (run *B*2). The solid and open squares show d_{14} on warming and cooling, respectively. The solid and open circles show the [011] length change on warming and cooling, uncorrected for background interferometer expansion. The smooth curves represent best fits to the experimental data over a wide temperature range. The points marked × (*a*), × (*b*), and × (*c*) correspond to three fitting choices (see Fig. 6). The zero position on the ΔL scale is arbitrarily chosen for display purposes.

IV. DISCUSSION

The principal objective of our data analysis will be to analyze the variations in ΔL and d_{14} over the range $-12 < T - T_c < -0.06$ K in terms of the critical exponents α' and β. But first, the unusual behavior in the immediate vicinity of the transition deserves some discussion. The basic question is what is the thermodynamic order of the transition in ND_4Cl at 1 atm. The first-order character observed in a neutron study[3] of a $N(D_{0.93}H_{0.07})_4Cl$ single crystal could very well be due to incomplete deuteration since investigations on powdered samples with 98%–100% deuteration[8,15] do not reveal any discontinuity in the volume. However, the role of crystal size and internal strains near a λ transition is not well understood.[7,16] The sensitivity of the detailed behavior very close to T_c is clearly indicated by Figs. 4 and 5. Since samples *A* and *B* were cut from the same large single crystal, the differences in their behavior must be due to slight differences in any defects present. The d_{14} oscillations shown in Fig. 4 indicate that major domain rearrangements occur in sample *A* very close to and *above* its transition temperature. However, the complex and reproducible variations in the length of sample *A* do not fit in with the first-order behavior observed in NH_4Cl at low pressures. In particular, it is unclear why the discontinuous "first-order" change in length is always associated with a second discontinuous change of opposite sign (which immediately precedes the first-order change on cooling and immediately follows it on warming). Moreover, in the case of sample *B*, the abrupt changes in the temperature dependence of d_{14} and ΔL near T_c correspond to classical (Ehrenfest) second-order behavior. For a substance as close to a "multicritical" point as ND_4Cl, it may be impossible to decide whether a departure from the smooth progression of a critical variable toward a critical point has been caused by some thermodynamic instability or some sudden sample-dependent change in domain structure. Indeed, finding the exact location of a multicritical point will be very difficult in such a substance.

In spite of complications very close to the transition, the piezoelectric data in the ordered phase can be well represented by a simple power law of the form

$$d_{14}=\mathcal{B}\,|\epsilon\,|^{\beta}, \qquad (5)$$

where β is the critical exponent for the order parameter [see Eq. (3)] and $\epsilon \equiv (T-T_c)/T_c$. Since ND_4Cl never actually reaches its critical point, it is necessary to treat the value of T_c as a fitting parameter which is adjustable over a narrow range. The best fit of the d_{14} data with Eq. (5) was achieved using a least-squares procedure to minimize the quantity

$$\chi^2=\frac{1}{n-p}\sum\frac{(d_{14}^{\text{expt}}-d_{14}^{\text{calc}})^2}{\sigma^2}, \qquad (6)$$

where n is the number of data points, p is the number of adjustable parameters, and σ is the standard deviation in the experimental values. Minimization of χ^2 was carried out with $\mathcal{B}$ and β as free parameters for various fixed values of T_c covering a range of 0.1 K. A minimum χ^2 value (≈ 1) was obtained for sample B when $T_c = 249.725$ K. This value for T_c is 65 mK above the "kink", where the curvature in the data clearly changes sign (see Fig. 5). Since data points above this kink cannot be used in the fitting procedure, there is an appreciable gap, and it is difficult to select an unambiguous critical temperature. Choices of 249.700 and 249.750 K for T_c gave fits with β values of 0.118 and 0.132, respectively, and χ^2 values of ~ 1.5. However, a systematic trend in the deviations became quite obvious for T_c values below 249.7 or above 249.75 K. Thus, our analysis of sample B gave $T_c = 249.725 \pm 0.025$ K and $\beta = 0.125 \pm 0.007$. It should be stressed that the error limits on β are not due to a lack of quality in the d_{14} data but to the ambiguity in the T_c value. A comparable analysis of the d_{14} data for sample A gave $T_c = 249.690 \pm 0.030$ K and $\beta = 0.127 \pm 0.005$. It should be noted that our β values are slightly smaller than the values (0.14–0.18) reported from neutron scattering measurements near the multicritical point in $N(D_{0.93}H_{0.07})_4Cl$.[3] However, those values may be quite sensitive to the treatment of the critical neutron scattering near T_c.

The thermal-expansion data can be analyzed only in the ordered phase since the magnitude and temperature range of the critical variation above T_c is very small and power-law fits in the disordered phase are too uncertain to be significant. Below T_c, the observed variation in the length of a ND_4Cl single crystal can be represented by

$$\frac{\Delta L}{L_0}=\left(\frac{\Delta L}{L_0}\right)_c-\alpha_b\,|T-T_c|-\frac{\mathcal{A}T_c}{1-\alpha'}\,|\epsilon\,|^{1-\alpha'}, \qquad (7)$$

where $(\Delta L/L_0)_c$ is the value expected at the critical point, and α_b is the sum of a noncritical background thermal expansion α_0 of the ND_4Cl crystal and the linear framework expansion of the interferometer. The critical contribution α_c to the thermal-expansion coefficient of ND_4Cl in the ordered phase has been assumed to have the form $\mathcal{A}\,|\epsilon\,|^{-\alpha'}$, where α' is the critical exponent associated with the heat capacity. Since the critical point is not actually achieved, the fitting procedure with Eq. (7) involves five adjustable parameters: T_c, α_b, $(\Delta L/L_0)_c$, $\mathcal{A}$, and α'.

The goodness of fit in terms of χ^2 values was systematically explored by holding T_c and α_b fixed at various values and carrying out a least-squares fit for the values of the other three parameters. An indication of the quality of these fits is shown in Fig. 6 for three sets of T_c and α_b values. The necessity of using five fitting parameters together with the impossibility of fitting the data very close to T_c (resulting from the abrupt departure of the experimental data from a smooth critical variation prior to reaching T_c) makes the choice of the best fit less certain than for the piezoelectric data. However, it was found that quite good fits were achieved when the T_c value for a given sample was set equal to the value previously determined in the d_{14} fitting procedure. It was also discovered that there was a close correspondence between the values of α' and $\mathcal{A}$ for samples A and B when $\alpha_b(B) = \alpha_b(A) + 4\times10^{-5}$, which is consistent with the differences observed in the linear expansion of the interferometer above the transition region for runs on these two samples. The choice within a spread of α_b values depends mostly on the physical plausibility of the $(\Delta L/L_0)_c$ value obtained. The

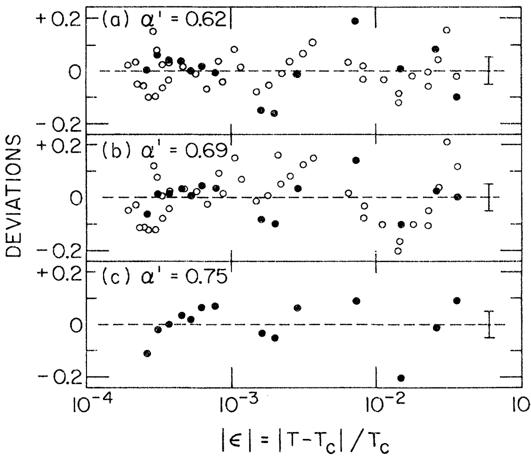

FIG. 6. Deviations $10^4(\Delta L/L_0^{\text{expt}} - \Delta L/L_0^{\text{calc}})$ for various fixed values of T_c and α_b. The solid dots represent run $B2$ warming with $T_c = 249.725$ K and (a) $\alpha_b = 11\times10^{-5}$ K^{-1}, (b) $\alpha_b = 14\times10^{-5}$ K^{-1}, and (c) $\alpha_b = 16\times10^{-5}$ K^{-1}. The open circles represent the combined data from runs $A5$ and $A6$ warming with $T_c = 249.690$ K and (a) $\alpha_b = 7\times10^{-5}$ K^{-1}, (b) $\alpha_b = 10\times10^{-5}$ K^{-1}. The error flag corresponds to an estimated standard deviation of 5×10^{-6} in the $\Delta L/L_0$ values.

smooth curves that terminate at $\times(b)$ in Figs. 4 and 5 represent the fits achieved with the appropriate sets (b) of fitting parameters, for which $\alpha' = 0.69$ and $\mathcal{A} = 7.1\times10^{-5}\ \mathrm{K}^{-1}$. Sets (a) and (c) give almost the same curve but predict different lengths at the critical point. None of these sets can be ruled out, but set (b) leads to values of the integral $\int_T^{T_c} \alpha_c\, dT$, in good agreement with those estimated from the data of Boiko[14] and Smits *et al.*[8] Thus we conclude that α' lies in the range 0.62 to 0.75 for both samples, with a probable value of ~0.69. This value is very similar to those reported for NH_4Cl at 1 atm, where $\alpha' = 0.67$ was obtained from an analysis of the heat capacity[17] and $\alpha' = 0.75$ was obtained from the thermal expansion.[18]

In summary, our analysis of the best power-law fit to the simultaneously measured piezoelectricity and thermal expansion leads to the critical exponents

$$\alpha' = 0.69 \pm 0.06 \quad \text{and} \quad \beta = 0.126 \pm 0.006, \tag{8}$$

with $T_c = 249.690 \pm 0.030$ K for sample A and 249.725 ± 0.025 K for sample B. This difference in T_c values is unexpected. Two samples cut from the same single crystal would be expected to have a common critical temperature even though sample-dependent effects might interrupt the critical variation in the properties at different distances from T_c. This does not seem to be the case since significantly better agreement between α', β, and all other fitting parameters for the two samples can be achieved by assuming different T_c values rather than forcing the T_c values to be the same for both samples.[19]

The exponents given in Eq. (8) clearly indicate that the multicritical point in ND_4Cl is not a Gaussian tricritical point, for which $\alpha' = \frac{1}{2}$ and $\beta = \frac{1}{4}$.[5,20] Even taking logarithmic corrections[20] into account (which would lead to an "effective" tricritical β value of ~0.19 over the range of reduced temperatures used in our fits) does not alter this conclusion. One can consider the formal possibility that ND_4Cl exhibits a Gaussian critical point of higher order $\mathcal{O}$, for which $\alpha' = \frac{2}{3}$ and $\beta = \frac{1}{6}$ when $\mathcal{O} = 4$ or $\alpha' = \frac{3}{4}$ and $\beta = \frac{1}{8}$ when $\mathcal{O} = 5$.[5] The latter set of values certainly resembles our experimental exponents, but it is difficult to visualize the five ordered phases which become identical simultaneously at such a fifth-order point. However, the presence of indirect interactions which favor antiparallel ordering[21–23] (as in the tetragonal phase of NH_4Br) in addition to the dominant direct interactions which cause parallel ordering does encourage one to think in terms of higher-order critical phenomena.

Neutron scattering experiments on high-quality, fully deuterated single crystals would be of great value in confirming our new value of β and determining the susceptibility exponents γ and γ'. If the mean-field values $\gamma = \gamma' = 1$ are valid for ND_4Cl, the Rushbrooke inequality $\alpha' + 2\beta + \gamma' \geq 2$ requires that $\alpha' + 2\beta \geq 1$. Since the present experimental values give $\alpha' + 2\beta = 0.94 \pm 0.07$, either $\gamma' > 1$ or α' must be close to its upper limit of 0.75. Direct measurements of the heat-capacity variation in ND_4Cl are now in progress to establish a more precise experimental value for α'.

Note added in proof. A good fit to the $d_{14}(T)$ data below the break (sample A) or kink (sample B) can also be achieved with a Landau model that involves a first-order transition at a temperature T_1. This Landau fit is based on the assumption that the free energy has the form

$$G = G_0 + \tfrac{1}{2} a_0 (T - T_\theta)\Psi^2 + \tfrac{1}{4} b \Psi^4 + \tfrac{1}{10} e \Psi^{10} ,$$

where a_0, $e > 0$, $b < 0$, and the "Curie" temperature T_θ is lower than T_1. From this free energy, one can easily derive the following expression for $\tilde{d}_{14} \equiv d_{14}(T)/d_{14}(T_1)$:

$$\tilde{d}_{14}^{8} - \tfrac{8}{5}\tilde{d}_{14}^{2} + \tfrac{3}{5}[(T - T_\theta)/(T_1 - T_\theta)] = 0 .$$

The best Landau fits were achieved with $T_1 - T_\theta = 0.040$ K and $T_\theta = 249.570$ K for sample A and $T_\theta = 249.615$ K for sample B, and these fits were as good in a χ^2 sense as those obtained with a pure power law. Note, however, that the $\tilde{d}_{14}$ equation is very close to a simple power law when $T - T_\theta$ is large. Thus the Landau fit works because $\beta \simeq \frac{1}{8}$ for our pure power-law fit. Indeed, if $\beta \simeq 1/2n$ such Landau fits will always work quite well when the final term in the free energy is chosen to be Ψ^{2n+2}.

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[1] C. W. Garland and B. B. Weiner, Phys. Rev. B 3, 1634 (1971); B. B. Weiner and C. W. Garland, J. Chem. Phys. 56, 155 (1972), and references cited therein.

[2] R. J. Birgeneau, W. B. Yelon, E. Cohen, and J. Makowsky, Phys. Rev. B 5, 2607 (1972); W. B. Yelon and R. J. Birgeneau, *ibid.* 5, 2615 (1972); M. Blume, V. J. Emery, and R. B. Griffiths, Phys. Rev. Lett. 29, 278 (1972); G. Goellner and H. Meyer, *ibid.* 26, 1534 (1971).

[3] W. B. Yelon, D. E. Cox, P. J. Kortman, and W. B. Daniels, Phys. Rev. B 9, 4843 (1974).

[4] A. Hüller, Z. Phys. 270, 343 (1974).

[5] T. S. Chang, A. Hankey, and H. E. Stanley, Phys. Rev. B 8, 346 (1973); 8, 1178 (1973); T. S. Chang, G. F. Tuthill, and H. E. Stanley, Phys. Rev. B 9, 4882 (1974).

[6] See the discussion and references cited at the end of Ref. 1.

[7] D. G. Thomas and L. A. K. Staveley, J. Chem. Soc. 1951, 1420 (1951).

[8] A. Smits, G. J. Muller, and F. A. Kröger, Z. Phys. Chem. B 38, 177 (1937).

[9] R. B. Griffiths, Phys. Rev. Lett. 24, 1479 (1970);

Phys. Rev. B 7, 545 (1973).

[10] S. Bahrs and J. Engl, Z. Phys. 105, 470 (1937).

[11] The ND_4Cl crystal was obtained from B. N. Brockhouse and was similar to the crystals used for neutron diffraction; see H. C. Teh and B. N. Brockhouse, Phys. Rev. B 8, 3928 (1973).

[12] D. E. Bruins, C. W. Garland, and T. J. Greytak, Rev. Sci. Instrum. (to be published).

[13] This uncertainty is due to possible drifts in the laser frequency and the possibility of slight irregularities in the expansion behavior of the interferometer background contribution to the over-all expansion.

[14] E. Mohler and R. Pitka, Solid State Commun. 14, 791 (1974).

[15] A. A. Boiko, Kristallografiya 14, 639 (1969) [Sov. Phys.-Crystallogr. 14, 539 (1970)]; P. Nissilä and J. Pöyhönen, Phys. Lett. A 33, 345 (1970).

[16] D. G. Thomas and L. A. K. Staveley, J. Chem. Soc. 1951, 2572 (1951); 1952, 1727 (1952).

[17] P. Schwartz, Phys. Rev. B 4, 920 (1971).

[18] G. E. Fredericks, Phys. Rev. B 4, 911 (1971).

[19] The assumption of a single T_c value does not, however, change the exponent values by more than the stated uncertainties. For example, the choice of $T_c = 249.690$ K for both samples gives $\alpha'_A = 0.69$ and $\alpha'_B = 0.65$ while the choice $T_c = 249.725$ K gives $\alpha'_A = 0.74$ and $\alpha'_B = 0.69$.

[20] E. K. Riedel and F. J. Wegner, Phys. Rev. Lett. 29, 349 (1972).

[21] A. Hüller, Z. Phys. 254, 456 (1972).

[22] Y. Yamada, M. Mori, and Y. Noda, J. Phys. Soc. Jpn. 32, 1565 (1972).

[23] M. Couzi, F. Denoyer, and M. Lambert, J. Phys. (Paris) 35, 753 (1974).