Optical soft mode in ferroelectric RbH_2AsO_4

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A Raman-scattering study of the optical coupled soft mode in $R_bH_2AsO_4$ is reported. It was found that in the temperature range 110–220 K the soft mode frequency has the behavior $\omega_1^2 = 29.5\ \mathrm{cm}^{-2}/\mathrm{K}$ (T-91 K). Therefore, there is a large gap between the temperature at which ω extrapolates to zero (91 K) and the transition temperature of the mechanically free crystal ($T_c = 110$ K). We predict that 91 K is the transition temperature of the mechanically clamped crystal, not yet measured, and that the large gap between these temperatures is the result of unusually large coupling between the optical soft mode and the shear xy acoustic mode. [S0163-1829(97)06934-8]

I. INTRODUCTION AND THEORETICAL REVIEW

The behavior of the optical soft mode in the ferroelectric crystals of the potassium dihydrogen phosphate (KDP) family has been very controversial and is not satisfactorily established, although several investigations were performed on the subject.[1–5] The optical soft mode is a coupled mode of symmetry B_2 which transforms, under the D_{2d} symmetry of the paraelectric phase, as z and also as xy. The atomic motions involved in the coupled mode are a correlated tunneling of the proton system (lowest mode) and a displacement of the heavy ions along the z axis. The double (vectorial and tensorial) character of the soft mode is a consequence of the fact that D_{2d} is a piezoelectric point group. This brings a new complication to the problem: the coupled optical soft mode also couples with the shear (xy) acoustic mode, resulting in a phase transition at T_c which is both ferroelectric and ferroelastic. It is well known that KDP presents a purely ferroelectric phase transition at a temperature T_c^x below T_c, when mechanically clamped to prevent the ferroelastic shear. This means that the crystal is a primary ferroelectric and a secondary ferroelastic. In a Landau theory of phase transitions in which critical fluctuations of the soft modes are neglected, the phase transitions can be described by the Gibbs free energy density expansion

$$G = G_0 + \frac{1}{2}(C^x)^{-1}(T - T_c^x)P^2 + \frac{1}{4}bP^4 + \frac{1}{2}C_{66}^p X_6^2 - h_{36}PX_6, \tag{1}$$

where C^x is the Curie constant for the mechanically clamped crystal, C_{66}^p is the shear elastic stiffness, and h_{36} is a piezoelectric coefficient.

Under zero electric field external bias the crystal presents phase transitions at T_c^x if mechanically clamped and at $T_c^x + C^x h_{36}^2 / C_{66}^p$ if mechanically free. The piezoelectric coupling produces a repulsion between the acoustic and optical modes near the center of the Brillouin zone. That is very important for the acoustic mode, owing to its low frequency, but the frequency displacement is relatively very small for the optical mode. The behavior of the optical soft mode is therefore almost independent of the clamping and its frequency varies as $\omega_s^2 \propto (T - T_c^x)$. Consequently, in a mechanically free crystal there is a temperature gap between the point at which the acoustic soft mode frequency goes to zero and the point at which the optical soft mode frequency extrapolates to zero.[6]

The phenomenon of critical fluctuations of optical and acoustic soft modes presumably gives origin to new complications. These fluctuations manifest in the system susceptibilities as the so called (intrinsic) central peak (CP), discovered[7] and intensively investigated in the 1970s. One possible consequence of the CP dynamics is that the soft modes slowing down saturates and their frequencies near the phase transition is higher than the predictions of the Landau theory. Lagakos and Cummins[4] investigated KDP and found that the optical soft mode behaves as predicted by the Landau theory, at least for $T \geqslant 132.5$ K. This should be compared with $T_c^x = 117.7$ K and $T_c = 122$ K. Scarparo *et al.*[5] investigated KDP, RDP, and RDA and found marked deviations from the classical soft mode picture, mainly for RDP and

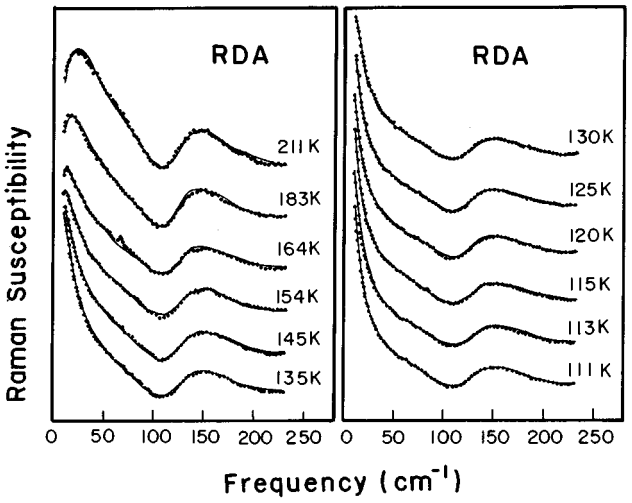

FIG. 1. Raman susceptibility of the coupled mode. The scattering configuration is $X(YX)Y$. The solid lines are best fit with formula (3). The fitting parameters are ω_1, γ_{12}, P_1, P_2. The parameters ω_1, γ_2 are fixed as explained in the text.

KDP. A recent microscopic theory of soft mode dynamics in the KDP family[8] produced predictions similar to the observations by Scarparo *et al.* That stimulates us to make experiments on this subject, which are here reported for the compound RDA.

The Raman spectra, in the configuration $X(YX)Y$ were measured by using the Dilor model XY triple spectrometer. The first two monochromators are arranged in a subtractive configuration and the light dispersed by the third monochromator is detected by an array of silicon diodes. The contrast of this spectrometer is much higher than that of the Spex double spectrometer used in the previous experiments. This allows more precise measurements of the low frequency Raman scattering and therefore makes possible improved experiments of the soft mode near the phase transition. A large crystal (1 cm×1 cm×1 cm) of optical quality, cooled in a cold finger cryostat, was used for the measurements. The temperature stability was better than 0.1 K and the precision of the reading, done at the cooper basis on which the crystal was mounted, was better than 0.3 K. The crystal was optically excited by the 514.5 nm line of an argon laser. The laser power was 200 mW and a spherical lens produced a focus of about 200 μm diameter inside the crystal. The laser heating of the crystal, as diagnosticated by the reading of the phase transition temperature, was about 2 K. We corrected our readings by this value, neglecting the probable fact that the heating changes with the crystal temperature.

The spectra are shown in Fig. 1. The solid lines are the theoretical fit with the linear coupled modes model. Following Katiyar *et al.*,[3] the coupled mode response function is taken as

$$\begin{pmatrix} \omega_1^2-\omega^2-i\omega\gamma_1 & -i\omega\gamma_{12} \\ -i\omega\gamma_{12} & \omega_2^2-\omega^2-i\omega\gamma_2 \end{pmatrix}\begin{pmatrix} G_{11} & G_{12} \\ G_{12} & G_{22} \end{pmatrix}=\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{2}$$

The Raman susceptibility of the system is

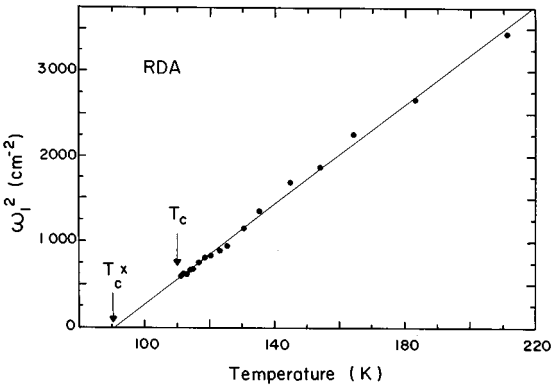

FIG. 2. Temperature variation of the soft mode ω_1. It is suggested that the temperature at which ω_1^2 extrapolates to zero is the transition temperature T_c^x of the mechanically clamped crystal.

$$\chi''(\omega)=\mathrm{Im}\sum_{ij} P_iP_jG_{ij}(\omega), \tag{3}$$

where P_i are optical coupling amplitudes. The Raman stokes intensity is

$$I(\omega)=[n(\omega)+1]\chi''(\omega),$$

where $n(\omega)$ is the Bose-Einstein factor.

The mode coupling in the expression for the susceptibility, Eq. (2), is taken as imaginary. That is because, as already discussed by Lagakos and Cummins,[4] at zero frequency the imaginary coupling disappears and consequently the temperature at which ω_1 extrapolates to zero is the same as that where $\chi'(0)$ diverges. This happens because as $\omega_1\to 0$, $\omega_p\to\omega_1$, where ω_p is the pole of $G_{ij}(\omega)$with smaller modulus.

II. RESULTS AND DISCUSSION

The Raman susceptibilities, as obtained from the Raman Stokes spectra, are shown in Fig. 1. The solid lines are best fits with the formula in Eq. (3). In the fitting procedure, we first allowed all the constants ω_1, γ_1, ω_2, γ_2, P_1, P_2 to vary as free fitting parameters. As there is considerable correlation between these parameters, this results in undesirable dispersion of the best fitting parameters. As it was easily recognized that ω_2 fluctuated around a fixed value as the temperature varied and γ_2 fluctuated around a straight line $\gamma_2=a+bT$, where b is very small, we did not allow the free variation of these two parameters. The result was a reduced dispersion of the other parameters without any noticeable deviation from the previous fittings. From Fig. 1 one notices that there is a systematic small deviation between the data and theory in the region near 100 cm^{-1}. That does not improve if we allow ω_2 and γ_2 to vary freely and should be taken as intrinsic limitation of the too-simple linear coupled oscillators model.

The temperature variation of the coupled mode parameters ω_1, γ_1, ω_2, γ_2, γ_{12} is shown in Figs. 2 and 3. As seen in Fig. 2, the obtained values of ω_1^2 fall around a straight line. The solid line is a fit with the formula $\omega_1^2=A(T-T_c^x)$. The value of T_c^x is 91 K, but a good fitting could also be obtained for any T_c^x in the range $T_c^x=(91$

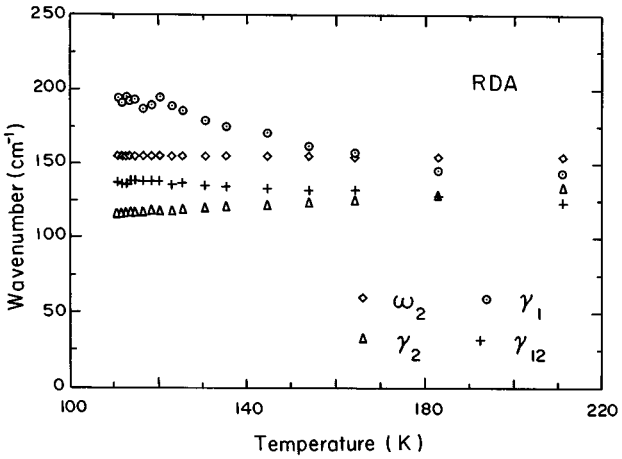

FIG. 3. Temperature variation of the parameters γ_1, ω_2, γ_2, γ_{12}.

± 2) K. Our results suggest an interpretation which is very distinct from that drawn by Scarparo *et al.*:[5] RDA seems to fit nicely in the classical Landau theory in which the critical fluctuations of the order parameter are neglected and in the closely related soft mode theory by Anderson[9] and Cochran.[10] However, apparently a very large coupling between the optical coupled mode and the acoustic mode creates a large gap between the clamped (T_c^x) and free (T_c) transition temperatures. Consequently, at the free-crystal transition temperature T_c the soft mode has a frequency $\omega_1 = (24 \pm 0.5)$ cm^{-1} which suggests (in our view, incorrectly) a hard core induced by the crystal dynamics. One should also notice that the theory drawn by Kokshenev and Chaves[8] is also not in agreement with our observations on the soft mode frequency ω_1. However, the linewidth γ_1 of the soft mode is shown in Fig. 3 to increase as we approach T_c and that is in agreement with the predictions of Kokshenev and Chaves. It should be noticed that the coupling with the acoustic mode in fact prevents the soft optical mode from entering in the truly critical region. This could be the reason for the deviation in the behavior of the soft mode frequency and for the fact that the predicted sudden decrease of $\gamma_1$very near T_c was not observed.

The gap between the two principal transition temperatures is $T_c - T_c^x = C^x h_{36}^2 / C_{66}^p$, and consequently can be obtained based on electric, elastic, and piezoelectric properties. Unfortunately, the values of the coefficients involved in the above expression are not available in the literature and hence the consistency of the Landau theory could not be checked. The constant A in the relation $\omega_1^2 = A(T - T_c^x)$ is 42.75 cm^{-2}/K for KDP (Ref. 4) and 29.5 cm^{-1}/K in RDA. This can partially explain the difference in the temperature gap, which is 4.3 K for KDP and 19 K for RDA, because the larger the value of A, the smaller is the Curie constant.

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