Nature of the Central-Peak Light Scattering in Potassium Dihydrogen Phosphate*

L. N. Durvasula and Robert W. Gammon
Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742
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The divergent intensity of the central peak observed in Brillouin scattering spectra in potassium dihydrogen phosphate has been studied in the paraelectric phase and found to be *VH* polarized and to show "speckle" interference fringes. This implies that the scattering centers have time-independent amplitudes and positions. Photographs of the scattering column at different temperatures near the phase transition show that the scattering-center configuration is temperature independent.

The soft-mode description of the structural phase transitions in ferroelectrics has been reexamined in recent years after the discovery of an extremely narrow quasielastic component, whose intensity diverges as the transition is approached in neutron and light scattering experiments on potassium dihydrogen phosphate[1] (KDP) and strontium titanate.[2,3] This additional structure in the low-frequency scattering spectrum was called the "central peak." Several theoretical models[4] were proposed to explain the central peaks and their role in structural phase transitions. The width of the central peaks predicted by these models varied by three orders of magnitude, i.e., 10^9 to 10^{12} Hz. So far the experimental studies of neutron and light scattering have failed to measure finite widths for the central peaks in the predicted range.

A possible explanation for the narrow widths of central peaks is that they have a nondynamic origin. Axe, Shapiro, Shirane, and Riste[5] suggested that the scattering is due to the temperature-dependent static distortion field surrounding the impurities or defects. Halperin and Varma[6] also considered the effect of defects on the central peak, classifying the defects into relaxing and frozen types. The mobile-defect case leads to a central peak whose width is determined by the time scale of hopping between positions which break the symmetry locally, while the frozen-defect case gives elastic scattering with a central peak of zero width.

A static description was previously used by Shapiro and Cummins[7] in discussing the critical opalescence of quartz near the α-β transition based on the observation of a granular or speckle interference pattern in the scattering column illuminated by laser light. The speckle interference pattern[8] is the grainy appearance of an area when illuminated by coherent laser light. This appearance results from constructive and destructive interference of light scattered with random fixed phase from defects or impurities with fixed spatial configurations. The graininess of the speckle interference pattern depends on the numerical aperture of the viewing system. If the amplitude and the spatial position of the scattering centers change with time the scattering column appears continuous and the scattering is dynamic. If the speckle interference pattern is static the scattering giving the speckle interference is purely static.

In this Letter we report the results on the appearance of the scattering column and measurements of the temperature dependence and polarization properties of the central-peak intensity near the transition temperature in KDP.

The apparatus consisting of a light scattering Dewar and the Fabry-Perot spectrometer is described elsewhere.[9] A y $-45°$ cut 10-mm cube of KDP was purchased from Quantum Technology Ltd.[10] Incident laser light, a single frequency at 5145 Å from a Spectra-Physics 165-3 argon ion laser, was along [101] and scattered light was along $[\bar{1}01]$ so that the scattered wave vector was along [100]. With polarization for incident light perpendicular to the scattering plane, the scattered light can be observed with polarization perpendicular to the scattering plane called *VV* spectra or polarization in the scattering plane called *VH* spectra. The temperature resolution was ± 0.001 K near the transition temperature.

A visual observation of the scattering column less than 1 K above the transition temperature, looking through the collecting lens with a telescope, showed a speckle interference pattern. This is in marked contrast to the observation reported by Lagakos and Cummins[1,11] that they saw a spatially uniform scattering column. As the transition temperature is approached, the scattering giving the speckle interference pattern increased strongly. When the scattering column

was viewed in the *VH* polarization, the scattering giving the speckle interference pattern was dominant. In the *VV* polarization, the scattering giving the speckle interference pattern disappears completely and only the visible inclusions appear. This shows that the scattering giving the speckle interference pattern is *VH* polarized like the x-y shear acoustic mode that softens as the transition temperature is approached.

We have photographed the speckle interference pattern in the scattering column near the transition temperature before and after the Fabry-Perot interferometer with a fine-grain film (Kodak Panatomic ASA 32). The transition temperature, T_{tr}, where the domains first appear in the light-scattering sample was found to be T_{tr} = 122.730 K on our Pt resistance-thermometer temperature scale. We report our observations in terms of temperature differences from T_{tr}. Figure 1 shows blown-up examples of the speckle interference patterns. The incident light power was 20 mW at 5145 Å for these photographs. These interference patterns were stable for the lengths of exposure used implying static scatterers and static configurations. Comparison of (a) and (b) in Fig. 1 shows the effect of collection aperture on the interference pattern at the same temperature. Photograph (c) was taken at 25-mK-higher temperature with a 2×-longer exposure to compensate for the reduced scattering intensity. Comparison of (b) and (c) shows a one-to-one correspondence of the minutiae of the

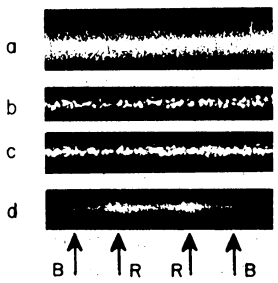

FIG. 1. Photographs of the scattering column in KDP: (a) at ΔT = 0.066 K, for collection aperture $f/3.8$, 7-sec exposure; (b) at ΔT = 0.066 K, for collection aperture $f/16$, 30-sec exposure; (c) at ΔT = 0.091 K, for collection aperture $f/16$, 56-sec. exposure. (d) Image taken through the Fabry-Perot interferometer, free spectral range 15 GHz, at ΔT = 0.2 K, 60-sec exposure. Arrows labeled R point to the speckled Rayleigh scattering while arrows labeled B point to the anti-Stokes Brillouin scattering component. The length of the photographs in (a), (b), and (c) corresponds to a distance along the laser beam in the crystal of 1.5 mm.

fringe patterns at the two temperatures. This implies that the number density and positions of the scatterers are independent of temperature. Photograph (d), showing the scattering column as seen through the Fabry-Perot, allows comparison between the coarse, granular appearance of the speckle interference pattern occurring on the elastic scattering Fabry-Perot fringes and the smooth Brillouin component fringes at the right and left extremes. The fine graininess of the Brillouin components is due to the film grain and half-tone reproduction.

The Fabry-Perot spectrometer was used to record Brillouin spectra of the central peak and the x-y shear acoustic mode above T_{tr} in the range of strong central-peak scattering. It was found necessary to use low incident laser powers of 3 to 10 mW in this range to avoid perturbing the sample temperature. The central peak observed in the *VH* polarized spectra was up to 20× larger than the *VV* scattering because of visible inclusions, surface polish, stray light from the Dewar windows, etc. A fit to the elastic Curie law of the elastic-constant data from the Brillouin spectra for C_{66}^{E} gives $T_c^{X} = 122.72 \pm 0.072$ K.

The observed temperature dependence of the elastic central peak in the paraelectric phase is similar to that reported by Lagakos and Cummins.[1] Figure 2 shows the central-peak temperature dependence obtained from Brillouin spectra. The intensity of the elastic central peak at 122.76 K has increased by two to three orders of magnitude from its value above 127 K where it is nearly temperature dependent. On entering the ferroelectric phase the intensity of the elastic central peak decreases sharply and becomes roughly independent of temperature, scattering being mainly from the domain walls. The temperature dependence is stable and reproducible, does not change on temperature cycles through the transition or back to room temperature, and does not seem to depend on the optical quality of the sample material. This is quite different from the observations recently reported for potassium trihydrogen selenite[12] in which the Rayleigh intensity decreased strongly for samples held at temperatures between −30 and −69°C. We attempted to fit the temperature dependence of the central-peak intensity to a power law $I \sim (T - T_c^{X})^{-\gamma}$ and find $\gamma = 1.5 \pm 0.2$. The intensity increasing faster than $\gamma = 1$, the exponent of the elastic Curie law, is probably due to the clamped Curie temperature anomaly[13,14] in the elasto-optic coeffi-

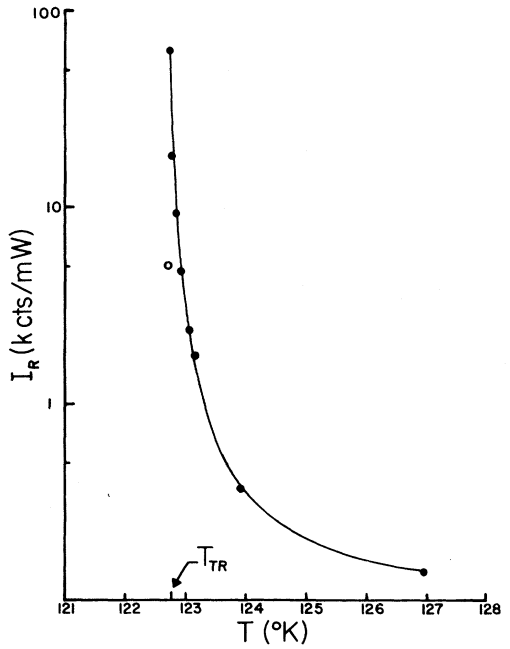

FIG. 2. Rayleigh intensity I_R vs temperature. Closed circles, paraelectric phase; open circle, ferroelectric phase.

cient $p_{66}{}^E$.

The observation of a speckle interference pattern in the scattering column and the *VH* polarization of this scattering agrees with the suggestion of Axe, Shapiro, Shirane, and Riste[5] of defect-induced scattering. The speckle interference pattern remains fixed with temperature which suggests that the defect scattering centers are spatially fixed. In KDP-type ferroelectrics it is the x-y shear elastic constant (C_{66}) that softens as the transition is approached. The x-y shear acoustic mode and any static x-y shear deformation contribute to the scattering only in the *VH* spectra. The observation of the central-peak scattering being essentially all *VH* polarized is then consistent with temperature-dependent x-y shear strain around defects as the mechanism of the scattering: a strain decoration of the defects.

If the defects were mobile like the clusters of Schneider and Stoll[4] or relaxing like the defects of Halperin and Varma,[6] then they would produce a dynamic central peak of nonzero width and the scattering column would appear continuous. The appearance of the speckle interference patterns in Fig. 1 shows that any such dynamic components must be much weaker than the observed speckled scattering. Recently Mermelstein and Cummins[15] have studied the KDP Rayleigh scattering using an interferometer with 15-MHz resolution. They found no dynamic component to occur along with the elastic central peak giving the speckle interference in the paraelectric phase but did detect the thermal diffusion mode as a dynamic central peak in the ferroelectric phase.

Further understanding of the central-peak scattering in KDP requires a more detailed model of the defects. The photographs in Fig. 1 indicate that the defects must be finely distributed throughout the sample. Unfortunately, the speckle density[8] gives no information about the defect density. We estimate a lower bound on the defect density of 4×10^9 defects/cm^3 based on the diffraction-limited resolution of the collecting lens since we do not see resolvable scattering centers and the speckle is fully developed and uniform along the beam. We know from ultramicroscopic examination in the laser beam at room temperature that the sample has $\leq 10^6$/cm^3 inclusions, voids and/or dislocations giving detectable scattering in a 100-mW focused 5145-Å beam. Thus we suspect that the defects giving the central-peak scattering must be something other than the inclusions, etc., isolated in the laser beam. One high-density defect has been suggested,[16] that of the natural abundance (0.02%) of deuterium-replaced hydrogen. Since the proton motion is directly involved in the unstable motions of the transition such an "impurity" might have a large effect near T_c. Deuterium enrichment experiments are necessary to test this suggestion.

The static nature of the central-peak scattering is difficult to reconcile with the NMR[17] and ultrasonic[18] reports of 10-MHz range relaxations in KDP. The fast-slow crossover in the NMR work occurs so far above T_c (60 K) that it may have little to do with the soft-mode fluctuations to a few degrees above T_c. The ultrasonic absorption results need to be reanalyzed to separate the acoustic scattering losses expected for strain decorated defects reported here from real absorption by coupling to the soft mode.

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High-Resolution Study of Low-Energy-Electron-Diffraction Threshold Effects on W(001) Surface

A. Adnot and J. D. Carette

Laboratoire de Physique Atomique et Moléculaire, Centre de Recherches sur les Atomes et les Molécules, Faculté des Sciences et de Génie, Université Laval, Québec, Canada, G1K 7P4

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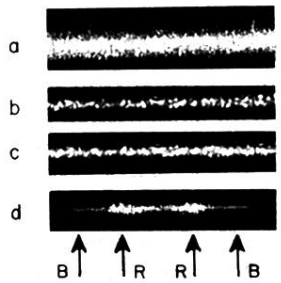
The simultaneous high-energy-resolution and high-angular-resolution (15 meV, 0.8°) measurements of the (00) beam diffracted from W(001) near 45° incident angles are reported. Apart from the well-known surface-state resonance previously identified, new features located in the close vicinity of the $(\bar{1}0)$ emergence energy are detected. They may remain undetected if one of the two high-resolution requirements is not fulfilled. The threshold effects are correlated with the $(\bar{1}0)$ beam emergence by angular distribution and I-V measurements, and possible interpretations are discussed.

The needs for high-resolution low-energy-electron-diffraction (LEED) experiments have been stressed by numerous authors: The knowledge of the exact position and shape of the surface-state resonances is of primary importance for the determination of the surface-potential-barrier parameters[1-5]; high-resolution measurements can help to make the distinction between surface-state resonances and beam threshold effects[6] and to clarify the origin of some singularities[7,8] in I-V curves; the limited resolution of conventional LEED equipment may blur[5] fine details of I-V curves; indeed, a sharp and highly localized effect just at the detection limit imposed by a 0.4-eV resolution has been recently reported.[7]

Working at very low energy presents the advantage that the dynamical effects for the first nonspecular diffracted beams are located below the strong inelastic surface and volume-plasmon thresholds. This inelastic scattering attenuates, broadens, and displaces the features.[9] Thus it becomes more difficult to determine true shape and position of the details, in the absence of a quantitative theoretical treatment of the adsorptive part of the potential. To our knowledge only one experiment[10] has so far been reported in the low-energy range with a 70-meV resolution at 53° incidence angle. The angular resolution was not given. It has been analyzed by many other autors.[5,9,11-13]

We report in this Letter the study of the (00) beam diffracted from W(100) for incidence angles near 45°, a 15-meV energy resolution, and an angular detector resolution better than 0.8°. This performance has permitted the detection and identification of new features whose widths are more



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