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SINGLE PARTICLE EXCITATIONS IN $RbAg_4I_5$

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ABSTRACT

In an inelastic neutron experiment on $RbAg_4I_5$ a broad quasielastic peak was observed throughout Q-space. As the temperature was lowered, the quasielastic peak became a broad propagating excitation with $\hbar\omega \sim 2.2$ meV. This excitation was measured along several symmetry directions and it exhibited little dispersion. This confirms that the original idea of a single particle excitation corresponding to the Ag^+ ions moving within a potential well created by the rest of the lattice. The temperature dependence of this excitation is consistent with recent calculations of neutron scattering in superionic conductors.

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DISCLAIMER

$RbAg_4I_5$ has one of the highest room temperature ionic conductivities of all known superionic conductors [1]. It is also known to undergo two phase transformations at T_2 = 208 K and T_1 = 122 K. At the former temperature, there is a change in symmetry from cubic to rhombohedral. The conductivity exhibits a small change, but there is a significant change in the activation energy at this temperature. The transition is a disorder-disorder transformation where the Ag^+ ions redistribute themselves over a different set of allowed sites, but still remain disordered. At T_1, the conductivity decreases by two orders of magnitude and the Ag^+ ions are considered ordered.

Most of the lattice dynamical studies of $RbAg_4I_5$ have been performed using light scattering [2] and ultrasonic [3] techniques. One important result of the ultrasonic studies is the anomalous temperature dependence of C_{44} near T_1. This anomaly was not observed in a neutron study [4] of the acoustic modes which probes a much higher frequency than ultrasonic methods. The Raman studies observed two broad excitations at 13.0 meV and near 2.5 meV which were assigned as motions of the iodine cage and "attempt vibrations" of the Ag^+ ions, respectively. It is remarkable that no other sharp features were observed since there are 117 optic vibrational modes. However, from group theory, motion of the Ag^+ atoms is involved in all the normal modes of the system. It appears, therefore, that the disorder of the Ag^+ atoms contribute to the "washing out" of the optical modes, a result consistent with the idea that the Ag^+ atoms being liquid-like.

In the neutron study of $RbAg_4I_5$, no soft mode associated with the transition at T_2 or T_1 was observed [4]. The interesting observation of this experiment is shown in Fig. 1. At room temperature, a broad quasielastic scattering is observed with a full width at half maximum(FWHM) of $\sim$ 6.0 meV. This feature is observed throughout reciprocal space which is suggestive of a local effect. As the temperature is lowered, the broad quasielastic scattering develops into a propagating mode. It is the purpose of this note to further characterize this excitation and to measure the phonon dispersion curves.

The crystals were grown from solution and were similar to those used in the previous experiment [4]. They possessed a narrow mosaic(0.25°) and at room temperature were untwinned. The sample volume was about 0.2 cm^3. The crystal was mounted in a variable temperature cryostat with the [110] axis perpendicular to the scattering plane. All measurements were made on a triple-axis spectrometer at the HFBR using either a fixed incident energy of 13.7 meV or 5.0 meV, or a fixed final energy of 14.7 meV.

In Fig. 1, we showed how the spectra evolved with temperature [4]. The evolution of the propagating mode depended more upon the absolute temperature than on any temperature relative to T_2 or T_1. Fig. 2 shows two energy scans corresponding to a longitudinal scan along [110] (top) and a transverse scan along [110] (bottom). The Brillouin zones are deliberately chosen where the structure factors for the acoustic modes are weak, so they would not interfere with our observations. The temperature is held constant at T = 125 K, just above T_1. Both spectra show an inelastic peak at $\hbar\omega \approx 2.0$ meV and a strong resolution limited intensity at $\hbar\omega = 0$. The latter is due mainly to the incoherent scattering from the Ag ions since Rb and I have almost no incoherent scattering cross section. At higher temperatures, an inelastic peak is no longer observable and the spectra resemble the 250 K curve of Fig.1. This excitation was measured at several q values along the [100] and [110] direction and the results are plotted in Fig. 3.

There is little dispersion along the [100] direction and along the [110] direction, the frequency reaches 3.0 meV at the zone boundary. Also shown in the figure are the measurements of some of the acoustic modes propagating along these directions. The dotted line represents the velocities of sounds as determined from the ultrasonic measurements [3]. Within the accuracy of the measurements, the values obtained from the neutron scattering are identical to the ultrasonic results. A search was made for optic modes above 2.0 meV and none was observed.

The almost dispersionless nature of the excitation suggests that we are observing an excitation which is mainly local in character, i.e. it corresponds to uncorrelated motion of individual ions. Most likely, we are observing motion of the silver atoms.

The temperature dependent features of our spectra were predicted in a theoretical treatment of the scattering of neutrons by superionic conductors [5]. This is a one-dimensional model where the motion of the mobile ion is described as a continuous diffusion process. In this model, the diffusion of the individual particles is treated as a Brownian motion in a periodic potential provided by the crystalline sublattice. The barrier height is on the order of kT. The interaction of the mobile ions with the phonons of the lattice is parametrized by a friction term in the equation of motion. For small friction, the spectra evolve with temperature in a way very similar to that shown in Fig. 1. Physically, these spectra relate how at temperatures higher than the barrier height, the particles can undergo a diffusive motion. The spectra should consist of broadened Lorentzians centered around $\hbar\omega = 0$ as shown in Fig. 1. As the temperature is lowered, the particle undergoes a more oscillatory behavior and a well-defined resonance appears. This is shown in Figs. 1 and 2.

The diffusion of the Ag^+ atoms would appear as a broadening of the scattering about E = 0. At these temperatures, the diffusion constant is less than 10^{-6} cm^2/sec [6] and any linewidth is much less than the instrumental resolution of $\Delta E = 0.8$ meV. Thus, contained in the scattering about E = 0 of Fig. 2 is the information about the diffusion process which can be studied only with ultrahigh resolution experiments.

The theoretical treatment also predicts interesting variations of intensities with q which have yet to be tested. The intensity of the inelastic peak should increase with increasing Q which appears to be the case, but has not been systematically studied. Also, in the small friction regime for larger Q values, second harmonics of the oscillatory frequency should also be present. These have not yet been observed.

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Fig. 1. Inelastic spectra of $RbAg_4I_5$ taken at several temperatures (from Ref. 4).

Fig. 2. Inelastic spectra of $RbAg_4I_5$ for q along [110] (top) a longitudinal scan (bottom) a transverse scan.

Fig. 3. Low frequency dispersion curves of $RbAg_4I_5$. The dashed lines are calculated from the elastic constants of Ref. 3.

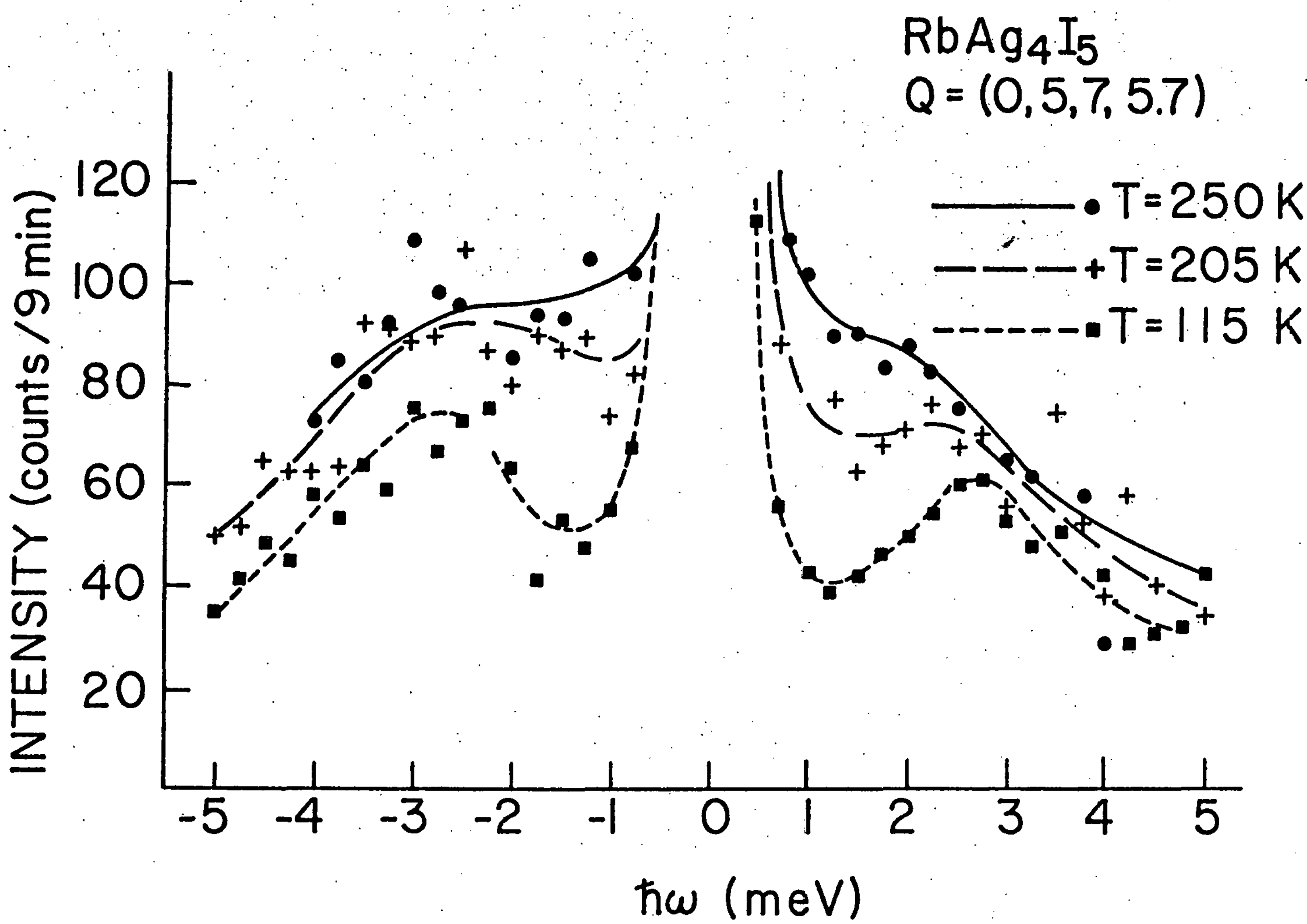

FIGURE 1

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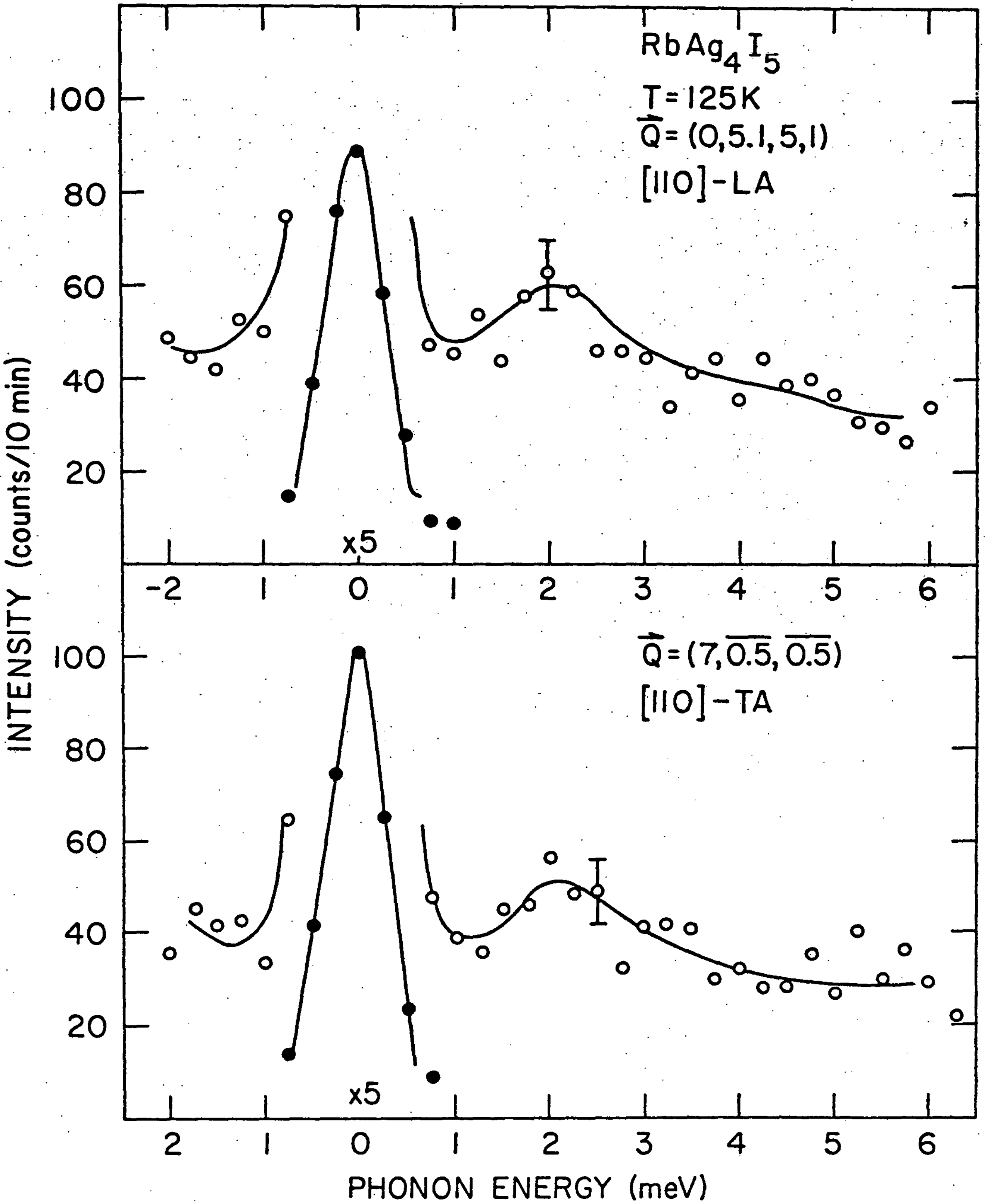

FIGURE 2

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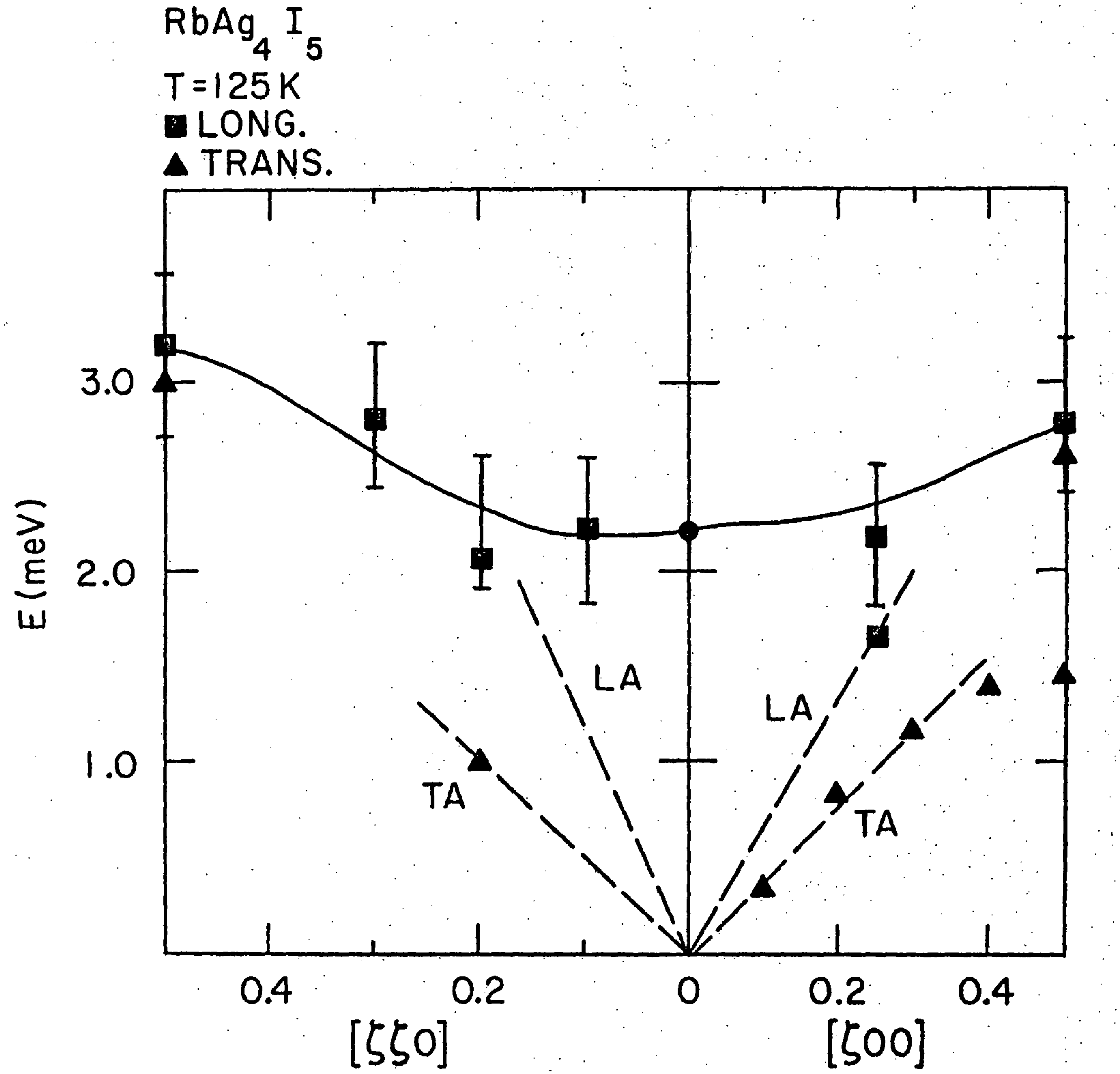

FIGURE 3

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