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Hypersonic studies in CsD_2AsO_4 and $\text{Cs}_{0.84}(\text{ND}_4)_{0.16}\text{D}_2\text{AsO}_4$ single crystals

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Abstract

The longitudinal (LA) Brillouin back-scattering spectra along the $[1\ 0\ 0]$ (a -axis) phonon direction have been measured as a function of temperature (80–300 K) for both CsD_2AsO_4 (DCDA) and $\text{Cs}_{0.84}(\text{ND}_4)_{0.16}\text{D}_2\text{AsO}_4$ (DCADA-0.16) single crystals. As the temperature decreases the acoustic phonon frequencies of both DCDA and DCADA-0.16 show a hardening (whose steepness is weaker in DCADA-0.16). A Landau–Khalatnikov-like maximum was observed in a pure crystal of DCDA and the polarization relaxation time is estimated to be $\tau \sim 2.0 \times 10^{-11}/T_c - T/s$, where $T_c \sim 206$ K is the ferroelectric transition temperature. In DCADA-0.16, the temperature-dependent frequency shift shows a gradually rising anomaly associated with a damping maximum near ~ 175 K. This phenomenon is attributed to coexistence of ferroelectric and paraelectric phases. © 1998 Elsevier Science B.V. All rights reserved.

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Keywords: Brillouin back-scattering; Mixed ferroelectric (FE)–antiferroelectric (AFE) crystals; Landau–Khalatnikov-like maximum; Polarization relaxation time

1. Introduction

The deuterated mixed ferroelectric (FE)-antiferroelectric (AFE) system $\text{Cs}_{1-x}(\text{ND}_4)_x\text{D}_2\text{AsO}_4$ (DCADA- x) belongs to the family of nonlinear materials with the general formula $\text{A}_{1-x}(\text{ND}_4)_x\text{D}_2\text{BO}_4$ ($A = \text{K}, \text{Rb}$ or Cs and $B = \text{P}$ or As) originating from KDP (KH_2PO_4)-type crys-

tals [1–5]. In this system, there is competition between ferroelectric and antiferroelectric orderings, each characterized by specific configurations of the acid deuterons. The random distribution of the K (or Rb, Cs) and ND_4 ions is the main cause of local structural fluctuations which can suppress long-range electric order. Therefore, instead of a typical FE or AFE phase transition, phase coexistence [such as FE/PE (paraelectric), AFE/PE, etc.] can be a characteristic of these mixed compounds. For instance, in $\text{Rb}_{0.9}(\text{ND}_4)_{0.1}\text{D}_2\text{AsO}_4$ the short-range antiferroelectric order due to the

freezing-in of the ND_4 reorientations can trigger a development of FE/PE phase coexistence [5].

KDP-type crystals (which contain two molecular units in a primitive unit cell) have a paraelectric (tetragonal structure)–ferroelectric (orthorhombic structure) phase transition with a change of symmetry $\bar{4}2m$ (space group $I\bar{4}2d-D_{2d}^{12}$)- $mm2$ (space group $Fdd2-C_{2v}^{19}$) [4]. The situation in the mixed system is more complicated than in the parent crystals, because some Rb (or Cs) ions have been substituted by ND_4 ions. For instance, $\text{Rb}_{1-x}(\text{ND}_4)_x\text{D}_2\text{PO}_4$ (DRADP- x) mixed crystals in the concentration range $0.3 \leq x \leq 0.7$ have tetragonal symmetry (space group $I\bar{4}2d-D_{2d}^{12}$) down to liquid-He temperature.

In principle, the acoustic coupling contributions include both static and dynamic effects. With decreasing temperature the dynamic coupling always produces a negative contribution (softening) to the real part of the complex elastic stiffness change Δc^* , but the static effect can have either sign depending on whether the phase transition is of first or second order. According to the Landau free-energy expansion with a single order parameter, a second-order transition gives a negative contribution in elastic stiffness change, but a first-order transition can give either a positive or negative contribution for both linear and quadratic couplings.

We report here the temperature dependences of acoustic phonon frequency and half-width (damping) for DCDA and DCADA-0.16 from 80 to 300 K. The polarization relaxation time is also estimated for a pure crystal of DCDA. In particular, direct evidence for acoustic phonon hardening behavior in both crystals is presented.

2. Experimental procedure

Single crystals of CsD_2AsO_4 and $\text{Cs}_{0.84}(\text{ND}_4)_{0.16}\text{D}_2\text{AsO}_4$ were grown from aqueous solutions of CsD_2AsO_4 and $\text{ND}_4\text{D}_2\text{AsO}_4$ (DADA). The ammonium concentration of DCADA-0.16 was determined using X-ray photoelectron spectroscopy (XPS). The Brillouin spectra were obtained from the back-scattering geometry with scattering configuration $X(Z, u)\bar{X}$, where “u”

means that the collection was not polarization discriminated. Here x and z correspond to the crystal a - and c -axis, respectively. The sample was illuminated along $[1\ 0\ 0]$ with an Innova 90 plus-A3 argon laser with $\lambda = 514.5$ nm (single line), so the longitudinal phonons with wave vector along $[1\ 0\ 0]$ were studied. According to the theoretical calculations for both point-group symmetries, $mm2$ and $\bar{4}2m$, there should be no transverse acoustic (TA) mode in the case of back-scattering due to the weak intensity factor [6]. Scattered light was analyzed by a Burleigh five-pass Fabry–Perot interferometer. To acquire accurate frequency shift and half-width data, the Brillouin doublets were adjusted to appear in the second order with respect to the Rayleigh line. The half-width of the laser line (for $\lambda = 514.5$ nm) is about 0.02 GHz determined by the spectrometer. The free spectral ranges of the Fabry–Perot interferometer were determined by measuring the LA phonon shift of fused quartz. The free spectral range was 18.96 GHz for the DCDA spectra and 18.99 GHz for the DCADA-0.16 spectra. The laser power incident on the samples was kept less than 120 mW. A Janis VPF-100 variable temperature pourfill cryostat was used with a LakeShore Model 321 temperature controller. The samples were heated from 80 K to room temperature by steps.

In order to determine the position and half-width of the Brillouin component, the damped harmonic oscillator model with the spectral response function [7],

$$S(\omega) = \frac{\chi_0 \Gamma \omega \omega_0^2}{(\omega^2 - \omega_0^2)^2 + \Gamma^2 \omega^2} \frac{1}{1 - e^{-\hbar\omega/kT}}, \quad (1)$$

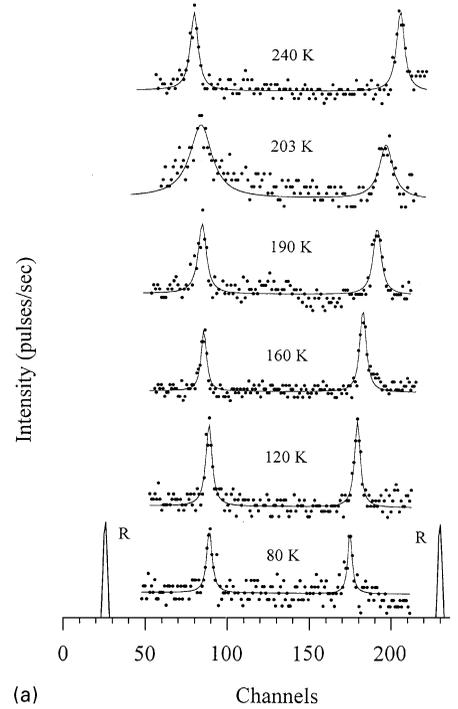
was used, where ω_0 and $\Gamma (= \Gamma_{\text{obs}})$ correspond to the phonon frequency and observed half-width, respectively, χ_0 is the susceptibility constant (in arbitrary units), k is Boltzmann’s constant and T is absolute temperature. For back-scattering, the broadening due to collection optics is negligible [5]. In this case, the natural-phonon half-width Γ_{ph} is given by $\Gamma_{\text{ph}} = \Gamma_{\text{obs}} - \Gamma_{\text{ins}}$ [5]. In our experiments, the half-widths of the Rayleigh line from fused quartz (which was assumed to have Gaussian distribution) was taken as the instrumental broadening $\Gamma_{\text{inst}} \sim 0.007$ FSR.

3. Results and discussion

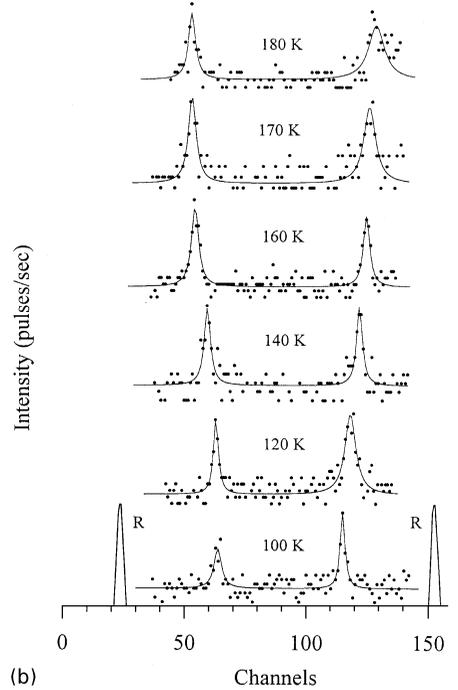
Actual temperature-dependent LA[1 0 0] phonon spectra of both anti-Stokes and Stokes Brillouin components are shown in Fig. 1a and b for DCDA and DCADA-0.16, respectively. The solid lines are fits of Eq. (1) from which the phonon frequency and half-width Γ_{obs} were obtained. Fig. 2a and b show the temperature dependences of the frequency shift and half-width Γ_{ph} for DCDA and DCADA-0.16, respectively.

As the temperature decreases, DCDA shows a discontinuous change in frequency shift near T_c associated with a sharp damping peak at $T \sim 203$ K. If the phase transition were second order, the phonon frequency should show a continuous variation as $T \rightarrow T_c^\pm$ like other ferroelectric crystals TGS (triglycine sulfate) and TSCC (tris-sarcosine calcium chloride) [8,9]. Thus, such an abrupt behavior in frequency confirms that DCDA possesses a first-order structural transition. This behavior is consistent with the results obtained from its isomorphous crystals (such as KD_2PO_4 and RbD_2AsO_4 in which a first-order phase transition has been observed) [10,11]. A compilation of parameters for KDP-type crystals gives $T_c - T_0 = 1.3$ K for DCDA, and shows that both the arsenate and deuteron substitutions increase the first-order nature of the transitions. In this family, only RbH_2PO_4 has a second-order transition [12]. A sharp damping maximum for longitudinal acoustic phonons can be connected with the Landau-Khalatnikov relaxation-type mechanism which is the characteristic of a linear $\eta\mu$ -type piezoelectric coupling [10]. Here, η is the order parameter and μ is the strain. In fact, because of the symmetries of the order parameter η and strain μ , a linear $\eta\mu$ -type coupling is allowed for KDP-type crystals as evidenced [10].

In the neighborhood of transition temperature T_c , both the magnitude and the relaxation time of

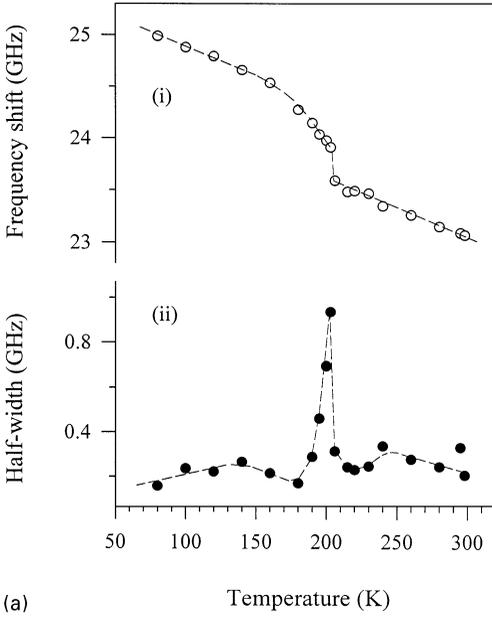


(a)

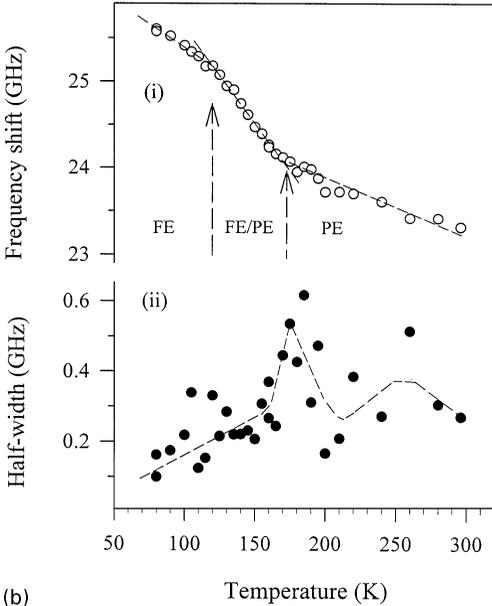


(b)

Fig. 1. Both Stokes and anti-Stokes Brillouin components of the LA[1 0 0] phonon frequency shift for (a) DCDA and (b) DCADA-0.16. The solid lines are fits to Eq. (1). The “R” indicates the position of the Rayleigh line. Here, the GHz/channel ratio is ~ 0.092 for the DCDA spectra and ~ 0.146 for the DCADA-0.16 spectra.



(a)



(b)

Fig. 2. (i) Frequency shift (open circles) and (ii) half-width Γ_{ph} (solid circles) versus temperature of the LA[1 0 0] phonons for (a) DCDA and (b) DCADA-0.16. The dashed lines are guides for the eye. The arrow-headed dashed lines are the estimates of various phase boundaries.

fluctuations in the order parameter (spontaneous polarization) become very large. According to Landau and Khalatnikov, the relaxation time τ is given by $\tau = A|T_c - T|^{-1}$ s [9]. Thus, if phonons couple to polarization linearly (i.e. a linear $\eta\mu$ -type piezoelectric coupling) [10], a temperature-dependent relaxation (in which a single relaxation time was assumed) is expected, which will produce a dispersion in the phonon velocity associated with a sharp Landau–Khalatnikov maximum in the attenuation coefficient, i.e. [8,9]

$$V^2 = V_\infty^2 - \frac{V_\infty^2 - V_0^2}{1 + \omega^2 \tau_0^2 t^{-2}}, \quad (2)$$

$$\alpha = \frac{\omega^2 \tau_0 t^{-1}}{2V^3} \frac{V_\infty^2 - V_0^2}{1 + \omega^2 \tau_0^2 t^{-2}}, \quad (3)$$

where $t = |T_c - T|/T_c$ is the reduced temperature, and τ_0 is the elementary individual-dipole relaxation time in the expression $\tau = \tau_0 t^{-1}$ for the relaxation time τ . The velocities V_∞ and V_0 designate the high- and low-frequency limit velocities, respectively. From Eq. (2) we can notice that there is an abrupt change (either up or down) in the velocity as $T \rightarrow T_c^\pm$. The relation between the phonon decay rate Γ or the Brillouin phonon half-width and the attenuation α is $\Gamma = \alpha V$. By using Eqs. (2) and (3), and $d\Gamma/dT|_{T=T_m} = 0$ with the approximation $V_\infty/V_0 \approx 1$ [13], one can obtain the relation

$$\omega \tau_0 \approx \frac{T_c - T_m}{T_c}. \quad (4)$$

From this relation we can estimate the elementary relaxation time τ_0 . Here, $T_m \sim 203$ K is the temperature at which the half-width is maximum and the FE transition temperature $T_c \sim 206$ K is defined as the point at which the frequency shift curve is steepest. For the LA[1 0 0] phonons of DCDA, we obtain the following results:

$$T_c - T_m \approx 3 \text{ K}, \quad \tau_0 \approx 1.0 \times 10^{-13} \text{ s},$$

$$\tau \approx \frac{2.0 \times 10^{-11}}{T_c - T} \text{ s}.$$

The elementary dipole relaxation time τ_0 obtained from the LA[1 0 0] phonons of DCDA is close to those of other order–disorder ferroelectrics. For instance, τ_0 is $\sim 1.2 \times 10^{-13}$ s for potassium

dihydrogen phosphate KDP and $\sim 1.3 \times 10^{-13}$ s for deuterated potassium dihydrogen phosphate KD_2PO_4 (DKDP) [8].

Instead of a sharp peak (Landau–Khalatnikov-like maximum), DCADA-0.16 exhibits a broader damping peak (shown in Fig. 2b), associated with a slowly rising frequency shift with decreasing temperature. Such a broad damping maximum is due partly to the transition being spread from 120 to 175 K, but the persistence of this maximum above 175 K indicates that fluctuations are the dominant dynamic mechanism. A qualitative estimate of the fluctuation contribution is given by the dashed curve in Fig. 2b with maximum near 175 K. The order-parameter fluctuations for longitudinal acoustic phonons are usually characteristic of an $\eta^2\mu$ -type electrostrictive coupling, squared in order parameter and linear in strain [10]. In the earlier Brillouin results for the $\text{Rb}_{1-x}(\text{ND}_4)_x\text{D}_2\text{AsO}_4$ (DRADA- x) system, the phonon frequencies of DRADA-0.10 and 0.28 showed a gradually rising anomaly associated with a broad damping peak which was attributed to the onset of PE/FE phase coexistence in DRADA-0.10 [5]. Thus, one can expect that the local structural competition between long-range FE and short-range AFE orderings is the origin of the strong broad damping anomaly (centered near 175 K) in DCADA-0.16. In other words, the damping maximum (near 175 K) is associated with the onset of short-range antiferroelectric order due to the freezing-in of the ND_4 reorientations associated with the development of PE/FE phase coexistence. In DCADA-0.16 the frequency jump seen at ~ 200 K in DCDA is replaced by a rapid but continuous increase as temperature drops from 175 to ~ 120 K. This is consistent with the rapid but continuous increase in spontaneous polarization P_s and decrease in a -axis permittivity ϵ_a seen in DRADA-0.08 and $\text{Rb}_{0.92}(\text{NH}_4)_{0.08}\text{H}_2\text{AsO}_4$ (RADA-0.08) [14], and the decrease in ϵ_a seen in $\text{Rb}_{0.88}(\text{NH}_4)_{0.12}\text{H}_2\text{AsO}_4$ (RADA-0.12) [15]. These behaviors were attributed to PE/FE phase coexistence. We conclude that in DCADA-0.16 a PE/FE phase coexistence begins to build up at ~ 175 K and below ~ 120 K (where the phonon frequency exhibits a different slope) the crystal transformation into the FE phase ceases as indicated in Fig. 2b). Whether the transformation is

complete is a question. In DRADA, an x at or slightly below 0.08 is required for complete transformation to the FE phase [14].

4. Conclusions

From the temperature dependences of phonon frequency and damping in DCDA and DCADA-0.16, we conclude qualitatively that order-parameter fluctuations grow and become the major dynamic damping mechanism as ND_4 concentration increases. By comparing with the earlier results of DRADA-0.10 and 0.28, a conclusion was reached for DCADA-0.16 that the PF/FE phase coexistence starts to evolve near 175 K associated with a broad damping maximum. A sharp Landau–Khalatnikov-like damping maximum with a step-up configuration in frequency shift was observed in pure crystal DCDA whose polarization relaxation time was also estimated.

Another main feature of the acoustic phonon spectra in DCADA ($x = 0$ and 0.16) for LA[1 0 0] phonons is that the frequency shift shows a positive coupling (hardening). The sign of the coupling contribution may be related to the temperature response of the lattice parameter $a(T)$. A smaller lattice constant is usually associated with a stiffer interatomic force constant and implies a contraction Δa which could lead to the LA[1 0 0] phonon hardening.

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