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NEUTRON SCATTERING STUDY OF THE SOLID ELECTROLYTE: $RbAg_4I_5$

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Neutron scattering experiments were performed on $RbAg_4I_5$ in order to probe: i) The lattice dynamics above and below the phase transition at T_2 = 208.5K; ii) The temperature dependence of the Ag^+ occupancies below T_2 and iii) The diffusion of the Ag^+ ions. No anomalous softening of the elastic constant C_{44} was observed as had been reported by ultrasonic studies. Careful examination of the phonon intensities above and below T_2 suggest that the transition is discontinuous. The behavior of allowed reflections below T_2 mirror the temperature dependence of the Ag^+ occupation factors. A broad overdamped excitation is observed throughout Q-space and becomes a propagating mode as the temperature is decreased. Nothing critical happens at T_2 or T_1.

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$RbAg_4I_5$ is an important Ag^+ based solid electrolyte since at room temperature it has one of the highest conductivities of all solid electrolytes.[1] It is also known that $RbAg_4I_5$ undergoes two phase transitions[2]: i) At $T_2 = 208K$, there is an abrupt change in the slope of the conductivity versus temperature and many properties exhibit a lambda-like behavior. The symmetry changes from cubic (O^7-$P4_132$ or O^6-$P4_332$) for $T > T_2$ to rhombohedral ($D_3{}^7$-R32) with very small changes in atomic positions.[3] The most significant differences between the two phases is the redistribution of the 16 Ag^+ ions over the 56 allowed sites.[3] ii) At $T_1 = 122K$ there is a discontinuous reduction by a factor of $\sim$ 100 in the ionic conductivity related to a more ordered structure of the Ag^+ ions in the low temperature phase. The symmetry is not completely known at this stage but is trigonal, the most probable space group being $D_3{}^2$-P321.[3]

By studying the changes in lattice dynamics at T_2 and T_1, one may correlate any changes directly with the behavior of the Ag^+ cations. Several Raman studies[4,5] of $RbAg_4I_5$ revealed no large changes in frequency at T_2 or T_1. The major change is the appearance of additional lines below T_1 where the selection rules are modified due to the tripling of the unit cell. In fact it has been emphasized[4] that the Raman spectra are remarkably simple and almost featureless. This is surprising when you consider that there should be 120 vibrational modes! The major critical dynamical feature thus far observed was the ultrasonic investigation of C_{44} which showed an anomalous softening and increase in damping near T_2.[6] The purpose of our present investigation is to explore by neutron inelastic scattering the observed softening and search for other dynamical effects which we can relate to the changes in ionic conductivity.

The crystals used in this experiment were grown from solution and had a volume of $\sim$ 0.25 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 Brookhaven National Laboratory's HFBR with an incident energy of either 13.7 or 5.0 meV.

Figure 1 shows a high resolution spectra of the [100]-TA above and below T_2. The polarization of this mode is along the [011] direction and corresponds to the elastic constant C_{44}. No observable shift is detected within an estimated detectability of 0.02 meV. The momentum transfer, $q = 0.075a^*$ ($a^* = 0.561 Å^{-1}$) was the minimum q we were able to measure without being contaminated by the strong elastic Bragg scattering. The value of C_{44} obtained is $C_{44} = 0.51 \pm .05 \times 10^{11}$ dynes/cm^2 which is in agreement with the high temperature ultrasonic measurements.[6] The observed softening in the ultrasonic measurements most likely are due to very long wavelength strains which are beyond the capabilities of neutron scattering measurements. One must also consider that the apparent softening of C_{44} could be due to the effects of domains interacting with the ultrasonic pulses.

The most striking feature of Figure 1 is the change in the phonon intensity as the sample is cooled below T_2. This is most surprising since there is no change in frequency and can only arise as a result of a change in structure factor of the fundamental Bragg peak, (222), about where this phonon was measured. Figure 2 shows the temperature dependence of the phonon intensity in the vicinity of T_2. The abrupt change in intensity and the observed hysteresis are strong evidence of a first order phase transition. This has been predicted on the basis of mean field theory but has hitherto been unobservable.[7] In fact most earlier evidence suggested a continuous transition.

Because of the change in symmetry many Bragg peaks show large changes in intensity at the phase transition. New Bragg reflections also appear because of the lower symmetry. Explicitly, for $T > T_2$ in the cubic phase, the reflections of type (h00) with $h \neq 4n$ are forbidden but become allowed in the low temperature phase. Figure 3 shows the temperature dependent behavior of the intensity of two such reflections. A monotonic, almost linear increase in intensity below T_2 is observed. Also there is a slight increase in intensity on cooling just above T_2. This behavior is very suggestive of an order parameter. The quantity representative of the order parameter is the fractional occupancy of the Ag^+ ions amongst the 56 allowed sites.[7] Because of the large number of different sites available in this intermediate phase it is difficult on the basis of these two reflections to determine which site occupancies contribute to these reflections. A more complete structure analysis at several temperatures is required. Some interesting facts nonetheless emerge. The appearance of some precurser critical scattering just above T_2 is consistent with the optical studies which showed some birefringence in cubic phase near T_2.[8] Within the instrumental resolution, ($\delta Q_{FWHM} \sim 0.02\text{Å}^{-1}$) no q width was observed which says that any correlation amongst the diffusing silvers is over distances greater than $\sim$ 100Å.

A search for a soft optic mode or some dynamical effects related to the phase transition was made. No soft mode was observed in the Raman scattering measurements.[4,5] We looked in several Brillouin zones within the energy range of 0 - 5 meV. At room temperature a broad feature centered around $\hbar\omega = 0$ with a 6.0 meV full width at half maximum was observed at every point studied. The intensity was also greater for the larger momentum transfers. As the temperature is lowered (Figure 4) a propagating mode becomes visible with $\hbar\omega \sim$ 2.8 meV. Figure 4 shows the spectra at $\vec{Q}$ = (0, 5.7, 5.7), a position in Q space where the intensity of the acoustic mode would be very weak. No critical change in linewidth or intensity occurs at either T_2 or T_1. Instead the behavior seems to depend more upon the absolute temperature than on temperature differences from the transition temperatures. Because a similar feature is observed at several unrelated Q values we tend to interpret this as an Einstein-like excitation related to the Ag^+ ions moving in an uncorrelated fashion. One of the few prominent features in the Raman spectra of $RbAg_4I_5$ is a broad feature centered around $\hbar\omega \sim$ 2.5 meV,[5] nearly the same frequency observed in the present experiment. On the basis of polarization studies this was presumed to be due to vibrations of the Ag^+ ions within an immobile cage set up by the I^- ions.[5]

We are currently continuing these measurements to probe in more detail the temperature and Q dependence of this excitation.

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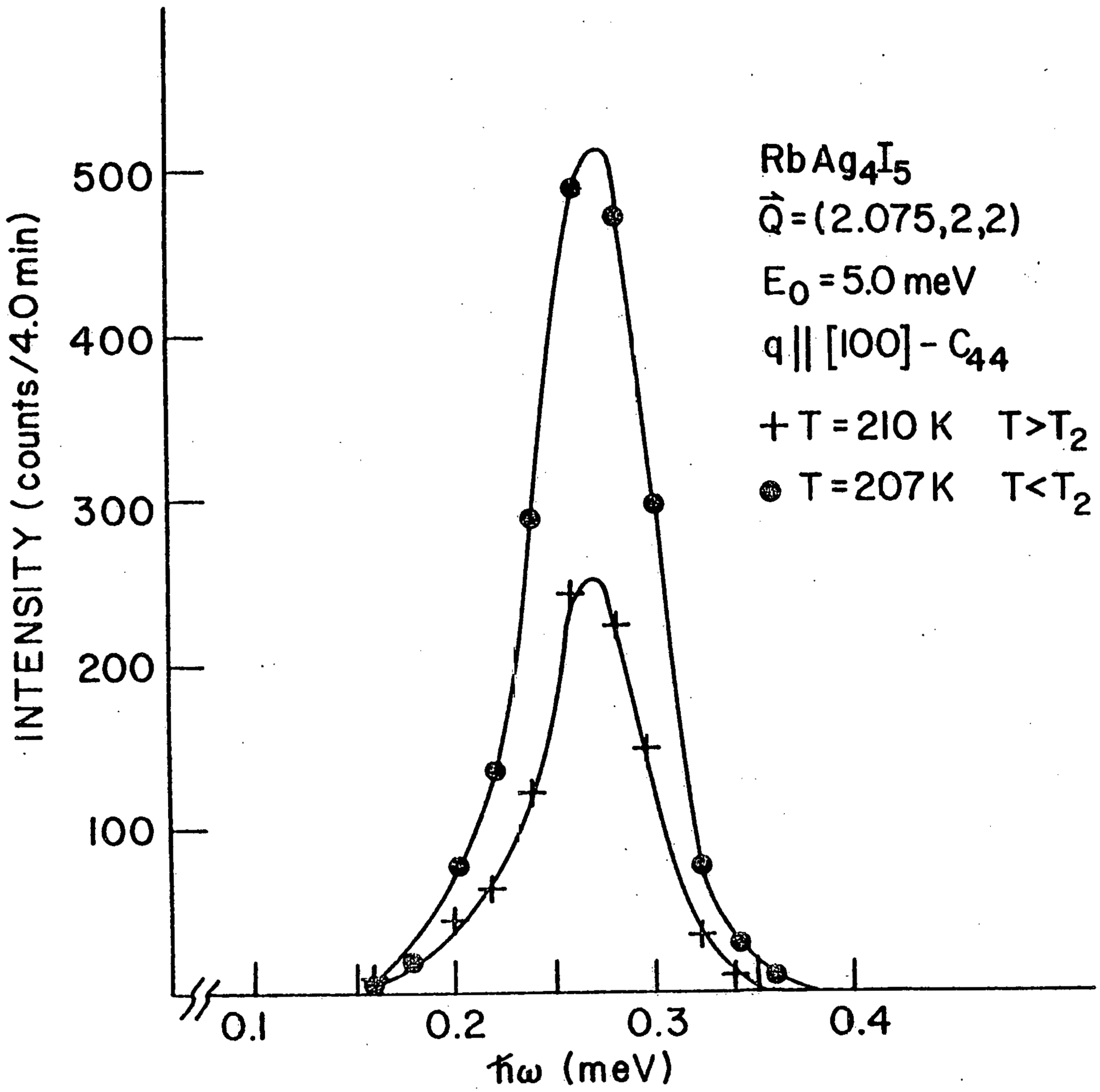
FIGURE CAPTIONS

FIGURE 1 Inelastic spectra of a TA mode propagating along [$\bar{1}$00] and polarized along [011] above T_2(+) and below T_2(●).

FIGURE 2 Temperature dpendence of the peak intensity of the phonon shown in Figure 1.

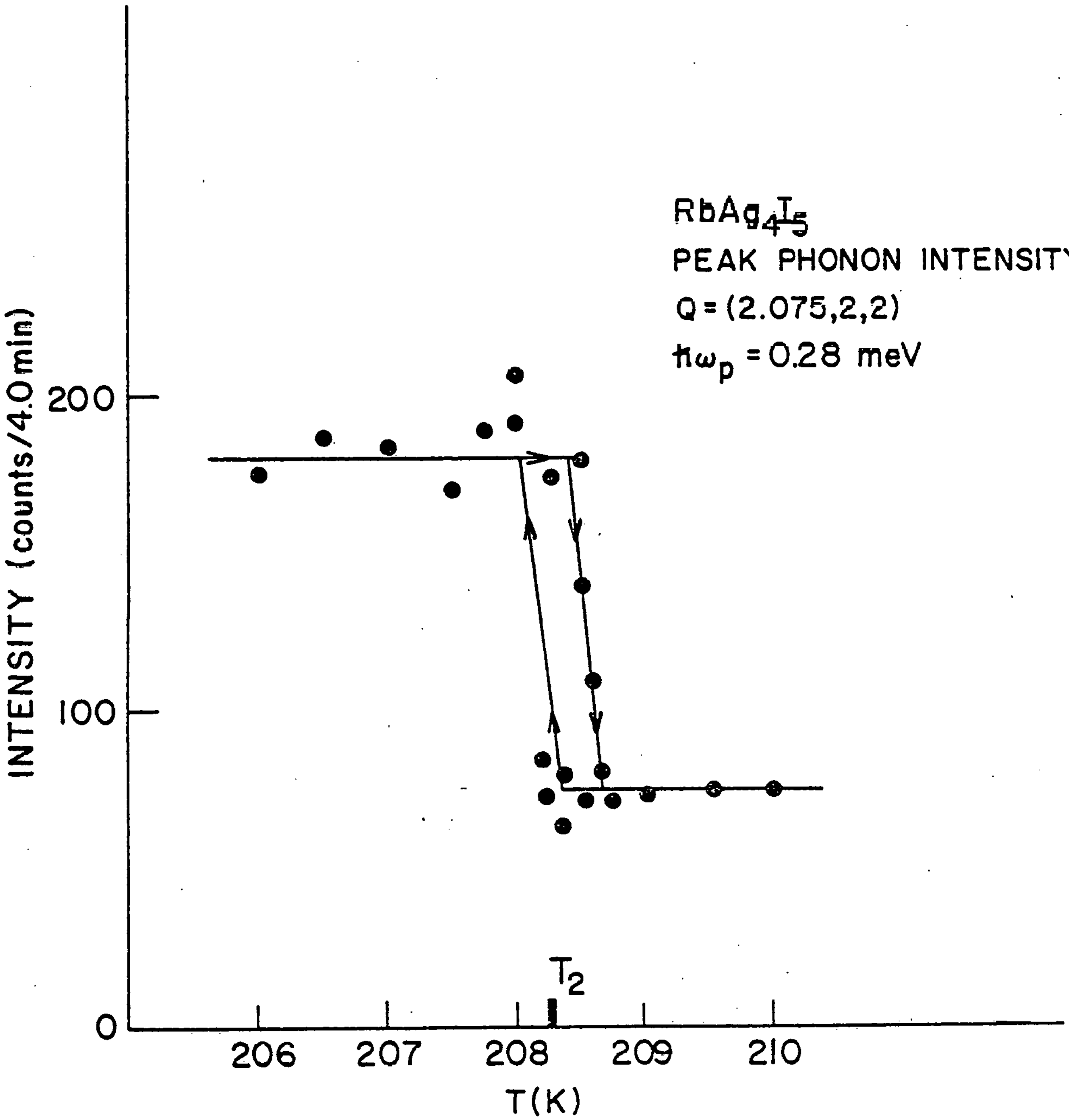
FIGURE 3 Temperature dpendence of the intensity of (600) (+) and (700) - (●) Bragg peaks. These peaks are forbidden by symmetry above T_2 .

FIGURE 4 Inelastic spectra at Q = (0, 0.57, 0.57) for T = 250 K > T_2(●), T_1 < T = 205 K < T_2(+), and T = 115K< T_1(□).



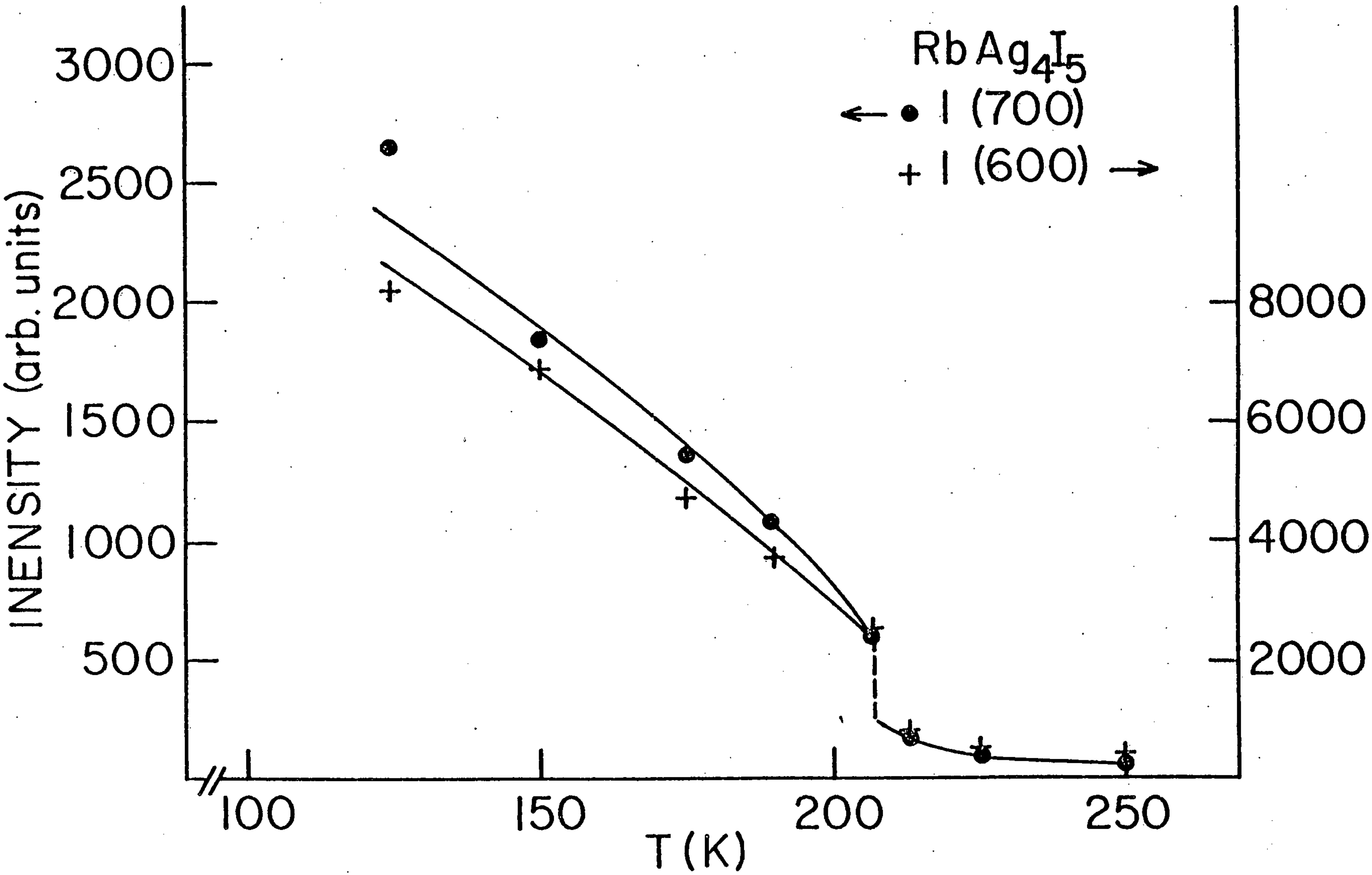
RbAg4I5
Q=(2.075,2,2)
E0=5.0 meV
q || [100] - C44
+ T = 210 K T>T2
● T = 207 K T<T2
INTENSITY (counts/4.0 min)
500
400
300
200
100
0.1
0.2
0.3
0.4
ħω (meV)

FIGURE 1



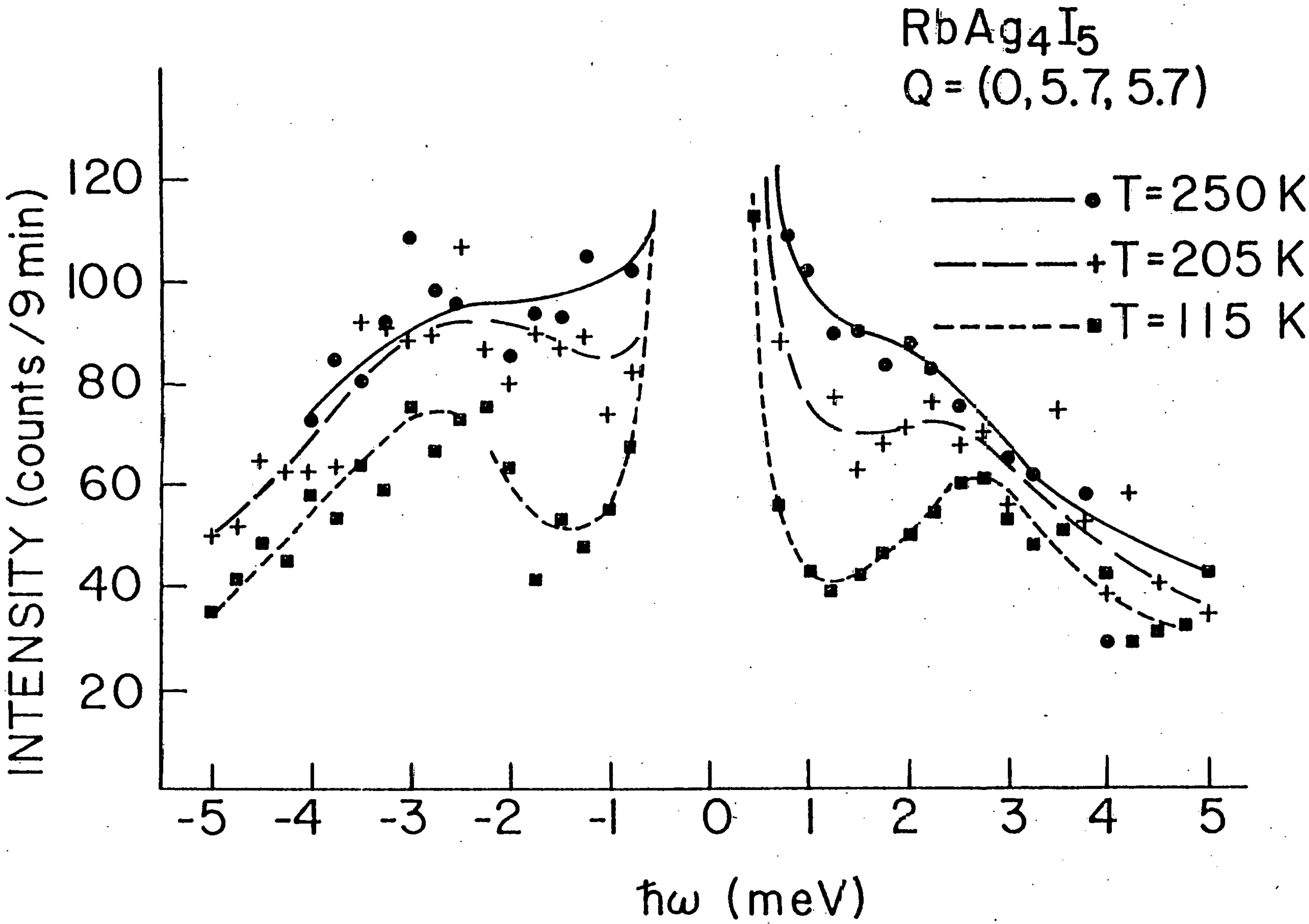
RbAg4I5
PEAK PHONON INTENSITY
Q = (2.075,2,2)
ħωp = 0.28 meV
INTENSITY (counts/4.0 min)
200
100
0
T2
206
207
208
209
210
T(K)

FIGURE 2



Rb Ag4I5
← • I (700)
+ I (600) →
INENSITY (arb. units)
3000
2500
2000
1500
1000
500
8000
6000
4000
2000
100
150
200
250
T (K)

FIGURE 3



RbAg4I5
Q = (0, 5.7, 5.7)
T=250 K
T=205 K
T=115 K
INTENSITY (counts/9 min)
120
100
80
60
40
20
-5
-4
-3
-2
-1
0
1
2
3
4
5
ħω (meV)

FIGURE 4