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Dynamic Central Peaks in a Crystalline Solid: $KTaO_3$

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Use of a computer-assisted normalization procedure and a resonant reabsorption technique has permitted frequency resolution of two central peaks in the quasielastic-light-scattering spectrum of $KTaO_3$ in the 0 to 3 cm^{-1} range. The intensities, and the polarization, temperature, electric field, and angular dependences of the linewidths indicate that the narrow component (2.3 ± 0.3 GHz at 300 K in right-angle scattering) is due to entropy fluctuations. A tentative identification of the broader component with two-phonon processes is made.

Over the past five years the existence and nature of quasielastic features (central peaks) in neutron- and light-scattering spectra of solids has generated considerable interest. Most attention has been paid to the possible role of central peaks in structural phase transitions.[1] To date such features in neutron experiments[2] and optical studies[3] have defied unambiguous spectral resolution or have been obscured by elastic-scattering or stray-light effects. The theoretical difficulty in accounting for dynamic processes in solids of sufficiently low frequency to escape spectral linewidth measurement has left open the possibility that central peaks in solids may be neither dynamic nor intrinsic to the crystal lattice. In this paper we report the first observation and spectral resolution of two kinds of central peaks in the quasielastic spectra of light scattered from crystalline solids in the frequency regime of interest in structural phase transitions. Our experimental technique permits detailed examination of weak spectral features beyond ± 500 MHz from the exciting laser frequency. Although both the linewidth and intensities of the central peaks exhibit considerable temperature dependence between 20 and 300 K, we find no evidence of divergent behavior for either feature upon approaching the ferroelectric or antiferroelectric structural transitions in the perovskites $KTaO_3$ and $SrTiO_3$. The observed results are essentially identical in the two materials. Because it remains in the simple perovskite structure ($O_h^{\,1}$) throughout the temperature range studied, and therefore has simpler lattice dynamics, the results in $KTaO_3$ will be emphasized here.

The spectra were excited by 150 mW of 5145-Å radiation from a single-mode Ar^+ laser. The data were obtained using a tandem Fabry-Perot interferometer with a resolution of 2 GHz and an effective free spectral range of 690 GHz (30 GHz $= 1\ cm^{-1}$). The 5145-Å radiation allowed the use of a molecular-iodine resonant absorption cell to remove light elastically scattered by sample imperfections. The apparatus is described elsewhere[4] as is the digital normalization technique[5] employed to remove the structure introduced into the spectrum by I_2 absorptions in the vicinity of the 5145-Å line. For the present purposes the important feature of this technique is that quantitative line-shape information may be obtained despite the strong subsidiary structure introduced by the use of the I_2 cell when operated at high peak attenuation ($> 10^7$).

Typical normalized spectra are shown in Fig. 1,

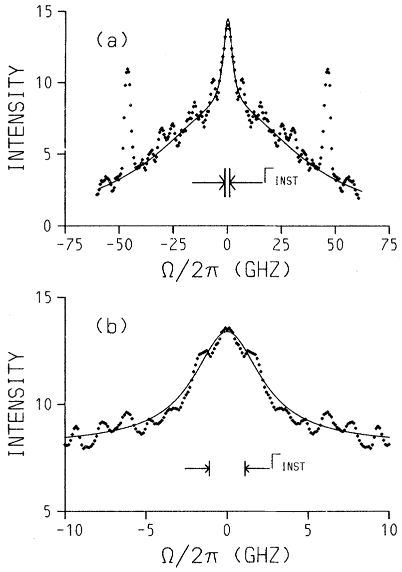

FIG. 1. (a) The polarized quasielastic spectrum of $KTaO_3$ taken at 182 K ($\theta = 90°$). The line represents a sum of two Lorentzians of full width at half-maximum 5.0 and 80.0 GHz, respectively. The LA Brillouin components appear at ± 47.5 GHz. (b) A more detailed spectrum of the narrow central component obtained at 300 K ($\theta = 135°$). The line represents a single Lorentzian of deconvolved width 3.0 GHz.

consisting of two features centered at zero frequency. The normalization procedure includes symmetrization, as shown in the figure. With the resolution evident in Fig. 1(a), the linewidth of the narrow component is insensitive to temperature, while the corresponding intensity decreases as the temperature is lowered. At room temperature, the deconvolved width (full width at half-maximum) of this feature [Fig. 1(b)] is 3.0 ±0.3 GHz in $KTaO_3$ for scattering angle θ of 135°. Within experimental error the linewidth and integrated intensity of the broad component (108 GHz at room temperature) vary linearly with temperature over the range 20–300 K, as shown in Fig. 2. Both components are observed to be strongly polarized. As is evident in Fig. 1(a), the fact that the Brillouin peaks are narrow with respect to the resolution of the instrument limits the accuracy of the normalization of their intensities.[5] However, the transmission of the I_2 cell for a *broad spectrum*, such as the central peaks seen here, is measurable. Using this information we find that the integrated intensity of the narrow component is about 0.06±0.03 that of the LA Brillouin peaks combined.

The most likely mechanism for the narrow component (Γ_n) is scattering from entropy fluctuations. As is well known, the linewidth of this Rayleigh scattering is given by $\Gamma_n = 2D_{\mathrm{th}}q^2$, where $D_{\mathrm{th}} = \Lambda/\rho C_p$ is the thermal diffusivity, Λ is the heat conductivity, C_p is the specific heat, and $q = (2\pi n/\lambda)\sin(\theta/2)$. For $KTaO_3$ the parameters are[6] $n = 2.3$, $\rho = 6.97$ g cm^{-3}; the room-temperature thermal conductivity[7] is $\Lambda = 0.15 \pm 0.01$ W/cm K, and from data on other perovskites[6] we may estimate $C_p \sim 25 \pm 3$ cal-mol K. We calculate $D_{\mathrm{th}} = 0.056$ cm^2 sec^{-1}. For right-angle scattering ($\theta = 90°$) this gives a calculated width of 2.8 ± 0.5 GHz, in good agreement with that observed (2.3 ± 0.3 GHz). A crucial test of this interpretation lies in the q^2 dependence of the linewidth. The linewidth of the central component was measured in more detail [spectra as in Fig. 1(b)] at scattering angles θ of 45°, 90°, and 135°. The results are shown in Fig. 3 where the line is drawn for $D_{\mathrm{th}} = 0.046$ cm^2 sec^{-1}, the best fit to the data. Clearly the interpretation of this peak as due to scattering from entropy fluctuations is well substantiated by both the magnitude of the linewidth and its q dependence.

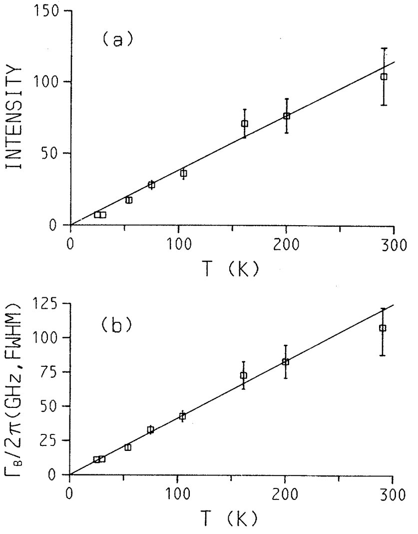

FIG. 2. (a) Integrated intensity of the broad central component in $KTaO_3$ as a function of temperature. (b) The linewidth of the broad component as a function of temperature.

In the approximation usually applied to liquids, the intensity we observe is anomalously high. The expected intensity of the entropy-fluctuation scattering may be obtained from thermodynamics as the ratio of the weight in the central component to that in the LA Brillouin peaks. For liquids this is accurately given by the Landau-Pla-

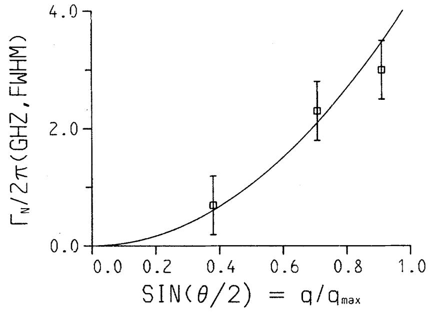

FIG. 3. Angular dependence of the narrow-component linewidth in the $KTaO_3$ at room temperature. The line $\Gamma_n = 2D_{th}q^2$ is drawn for $D_{th} = 0.046$ cm^2 sec^1 and $q_{max} = 5.44\times 10^5$ cm^{-1}.

cek ratio $I_c/2I_B = \alpha^2 T/\rho C_p \beta_s = R_{LP}$, where α is the thermal expansivity and β_s is the compressibility. This gives a value of $R_{LP} \leq 0.005$ for $KTaO_3$ at room temperature, far less than we observe. The approximation involved here ignores the explicit dependence of the dielectric susceptibility on temperature, $(\partial\epsilon/\partial T)_\rho$. While this is valid in liquids and plastic crystals,[8] it fails severely in crystalline solids. The exact thermodynamic result is[9]

$$\frac{I_c}{2I_B} = R_{LP}\left[\frac{(\partial\epsilon/\partial T)_p}{\alpha\rho(\partial\epsilon/\partial\rho)_s}\right]^2 . \qquad (1)$$

While all the data necessary to evaluate the right-hand side of Eq. (1) are not available for $KTaO_3$, they are for $SrTiO_3$. Klein and Wehner[10] have estimated an enhancement of R_{LP} for $SrTiO_3$ by a factor of 16. Given the reasonable prospect that the enhancement for $KTaO_3$ is similar, we estimate $I_c/2I_B \sim 0.08$ which is in good agreement with experiment. Thus, the observed intensity provides additional evidence that the narrow peak is due to entropy fluctuations.

We now consider the broad peak. The most striking aspect of its behavior is the temperature dependence of the linewidth, $\Gamma_B/2\pi$, shown in Fig. 2(b). This linewidth exhibits no q dependence. No aspect of the spectrum was found to vary with applied electric field, even at 25 K and 8 KV/cm—conditions under which the frequency and Raman scattering strength of the soft ferroelectric mode are strongly influenced.[11] Thus the soft TO-ferroelectric mode plays no significant role in this spectrum.

Our identification of the mechanism for this central peak is at this stage speculative. Recent suggestions of mobile-defect-induced scattering[12] could produce a central peak whose linewidth lies in the observed range. However, the observed linear temperature dependence of Γ_B and the fact that identical experimental spectra are obtained in samples of different origin, prepared by different techniques, argue against this explanation. A second possibility—that the broad component is a wing on the entropy-fluctuation scattering caused by frequency dependence of C_p, or Λ, etc.—would require severe relaxation of the thermodynamic parameters in the 10–100 GHz range, and has difficulty accounting for the much larger scattered intensity in the broad component than in the narrow one.

A more attractive possibility is that the broad peak arises from a higher-order process involving pairs of phonons. Such a process, described as "phonon density fluctuations," has been postulated theoretically[10] but never definitively observed. It may be more simply viewed as two-phonon difference Raman scattering, arising from simultaneous creation of a phonon at ω, k and destruction of a phonon at $\omega+\Omega, -k+q$ on the same branch. The resulting spectral line shape would be determined by the weighted Brillouin-zone averages of the phonon group velocities and the k-dependent linewidths. Since we see no evidence for splitting of this component, the contribution from the phonon dispersion must be small compared to the linewidth contribution. For example an undamped dispersionless branch, $\omega(k) = \omega_0$, would contribute a spectral δ function at $\Omega = 0$, with a temperature-dependent intensity varying in the simplest case as $n(\omega_0)[n(\omega_0)+1]$, where n is the phonon occupation number. The corresponding two-phonon *sum* processes dominate the familiar second-order Raman spectrum,[13] which is particularly strong in $KTaO_3$ and which exhibits quite a narrow peak at 123 cm^{-1}. This feature has been attributed to two phonons from the very low-frequency TA branch which is quite flat over most of the Brillouin zone[14] in $KTaO_3$ and whose zone-boundary frequency is ~ 62 cm^{-1}. The intensity of the difference process from this branch would drop sharply for $T < \hbar\omega_{TA}/k_B = 90$ K, and should approach a quadratic temperature dependence at higher temperatures. The facts that such behavior is not observed and that the TA-phonon linewidth is not known for large k preclude a definitive assignment of this mechanism without further experimental and theoretical work. For example, the possibility of interactions between members of the phonon pairs remains to be considered quantitatively.

In summary we have shown experimentally that the light-scattering spectra of the crystalline solids $KTaO_3$ and $SrTiO_3$ exhibit two temperature-dependent dynamic central pekas. Neither behaves in a singular manner upon approach to the known structural phase transitions in these materials. The narrower peak is rather firmly established as due to scattering from entropy fluctuations, with an expected but previously unobserved enhancement due to the direct temperature dependence of the polarizability at constant density. The broader peak exhibits a strongly temperature-dependent linewidth and is tentatively identified as arising from two-phonon processes. What connection, if any, these dynamic central peaks have with the frequently reported unresolved central peaks in phase-transition studies is now being explored in other crystals.

We are grateful to P. C. Hohenberg for helpful discussions and to H. L. Carter for assistance in various phases of the experiment.

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Formation of the Upper Hubbard Band from Negative-Donor-Ion States in Silicon

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The spectral response from shallow negative donor ions in silicon has been studied over a range of donor concentrations between 1×10^{14} and 1×10^{17} cm^{-3}. At low donor concentrations the binding energy of the negative-ion state is well described by the effective-mass theory. The formation of the upper Hubbard band out of these states is observed at a donor concentration of 3×10^{15} cm^{-3}—about three orders of magnitude lower than the concentration at which the metal-insulator transition occurs in this material.

In this Letter I would like to report the first experimental observation of the onset of formation of the upper Hubbard band in an impurity-doped semiconductor. The upper and lower Hubbard bands are formed out of impurity-state wave functions when the concentration of impurities in the material is sufficient to produce a critical overlap of the wave functions from adjacent impurity atoms. The familiar metal-insulator transition in these materials occurs at still higher concentrations when the upper and lower Hubbard bands overlap each other,[1] giving a continuous spectrum of unoccupied states in which the impurity electrons can move. Transitions between the upper and lower Hubbard bands have been observed previously, for example in the hopping-conductivity activation energy ϵ_2,[2] and in optical absorption and photoconductivity[3] resulting from excitation