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Proper Ferroelastic Transition in Piezoelectric Lithium Ammonium Tartrate

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(Received 13 June 1977)

Dielectric and Brillouin scattering experiments on a lithium ammonium tartrate crystal have shown that the transition in this crystal is described by the free energy of a piezoelectric crystal,

$$F=\tfrac{1}{2}(\chi^x)^{-1}P^2+aPx+\tfrac{1}{2}\beta(T-T_0)x^2,$$

where the primary order parameter is the homogeneous strain, which gives rise to ferroelectricity through the piezoelectric coupling with the polarization.

At present, ferroelasticity is a well-accepted concept. However, many ferroelastic crystals so far reported do not undergo the "proper ferroelastic" transition in which the primary order parameters is the homogeneous strain x. Here, we treat the ferroelastic transition, which is described by the free energy with a bilinear coupling term,

$$F=\tfrac{1}{2}(\chi^x)^{-1}P^2+aPx+\tfrac{1}{2}C^Px^2, \quad (1)$$

and we conclude that the transition of $LiNH_4C_4H_4O_6 \cdot H_2O$ (LAT) at 98 K is a "proper ferroelastic" transition.

In KH_2PO_4, the transition is well described by the free energy

$$F_1=\tfrac{1}{2}\alpha(T-T_0)P^2+aPx+\tfrac{1}{2}C^Px^2, \quad (2)$$

where the piezoelectric coefficient a and the elastic stiffness at constant polarization, C^P, are independent of temperature. In the early stages of the investigation of $Gd_2(MoO_4)_3$, the transition was suggested to be described by the free energy

$$F_2=\tfrac{1}{2}(\chi^x)^{-1}P^2+aPx+\tfrac{1}{2}\beta(T-T_0)x^2, \quad (3)$$

where a and the clamped inverse susceptibility $(\chi^x)^{-1}$ are independent of temperature. $Gd_2(MoO_4)_3$ was, however, shown to undergo the transition because of the softening of zone-boundary phonons,[1] and is not described by Eq. (3).

The present work reports the observation of the ferroelastic transition, described by the free energy F_2 [Eq. (3)], in the crystal $LiNH_4C_4H_4O_6 \cdot H_2O$. LAT undergoes the transition at $T_c=98$ K, the ferroelectric phase below T_c belongs to $P12_11$, and the paraelectric phase above T_c belongs to $P2_12_12$. According to the ESR study of Cr^{3+} in

LAT,[2] each resonance line gives rise to splitting when the sample is lowered into the ferroelectric phase. The number of split lines can be completely explained by taking account of both the lowering of the point-group symmetry and the formation and switching of ferroelectric domains. Comparison with ESR experiments on ammonium rochelle salt excludes the possibility of the multiplication of the primitive unit cell in LAT. We observed no TO soft mode, characteristic of the lattice dynamical transition, and no anomalous temperature dependence of Raman-active mode through the phase-transition point.

From the free energy with a piezoelectric coupling term [Eq. (1)], the free inverse susceptibility $(\chi^X)^{-1}$ and the elastic stiffness at constant electric field E are given, respectively, by

$$(\chi^X)^{-1} = (\chi^x)^{-1} - a^2/C^P,\quad C^E = C^P - a^2/(\chi^x)^{-1}. \tag{4}$$

From Eqs. (4), the relation

$$C^E/C^P = (\chi^X)^{-1}/(\chi^x)^{-1} \tag{5}$$

is obtained.

Now, we are interested in the comparison between the two cases: Case I is the dielectric instability transition described by the free energy F_1 [Eq. (2)], in which

$$(\chi^x)^{-1} = \alpha(T - T_0); \tag{6}$$

from Eqs. (4) and (6),

$$(\chi^X)^{-1} = \alpha(T - T_c) \tag{7}$$

and

$$C^E = C^P(T - T_c)/(T - T_0) \tag{8}$$

should result, where the transition point T_c is the temperature at which χ^X diverges, and

$$T_c - T_0 = a^2/\alpha C^P. \tag{9}$$

This situation is schematically shown in Fig. 1(a), as confirmed by Bordy and Cummins in potassium dihydrogen phosphate.[3]

Case II is the elastic instability (proper ferroelastic) transition described by F_2 [Eq. (3)], in which

$$C^P = \beta(T - T_0); \tag{10}$$

from Eqs. (4) and (10),

$$(\chi^X)^{-1} = (\chi^x)^{-1}(T - T_c)/(T - T_0), \tag{11}$$

$$C^E = \beta(T - T_c), \tag{12}$$

should result, as schematically shown in Fig. 1(b), where the transition point T_c is the temperature at which C^E vanishes, and

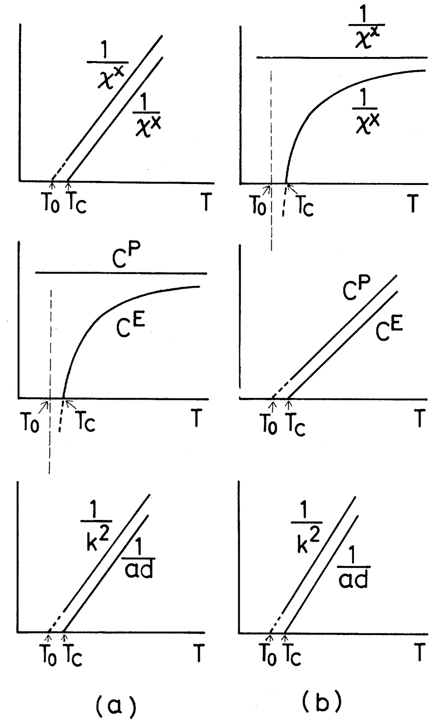

FIG. 1. Schematic representation of temperature dependence of $(\chi^x)^{-1}$, $(\chi^X)^{-1}$, C^E, C^P, k^{-2}, and $(da)^{-1}$; (a) for the dielectric instability transition, (b) for the elastic instability (proper ferroelastic) transition. The dashed line $T = T_0$ is the asymptote of a hyperbola.

$$T_c - T_0 = a^2/[\beta(\chi^x)^{-1}] \tag{13}$$

[as can be seen from Eqs. (4), (10), and (12)]. C^P and C^E have the same slope [as can be seen from Eqs. (10) and (12)].

Our dielectric measurements in LAT have shown that the clamped susceptibility $(\chi_{22}{}^x)^{-1}$ (measured at 2 MHz) is essentially temperature independent, and the free susceptibility $(\chi_{22}{}^X)^{-1}$ (measured at 2 kHz) has been well fitted by a hyperbola [Eq. (11)] with the asymptote $T = T_0$, as shown in Fig. 2(a), which bears all the traits of the dielectric properties of the elastic instability transition seen in Fig. 1(a). The temperature T_0 was estimated to be 4 K lower than T_c. Equation (11) can be rewritten in the form of the Curie-Weiss law,

$$\chi_{22}{}^X = \chi_{22}{}^x + C/(T - T_0), \tag{14}$$

with the Curie-Weiss constant $C = \chi_{22}{}^x(T_c - T_0)$. By replotting the experimental data given in Fig. 2(a), Eq. (14) has been found to hold well in LAT,

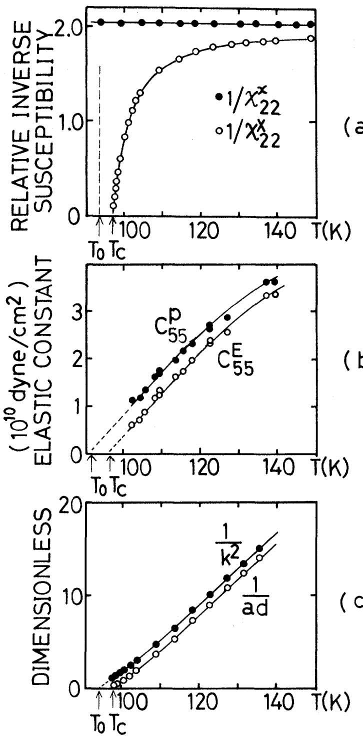

FIG. 2. Temperature dependence of (a) $(\chi^x)^{-1}$ and $(\chi^X)^{-1}$ (relative susceptibilities); (b) C^E and C^p; and (c) k^{-2} and $(da)^{-1}$ in $LiNH_4C_4H_4O_6 \cdot H_2O$. Quantities in (a) and (c) are dimensionless.

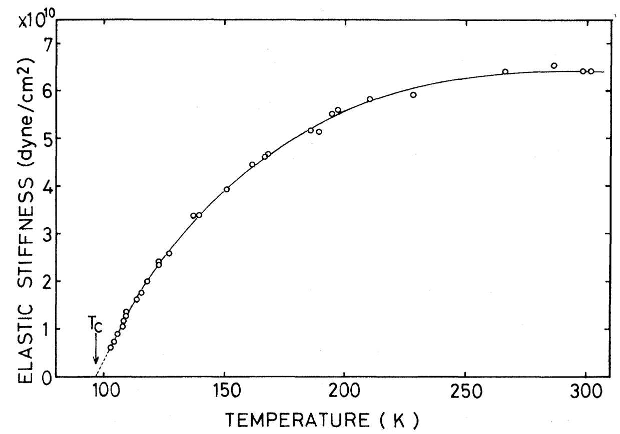

FIG. 3. Temperature dependence of elastic stiffness C_{55}^E of LAT.

and the value of C has been determined to be 2 K (extremely small). This value is in good agreement with the value calculated from $C = \chi_{22}^x(T_c - T_0)$ with use of the experimental value $\chi_{22}^x = 0.5$ at 2 MHz and the difference $(T_c - T_0) = 4$ K. These results of dielectric measurements provides strong support to our proposal that the free energy of LAT can be described by Eq. (3). From Raman scattering experiments our finding that soft phonon does not exist is reasonable, judging from the fact that tartrate-class ferroelectrics undergo the order-disorder transition. Furthermore, the possibility of the order-disorder transition in LAT is excluded because χ_{22}^x is very small (0.5) at 2 MHz and no relaxation is expected in the microwave region.

Brillouin scattering experiments in LAT by Udagawa, Kohn, and Nakamura[4] have been done in a right-angle scattering geometry, with excitation provided by a stabilized single-mode argon-ion laser operating at 5145 Å. The spectra were obtained using a double-pass pressure-scanned Fabry-Perot interferometer. Temperature was controlled within 0.1 K. No refractive-index-matching liquid was used. The observed components are longitudinal C_{11}, C_{22}, and C_{33} modes, and the transverse C_{55} mode. The elastic stiffness C_{55}^E is highly temperature dependent (Fig. 3), while C_{11}, C_{22}, and C_{33} only slightly increase with decreasing temperature from room temperature to 98 K. The elastic stiffness C_{55}^E as a function of temperature is fitted by a straight line [Eq. (12)] in the temperature range $(T - T_c) \sim 20$ K [Fig. 2(b)], by observing the softening of the acoustic phonon towards T_c. This is what is expected for the elastic instability transition [Fig. 1(b)]. By introducing temperature dependence into the experimental value of χ_{22}^x, χ_{22}^X, and C_{55}^E in Eq. (5), C_{55}^P has been obtained as a function of temperature. In the temperature region $(T - T_c) \sim 20$ K, $C_{55}^P(T)$ is represented by a straight line,

$$C^P = \beta(T - T_0), \qquad (15)$$

which crosses with the temperature axis at T_0. This relation is identical with the primary attribute of elastic instability transition, Eq. (10) [see also Fig. 1(b)]. Note that this relation [Eq. (10)] may be an approximation valid only for the temperature region just in the vicinity of T_0. The deviation of the curves in Fig. 2(b) from straight lines does not contradict assumption (10). The slope of $C_{55}^P(T)$ is equal to that of $C_{55}^E(T)$. The difference $(T_c - T_0)$ [given by Eq. (13)] has been found to be 5 K, in agreement with that estimated from the dielectric measurements.

From the dielectric measurements above, the inverse electromechanical-coupling factor k^{-2} and the quantity $(da)^{-1}$ (with d the piezoelectric modulus) have been found to be both straight lines in the vicinity of T_c [Fig. 2(c)]:

$$k^{-2} \equiv \chi_{22}{}^X/(\chi_{22}{}^X - \chi_{22}{}^x) = A(T - T_0), \tag{16}$$

$$(d_{25}a_{25})^{-1} \equiv \chi_{22}{}^x/(\chi_{22}{}^X - \chi_{22}{}^x) = A(T - T_c). \tag{17}$$

From the free energy F [Eq. (1)], the relations

$$k^{-2} = C^P(\chi^x)^{-1}/a^2, \tag{18}$$

$$(da)^{-1} = C^P(\chi^x)^{-1}/a^2 = C^E(\chi^x)^{-1}/a^2, \tag{19}$$

are derived. In both cases I and II, k^2 and da diverge (Fig. 1). Therefore, the experimental results (16) and (17) provide strong support that LAT is described by the free energy F_2 [Eq. (3)]. Furthermore, the temperature dependence of χ^X, χ^x, C^E, and C^P clearly shows that LAT belongs to case II.

So far many crystals have been reported to undergo the transition at which the elastic stiffness vanishes. In some crystals such as $TbVO_4$ [5] and Nb_3Sn,[6] the transition is known to take place primarily as a result of the Jahn-Teller instability; and because of the coupling between such mechanism and strain, the softening of the acoustic phonon is induced (that is, not "proper ferroelastic"). In some crystals such as TeO_2,[7] $PrAlO_3$[8] and $KH_3(SeO_3)_2$[9] it has been reported that the homogeneous strain is the sole order parameter for the transition. On the other hand, in the piezoelectric crystals such as the LAT under study here, the distinction between whether it is "proper ferroelastic" or not is very clear—constant χ^x and vanishing C^P constitute the sufficient conditions for the "proper ferroelastic" transition. This result and its implication do not appear to have been emphasized earlier.

One of the authors (M.U.) is grateful to Professor K. Kohn for his continual guidance and encouragements.

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Quadrupole Influence on the Dipolar-Field Width for a Single Interstitial in a Metal Crystal

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(Received 23 May 1977)

The dipolar broadening of the magnetic field sensed by an interstitial impurity in a rigid lattice is calculated with the electric-field gradient set up by the impurity taken into account. This is shown to give a strong dependence of the dipolar width on the applied magnetic field. The theory is especially applicable to the linewidth of precessing muons in metals.

The broadening, due to dipolar coupling, of magnetic resonance lines of nuclear spins I in solids was derived by Van Vleck[1] to be

$$\overline{\Delta\omega_I{}^2} = \tfrac{3}{4}\gamma_I{}^4\hbar^2 I(I+1)\sum\frac{(3\cos^2\theta - 1)^2}{r^6} \tag{1}$$

for the broadening due to like spins, and

$$\overline{\Delta\omega_I{}^2} = \tfrac{1}{3}\gamma_I{}^2\gamma_S{}^2\hbar^2 S(S+1)\sum\frac{(3\cos^2\theta - 1)^2}{r^6} \tag{2}$$

for the broadening due to unlike spins, i.e., gyromagnetic ratios $\gamma_I \neq \gamma_S$. The equations are valid if the spins are subject to a static magnetic field $B_0 = B_z$ substantially larger than the dipolar fields, which are typically of the order of 1 G for nuclear spins in solids.

In Eq. (2), spin-flip terms of the type I_+S_- are absent, and it can be considered as the random sum of the dipolar fields from all the spins S at