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Dielectric and ultrasonic measurements in CsH_2AsO_4[†]

Richard J. Pollina and Carl W. Garland
Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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The shear elastic constants c_{44}^E and c_{66}^E and both the free and clamped c-axis dielectric constant have been measured in the paraelectric phase of single-crystal cesium dihydrogen arsenate. The temperature variation of c_{66}^E is well described by an elastic Curie expression arising from linear piezoelectric coupling. A 20-K difference between the free and clamped Curie temperatures is obtained from an analysis of the elastic measurements and directly from the c-axis dielectric measurements. The a-axis dielectric constant, which has been measured between 90 and 300 K, shows antiferroelectric characteristics and exhibits a well-defined first-order discontinuity.

I. INTRODUCTION

Coupling between the soft mode and acoustic lattice modes plays an important role in the ferroelectric transition in KH_2PO_4 and its structural isomorphs. Experiments on cesium dihydrogen arsenate (CDA) are of considerable interest since several Raman-scattering studies[1-3]have shown that the frequency of an over-damped soft mode extrapolates to zero at a temperature T_0, which is considerably below the transition temperature. This effect has been analyzed in detail by Cowley and Coombs[4] on the basis of an anharmonic phonon model involving coupling between the soft mode and fluctuations in the acoustic-phonon occupation numbers. More recently, Young and Elliott[5,6] have extended the Kobayashi pseudospin model to include a nonlinear coupling between the spin mode and pairs of phonons. In both models, the c-axis dielectric response function is identical in structure, and the difference between the static and high-frequency response is attributed to a large relaxing contribution to the self-energy of the ferroelectric mode.

As a result of the present investigation and a parallel study of the Raman and Brillouin scattering by Lagakos and Cummins,[7] it appears that the properties of CDA can be understood on the basis of a simple model involving linear piezoelectric coupling without invoking any relaxing self-energy term. In this case, T_0 should be identical with the clamped Curie temperature, and the large difference between T_0 and the transition temperature is primarily due to the very low shear stiffness of CDA.

Actually, there is a small latent heat associated with the transition in CDA, and a first-order transition takes place.[8] Thus, we need to define three characteristic temperatures: $T_c^x < T_c^X < T_1$, where T_c^x is the clamped Curie temperature corresponding to constant strain x, T_c^X is the free Curie temperature at constant stress X, and T_1 is the temperature of the first-order transition. For notational convenience, we shall use T_c without a superscript to represent $T_c^{X=0}$.

The present investigation involves measurements of the shear elastic constants $c_{44}{}^E$ and $c_{66}{}^E$, the free and clamped c-axis dielectric constants, and the a-axis dielectric constant. An analysis of the c_{66} elastic data and the direct measurements of c-axis dielectric constants both show that $T_c - T_c^x = 20$ K. A comparison of ultrasonic and hypersonic[7] elastic data shows that there is no critical dispersion up to a few gigahertz. Indeed, the acoustic velocity and attenuation variations with $T - T_c$ are very similar to those observed in potassium dihydrogen phosphate (KDP).[9,10]

II. EXPERIMENTAL DETAILS

The oriented single crystals of CDA were obtained from Quantum Technology, Ltd.[11] After these were used for acoustic measurements, two thin slabs were cut from each of them for dielectric measurements along the a and c axes. Small cleavage cracks developed when the crystals were cooled through the transition. Such cracks interfered with measurements of acoustic attenuation but had very little, if any, effect upon the other measurements.

A pulse-echo method with a calibrated delayed comparator pulse was used to measure the ultrasonic attenuation and velocity.[9,10] Both crystal 1 with an acoustic path length $2L = 1.458$ cm and crystal 2 with $2L = 0.385$ cm were used to determine c_{66}. Data on c_{44} were obtained with a third crystal ($2L = 2.049$ cm) lent to us by Cummins.[12] All acoustic measurements were made at constant field ($E = 0$) by shorting the c-axis faces. Since the thermal expansion of CDA is not accurately known, the weak temperature dependence of c_{ij} due to changes in the path length and density has been neglected. The room-temperature density[13] was taken to be 3.43 g cm^{-3}.

Low-frequency (300-Hz) dielectric constants were measured using a General Radio 1615 three-lead capacitance bridge with phase-sensitive detection of the bridge voltage. The sensitivity was 10^{-3} pF with an applied field which never exceeded 5 mV cm^{-1}. The high-frequency dielectric constant was measured at 5 MHz on a General Radio 716-*CS*1 capacitance bridge. The accuracy of the latter measurements was poor (about ±0.1 pF) because of the large lead capacitance which must be subtracted in order to obtain the capacitance of the sample. Most of our dielectric measurements were made on two small crystals cut from crystal 2: Crystal 2a with dimensions $(a \times b \times c)$ 0.74 $\times$1.92$\times$10.0 mm was used for a-axis measurements and crystal 2c with dimensions 1.94$\times$8.89$\times$3.34 mm for c-axis measurements. The value of the vacuum capacitance C_0 was 0.23 pF for crystal 2a and 0.046 pF for crystal 2c. The appropriate faces of each sample were plated with an indium-gallium eutectic film and lightly clamped between metal plates. Since no guard ring was used, a small correction was made for fringing effects. This correction was determined for each sample by measuring the capacitance of a polystyrene dummy of identical shape.

III. RESULTS AND DISCUSSION

A. Elastic measurements

The constant-field elastic constants c_{44}^E and c_{66}^E are shown as a function of temperature in Fig. 1. The c_{66} data are shown as reduced values $\tilde{c}_{66}$, where $\tilde{c}_{66}(T) \equiv c_{66}(T)/c_{66}^E(170\text{ K})$, since the measured values of c_{66}^E varied substantially from crystal to crystal and even from run to run on a given crystal. For the two runs on crystal 2 which are shown in Fig. 1, we found $c_{66}^E(170\text{ K}) = 0.93 \times 10^{10}$ dyn cm^{-2} for the 5-MHz run and 1.05×10^{10} for the 10-MHz run. In the case of several 10-MHz runs on crystal 1, we found values ranging between 1.12×10^{10} and 1.17×10^{10} dyn cm^{-2}. Moreover, hypersonic Brillouin measurements[7] gave $c_{66}^E(170\text{ K}) = 1.25 \times 10^{10}$ dyn cm^{-2} for the one crystal studied in that investigation.[14] The reason for these sizable differences in elastic stiffness is unclear, but they may be due to strains generated when the crystals were originally cut by the manufacturer.

In spite of the ambiguity about $c_{66}^E(170)$, it is clear from Fig. 1 that no critical velocity dispersion is observed near the ferroelectric transition. Indeed, the acoustic behavior is very similar to that observed in KDP,[9,15] although CDA is a much softer crystal. (The essentially constant c_{44}^E value of 6.65×10^{10} dyn cm^{-2} is one-half that of KDP, whereas the c_{66} values are only about one-quarter those in KDP.)

As in the case of KDP, one can analyze the tem-

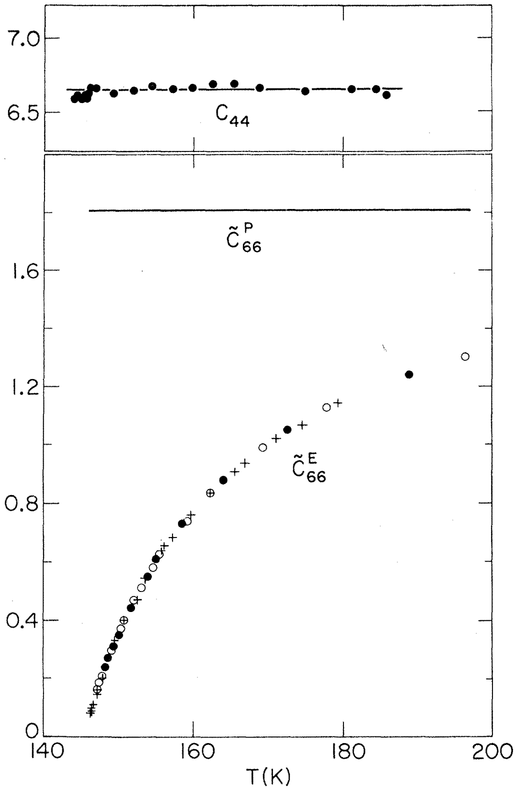

FIG. 1. Temperature dependence of c_{44}^E and c_{66}^E, along with an estimate of the value of c_{66}^P. Ultrasonic data for c_{44}^E were obtained at 10 MHz, and those for c_{66}^E were obtained at both 5 (○) and 10 (●) MHz. Hypersonic data varying from 0.75 to 3 GHz (+) were obtained from Brillouin measurements (Ref. 7). Tilde on $\tilde{c}_{66}^E$ and $\tilde{c}_{66}^P$ denotes dimensionless reduced values (see text); units for c_{44}^E are 10^{10} dyn cm^{-2}.

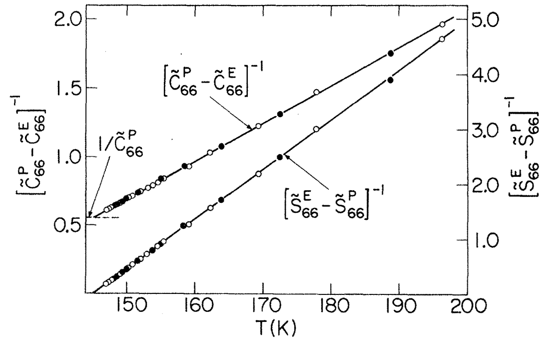

FIG. 2. Elastic Curie plots of the c_{66} ultrasonic data. Symbols have the same meaning as in Fig. 1.

perature dependence of the c_{66}^E data in terms of either of two equivalent elastic Curie expressions

$$c_{66}^P - c_{66}^E = a_{36}^2 \chi_3^x = D_0/(T - T_c^x), \quad (1)$$

$$s_{66}^E - s_{66}^P = b_{36}^2 \chi_3^X = D/(T - T_c), \quad (2)$$

where a_{36} and b_{36} are, respectively, the piezoelectric stress and strain constants; χ_3^x and χ_3^X are the clamped and free dielectric susceptibilities along the ferroelectric c axis; T_c^x and T_c are the corresponding clamped and free Curie temperatures; D and D_0 are given in the terms of the Curie constant C by $D_0 = a_{36}^2 C/4\pi$ and $D = b_{36}^2 C/4\pi$; and $s_{66} \equiv 1/c_{66}$ denotes the elastic compliance.[10] In order to carry out such an analysis, we have used the reduced values $\tilde{c}_{66}$, and have assumed that $\tilde{c}_{66}^P \equiv c_{66}^P/c_{66}^E(170)$ has the temperature independent value 1.81. This value, which was chosen to achieve the best linearity of the plots of $(\tilde{c}^P - \tilde{c}^E)^{-1}$ and $(\tilde{s}^E - \tilde{s}^P)^{-1}$ versus temperature, is a reasonable but essentially arbitrary choice. Fortunately, Fig. 2 shows that both elastic plots are well represented by a linear variation over a range of 50 K. Furthermore, the slopes of these two lines are internally consistent with the chosen value of $\tilde{c}_{66}^P$. The identity $D_0/D \equiv (c^P)^2$ can be rewritten in the form $[D_0/c^E(170\text{ K})]/[Dc^E(170\text{ K})] \equiv (\tilde{c}^P)^2$; the left-hand side, as determined from the ratio of slopes in Fig. 2, is 3.27, while $(\tilde{c}^P)^2$ is 3.28. This gives us confidence in the choice of $\tilde{c}_{66}^P$ and the resulting values of the free ($T_c = 145.1$ K) and clamped ($T_c^x = 125.1$ K) Curie temperatures. The difference $(T_c - T_c^x) = 20.0$ K agrees well with the difference directly obtained from the dielectric measurements (see Sec. III B). This unusually large difference between T_c and T_c^x is due to the very low shear stiffness of CDA.

If we adopt the average ultrasonic value of 0.99×10^{10} dyn cm^{-2} for $c_{66}^E(170\text{ K})$, the resulting values of D and D_0 are $D = 11.1\times10^{-10}$ dyn^{-1} cm^2 K and $D_0 = 35.6\times10^{10}$ dyn cm^{-2} K. The piezoelectric constants of CDA, obtained from these values and the Curie constant 2700 K, are $a_{36} = 4.1\times10^4$ and $b_{36} = 23\times10^{-7}$ in cgs units. The corresponding values for KDP are 3.4×10^4 and 4.95×10^{-7}. The marked increase in $b_{36} = a_{36}/c_{66}^P$ is another reflection of the change in shear stiffness on going from KDP to CDA.

It is appropriate to comment briefly on the acoustic absorption. Although ultrasonic velocity measurements could be made down to ~147 K, the echo pattern near the transition temperature was distorted by spurious modes which caused a nonexponential variation in the echo amplitudes. In addition, the temperature dependence of the attenuation increased markedly below ~147.5 K, suggesting the onset of some kind of scattering mechanism. Thus, it was not possible to carry out a reliable analysis of our ultrasonic attenuation data. However, the hypersonic attenuation obtained from Brillouin linewidths[14] can be fairly well represented by $\alpha/\omega^2 = 17.5\times10^{-16}(T - T_c)^{-1.6}$, when T_c is taken to be 145.1 K. Our analysis of these hypersonic data on the basis of a single relaxation formalism [see Eq. (8) of Ref. 10] yields

$$\tau_{S,X} = 55\times10^{-12}(T - T_c)^{-1}\ \text{sec} \quad (3)$$

for the adiabatic relaxation time at constant (zero) stress. This result is comparable to the corresponding variation $\tau = 24\times10^{-12}\Delta T^{-1}$ for KDP.[9]

B. Dielectric measurements along the *c* axis

The free c-axis dielectric constant measured at 300 Hz is well represented by

$$\epsilon - \epsilon_0 = C/(T - T_c), \quad (4)$$

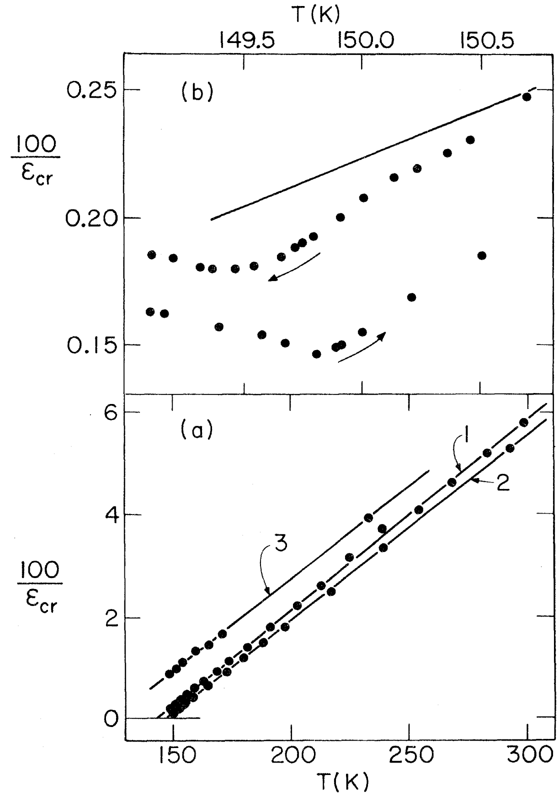

FIG. 3. Curie plots of the temperature variation in $\epsilon_{cr} \equiv \epsilon - \epsilon_0$ along the c axis. (a) Runs 1 and 2 show 300-Hz measurements of the free dielectric constant and indicate the variations observed from different cooling runs on crystal 2c; run 3 represents 5 MHz measurements of the inertially clamped dielectric constant. (b) Behavior of ϵ_{cr} near its maximum during run 1 and subsequent warming. Line is identical to that shown for run 1 in part (a).

where ϵ_0 is a temperature-independent background contribution and the Curie constant $C = 2700 \pm 75$ K. As shown in Fig. 3(a), different runs on crystal 2c gave surprisingly different values for the free Curie temperature and slightly different values for the other parameters. For run 1, $T_c = 144.0$ K, $\epsilon_0 = 9.65$, and $C = 2678$ K; for run 2, $T_c = 147.0$ K, $\epsilon_0 = 8.77$, and $C = 2757$ K. The detailed behavior of ϵ near its maximum value is shown in Fig. 3(b). On cooling, ϵ reaches a maximum value of 550 at 149.4 K and then very slowly decreases to 420 at 140 K (the lowest temperature for that run). On warming, a maximum ϵ value of 675 is observed at 149.8 K. In spite of the fact that only a small shift was observed in the temperature corresponding to $\epsilon_{\max}$, the warming data over the temperature range 155–300 K are represented by Eq. (4) with $T_c = 145.8$ K, which represents a shift of 1.8 K in T_c. Such shifts in T_c from run to run have also been observed by Lowndes and Spillman.[16]

The clamped c-axis dielectric constant is also shown in Fig. 3(a). In run 3, the capacitance was measured simultaneously at low frequency (300 Hz) and high frequency (5 MHz). Both sets of data obeyed Eq. (4) with the same Curie constant (2768 K), and the clamped Curie temperature T_c^x was found to be 125 K, whereas $T_c = 145$ K. Thus the difference $T_c - T_c^x = 20$ K is in very good agreement with that obtained from the analysis of the ultrasonic velocity.

The Curie constant obtained from these measurements is similar to that reported by others[7,16] who have studied CDA crystals obtained from Quantum Technology, Ltd. However, our results are rather different from those reported by Blinc, Burgar, and Levstik[17] and by Strukov and coworkers.[8] These investigators report $C = 3380$ and 3200 K, respectively, and show small discontinuous changes in ϵ at a first-order transition temperature T_1. Blinc *et al.* report $T_1 = 146.34$ K and $T_c = 141.79$ K, while the data of Strukov *et al.* give $T_1 = 145.4$ K and $T_c = 144.5$ K. In view of these comparisons, it is clear that the dielectric behavior in CDA is quite sample dependent. This is partially confirmed by measurements on a sample cut from crystal 1, which gave $T_c = 143$ K, $\epsilon_0 = 9.1$, and $C = 2630$ K with a maximum in ϵ at 148.25 K. A summary of the information presently available from various c-axis dielectric measurements is given in Table I.

It should also be noted that measurements obtained as a function of frequency over the 30–3000-Hz range indicate the presence of a low-frequency dielectric relaxation *above* the transition temperature in CDA, similar to that observed in KDA.[18] However, the 300-Hz data were unaffected by this relaxation, which is centered at frequencies below 30 Hz.

C. Dielectric measurements along the *a* axis

The variation in the a-axis dielectric constant ϵ^a between 90 and 300 K is shown in Fig. 4. The behavior of these ϵ^a data is in marked contrast to that of the c-axis dielectric constants. First of all, no shift was observed in ϵ^a values from run to run on crystal 2a. Secondly, as indicated by the expanded plot of data points close to the transition, there was a substantial discontinuity in ϵ^a at a well-defined transition temperature $T_1 = 149.75$ K. This temperature was stable with cycling through the transition but varied from one crystal to another in the same manner as the temperature of the maximum in the c-axis dielectric constant (ϵ^a measurements on a sample cut from crystal 1 gave $T_1 = 148.1$ K). Finally, there was a pronounced asymmetry in the equilibration times for ϵ^a measurements near T_1. On cooling, the crystal always came to equilibrium very rapidly (within ~30 sec). On warming, the equilibration times just below the transition were on the order of 8 h (as long as 12 h was needed to achieve equilibrium after slowly warming through the transition). This makes it difficult to investigate hysteresis in the value of T_1; however, we estimate that such hysteresis (if any) is less than 0.05 K.

The high value observed for T_1 is rather puzzling in view of the fact that several investigators[7,8,17] have reported first-order transition temperatures lying in the range 145.4–146.4 K. In addition, our own ultrasonic measurements give no indication of a transition in the vicinity of 148–150 K. Possibly cutting the small samples for dielectric measurements introduced strains which shifted the transition.

As shown by Fig. 5, the ϵ^a data in the paraelec-

TABLE I. Curie constant C, free Curie temperature T_c, first-order transition temperature T_1, and the difference $T_c - T_c^x$ between the free and clamped Curie temperatures for CDA. All quantities are expressed in K.

Source	C	T_c	T_1	$T_c - T_c^x$
Present work[a]	2700 ± 75	145 ± 2	149 ± 1	20.0 ± 0.2
Ref. 7[a]	2525	142 – 145	146	20
Ref. 16	2835	147.8	148.4	···
Ref. 8	3200	144.5	145.4	···
Ref. 17	3380	141.8	146.3	···

[a] All values except $T_c - T_c^x$ are sample dependent. In the case of the present work, the stated limits indicate the range of values observed for different samples.

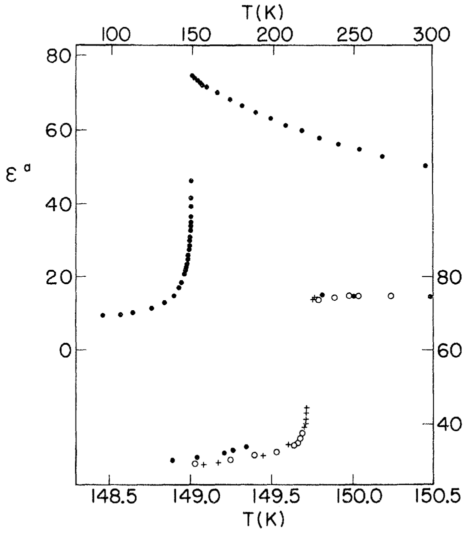

FIG. 4. Dielectric constant along the a axis. Data points obtained near the transition temperature in three different runs on crystal 2a are shown on a greatly expanded temperature scale (● and ○ data obtained on cooling; + data obtained on warming).

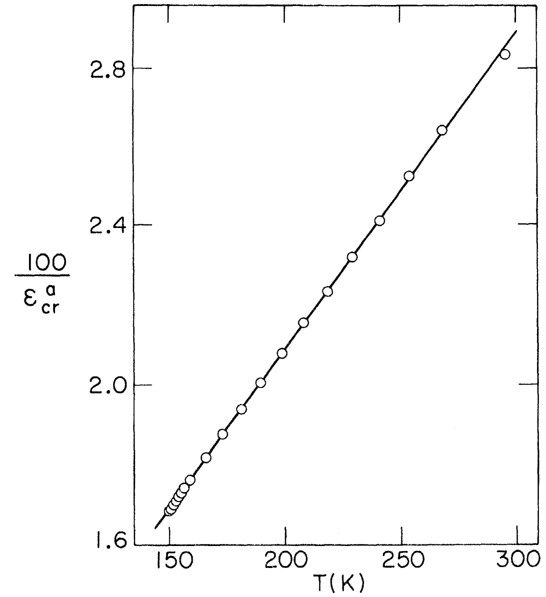

FIG. 5. Temperature dependence of $1/\epsilon^a_{cr}$ in the paraelectric phase, where $\epsilon^a_{cr} \equiv \epsilon^a - 15.3$.

tric phase can be well represented by

$$\epsilon^a = \epsilon^a_0 + C^a/(T+\Theta), \tag{5}$$

where ϵ^a_0 is a temperature-independent contribution equal to 15.3 for crystal 2a, $C^a = 12,450$ K, and $\Theta = 60.6$ K (corresponding to a *negative* critical temperature for the a-axis susceptibility). This behavior for ϵ^a is very similar to that observed in the antiferroelectric $NH_4H_2PO_4$ (ADP), for which $\epsilon^a_0 = 6$, $C^a = 18\,000$ K, and $\Theta = 55$ K.[19] Indeed, Havlin, Litov, and Uehling[20] have interpreted the a-axis susceptibility of ferroelectric crystals of the KDP family in terms of antiferroelectric ordering in the a-b plane. They have derived an expression for $\epsilon^a_{cr} \equiv \epsilon^a - \epsilon^a_0$ in terms of a mean-field interaction parameter J, a tunneling integral Γ, and an effective a-axis dipole moment μ_2 associated with the off-center positions of the hydrogens in their O–H$\cdots$O bonds. An analysis of our data in terms of this model gives $J = 150$ K, $\Gamma = 45$ K, and $\mu_2 = 3.64D$ for CDA. These values can be compared to $J = 204$ K, $\Gamma = 185$ K, $\mu_2 = 3.90D$ for KDP and $J = 101$ K, $\Gamma = 40$ K, and $\mu_2 = 4.05D$ for KDA,[20] which indicates that tunneling is much less important in the case of arsenates than phosphates.

The behavior of ϵ^a below T_1 is not well represented by the Havlin, Litov, and Uehling model, and we have carried out an analysis in terms of the phenomenological expression

$$1/\chi^a = 1/\chi^a_1 + A(T_1 - T)^n, \tag{6}$$

where $4\pi\chi^a = (\epsilon^a - 1)$ and χ^a_1 is the limiting value of the a-axis susceptibility on approaching T_1 from below. Equation (6) is analogous to an expression obtained by Kittel[21] from a Landau-type expansion of the free energy of an antiferroelectric crystal with a first-order transition, in which case the exponent n has the mean-field value of 1. Figure 6 shows that Eq. (6) is valid over a considerable range when χ^a_1 is taken to be 3.5 (in agreement with $\epsilon^a_1 = 45$ as indicated by the data in Fig. 4). However, the exponent n has the nonclassical value[22]

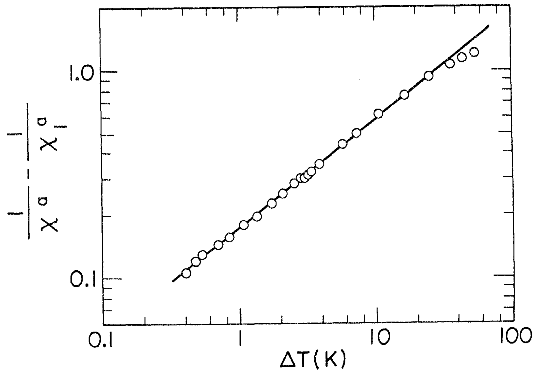

FIG. 6. Log-log plot of $1/\chi^a - 1/\chi^a_1$ vs $\Delta T = T_1 - T$. Straight line corresponds to the values $A = 0.178$ and $n = 0.52$ for the parameters in Eq. (6).

0.52. This suggests the possibility of tricritical behavior in CDA with competition between the two kinds of hydrogen ordering observed in KDP and ADP. Indeed, neutron-scattering measurements on CsD_2AsO_4 have recently provided evidence for a complex structure in the ferroelectric phase of that crystal,[23] which raises questions about the nature of the ordered phase in CDA.

ACKNOWLEDGMENT

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[22] This exponent seems to be consistent with the expectation that the dominant contribution to the temperature dependence of $1/\chi^a - 1/\chi_1^a$ should come from the term $P_s^2 - P_{s1}^2$, where P_s is the spontaneous polarization and P_{s1} is its value on approaching T_1 from below. A rough estimate based on values read from a plot of P_s vs ΔT given in Ref. 8 indicates that $P_s^2 - P_{s1}^2$ varies like $\Delta T^{0.55}$ in CDA.

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