

Raman Scattering and Short-Range Order in Ammonium Bromide at the λ Transition

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The decay of short-range ordering of NH_4^+ ions below T_λ (235°K) in NH_4Br is shown to be responsible for both the specific-heat anomaly and the Raman scattering of a polarized low-frequency mode at 56 cm^{-1} . The temperature-weighted integrated Raman intensity is quantitatively compared with the residual specific heat below T_λ .

It is well established that the λ transition at 235°K (T_λ) in NH_4Br is an order-disorder transition. Above T_λ , an x-ray diffraction study¹ indicates that the crystal has a CsCl-type cubic structure with the NH_4^+ ions randomly distributed between two energetically equivalent orientations. Below T_λ the unit cell undergoes a small distortion (c/a ratio = 1.003), and the NH_4^+ ions assume ordered orientations. The identically oriented NH_4^+ ions form chains along the tetragonal direction with neighboring chains oppositely oriented. In this sense the NH_4Br ordered phase is analogous to an antiferromagnet and is therefore more complicated than the ordered phase of NH_4Cl , which is analogous to ferromagnetic order.

In spite of the general understanding regarding the origin of λ transition in NH_4Br , the mechanism underlying the phase transition is not yet clear. Many different experiments have been undertaken in trying to understand the mechanism associated with the phase transition at 235°K.² Up to the present, although the overall effect of the onset of the λ transition has been manifested in several physical properties, there seems to be no correlation between them. This Letter reports the effect of short-range order on a Raman spectrum in NH_4Br . The results provide a quantitative correlation of the specific-heat anomaly and the integrated intensity of a low-frequency mode at 56 cm^{-1} and contributes to a better understanding of the λ transition in NH_4Br in terms of a more unified picture. A similar picture is also expected for other ammonium halides.

The Raman spectrum was obtained using a constant intensity (120 mW) argon ion source oscillating at 5145 \AA , a double monochromator for dispersion, and a photon-counting detection system. A good optical quality NH_4Br crystal ($\sim 1\text{ cm}^3$), grown from aqueous solution with urea added as a habit modifier, was mounted in a Cryotip refrigerator for temperature variations. Sample temperature was monitored simultaneously at the base and side of the crystal by two Chromel-

Constantan thermocouples. The spectrum was taken only when the two temperature readings differed by less than 1°K. The temperature stability of the refrigerator was maintained to $\pm 0.3^\circ\text{K}$.

The Stokes spectrum obtained with the $x(zz)y$ configuration in the $20\text{--}85\text{ cm}^{-1}$ region is shown in Fig. 1 for several temperatures above and below T_λ . Above T_λ , there is no corresponding scattering observed at the 56 cm^{-1} region in the $x(zx)y$ or other depolarized configurations. At 150°K the depolarized (as well as the polarized) spectrum shows no band at 56 cm^{-1} but, instead, two much weaker peaks at 67 and 76 cm^{-1} . This is consistent with the earlier Raman results by Wang and Fleury.³ However, the small leakage

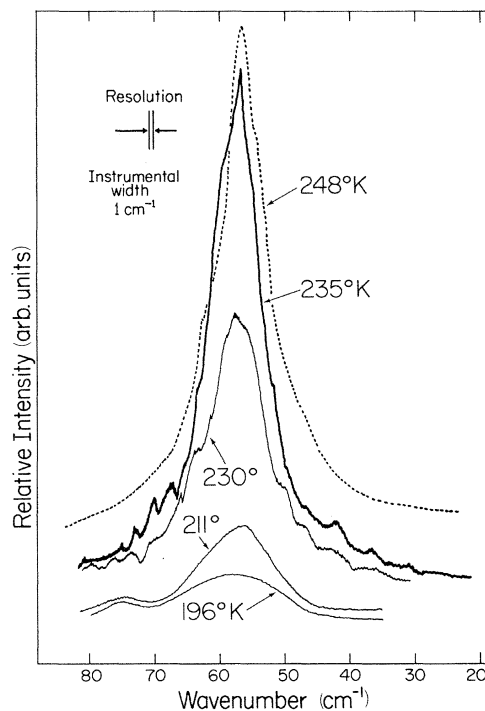


FIG. 1. The $x(zz)y$ Raman spectrum of NH_4Br single crystal in the region $20\text{--}90\text{ cm}^{-1}$ at various temperatures above and below T_λ . The configuration $x(zz)y$ gives a transverse phonon with the A symmetry propagating in the x - y plane of the crystal.

of the 56-cm^{-1} band in depolarized spectrum reported in Ref. 3 appears to be due to the imperfection in the light-gathering optics and the crystal orientation as it did not appear in the present measurement. Therefore, the 56-cm^{-1} band is established to be of a totally symmetric mode.

Although all the Raman bands measured in NH_4Br single crystals at temperature below T_λ have all been identified and assigned,³ the occurrence of a totally symmetrical mode at 56 cm^{-1} above T_λ is rather puzzling. In the cubic disordered phase the selection rule for the first-order Raman effect is not, strictly speaking, valid because the random orientation of NH_4^+ ions has the effect of destroying the translational invariance in the lattice (but due to the tetrahedral symmetry of the NH_4^+ ions, regardless of the disorder the group theory predicts a limiting lattice mode of F_2 symmetry at 130 cm^{-1}). As a result, without the restriction of $\vec{K}=0$, one should observe scattering from all the even-parity phonons. The resulting Raman spectrum should then mirror the one-phonon density of states—which is in general not a symmetrically shaped nor a sharp function. Therefore, in order to explain the sharp and symmetrically shaped spectrum at 56 cm^{-1} , Wang and Fleury³ proposed, on the basis of the phonon dispersion curves for CsI by Karo and Hardy,⁴ that the 56-cm^{-1} scattering is due to scattering from a large-wave-vector phonon at the zone boundary, possibly an acoustic mode at the X point. The mech-

anism which allows coupling of the zone-boundary phonon with the light wave is considered to be due to the existence of short-range order above T_λ .

A direct verification of the short-range order would be a measurement of the phonon dispersion curves in NH_4Br by neutron scattering to see if the X -point frequency agrees with the 56-cm^{-1} value, but there has been no such study ever reported since the proposal was made. Another possible test of the proposed picture would be the study of the 56-cm^{-1} mode below T_λ by the Raman or infrared (IR) intensity measurement. If the 56-cm^{-1} feature is indeed due to short-range ordering, one would expect that below T_λ the replacement of the short-range order by the long-range order would be manifested by the decay of the 56-cm^{-1} mode.

We have measured the integrated intensity of the 56-cm^{-1} mode at several different temperatures above and below T_λ . The integrated intensity divided by $n(\omega_0) + 1$, which is called I_{int} , is shown by open circles in Fig. 2. The intensity data are obtained by averaging values from four consecutive measurements and are accurate to within 4%. The same results were obtained irrespective of approaching the phase transition from above or from below. There is no thermal hysteresis observed in the λ -transition region.

In the short-range-order picture the light scattering which arises as a result of the correlation of an NH_4^+ ion with its nearest neighbor

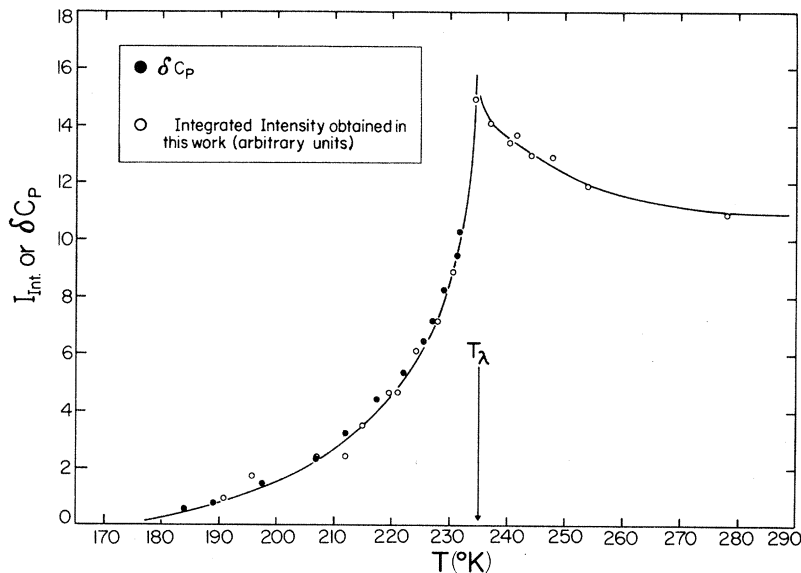


FIG. 2. The temperature-weighted Raman integrated intensity plotted versus the absolute temperature in the vicinity of the λ transition. The residual specific-heat data (in units of $1.676\text{ cal/mole deg}$) obtained from Ref. 8 are included for comparison.

is most conveniently considered as due to the spontaneous fluctuation of a system of microscopic dipole moments associated with the NH_4^+ ion pairs. The spectral density $J(\omega)$ of the fluctuation, which is proportional to the Raman scattering intensity, is related to the imaginary susceptibility according to the fluctuation dissipation theorem by⁵

$$J(\omega) = 2\hbar[n(\omega) + 1]\text{Im}\chi(\omega) \quad (1)$$

and, below T_λ , $J(\omega)$ is proportional to the Fourier transform of the correlation function of the dipole moment associated with the NH_4^+ ion pair:

$$J(\omega) = \rho(T) \int_{-\infty}^{\infty} d\tau \langle P(\tau)P \rangle e^{i\omega\tau}, \quad (2)$$

where $\rho(T)$ is the fraction of the correlated pair of nearest neighbors per unit volume. The $\rho(T)$ may be regarded as an order parameter describing the short-range order. $n(\omega)$ is the average occupation number given by $[\exp(\hbar\omega/kT) - 1]^{-1}$. In writing out Eqs. (1) and (2), the tensorial property of the susceptibility is ignored because the 56-cm^{-1} mode is totally symmetrical. The integrated spectral density is equal to

$$J = \int J(\omega) d\omega = \langle P^2 \rangle \rho(T); \quad (3)$$

and if the fluctuation is small, one can then expand P in terms of the displacement from the equilibrium position and carry out the ensemble average to yield

$$\begin{aligned} J &= \rho(T) (\partial P / \partial q)^2 [n(\omega_0) + 1] \\ &= I_{\text{int}} [n(\omega_0) + 1], \end{aligned} \quad (4)$$

where only one mode of vibration at frequency ω_0 ($= 56\text{ cm}^{-1}$) is assumed. Therefore, according to Eq. (4), the integrated intensity divided by $n(\omega_0) + 1$ gives the measure of the correlated pair density $\rho(T)$ which is shown in Fig. 2.

According to the theory of the specific-heat enhancement of a disordered crystal, the residual specific heat at constant volume due to an impurity is proportional to the impurity concentration.⁶ While the theory given in Ref. 6 is designed for small concentrations of isotopic impurity, in the present case the impurity is due to disordering of the NH_4^+ ions; and, therefore the impurity concentration associated with the disorder is a function of temperature. Below T_λ , the impurity concentration function $\rho(T)$ can, in principle, be calculated according to the Bethe-Peierls approximation of the three-dimensional Ising model.⁷ In this approximation the expression for the residual specific heat can be written

as

$$\delta C_p \approx \delta C_v = \gamma \epsilon \rho(T), \quad (5)$$

where δC_p is the additional molar specific heat due to the ordering of NH_4^+ ions, γ is the number of nearest neighbors of any NH_4^+ ion site, ϵ is the interaction energy, and $\rho(T)$ is equal to the temperature derivative of the difference between the long-range and short-range order parameters.⁷

Therefore a critical test for the proposed picture is to plot δC_p (with a suitable normalization) as a function of temperature and compare it with the Raman intensity result. A plot of δC_p vs T is shown by the solid circles in Fig. 2. The δC_p was obtained from the specific-heat data measured by Sorai *et al.*,⁸ by subtracting the measured specific heat of NH_4Br from a smooth-curve baseline representing all the nonconfigurational contributions to C_p (such as lattice vibrations, libration of the NH_4^+ tetrahedra, and internal motions of the NH_4^+ ion). As clearly shown in Fig. 2, the excellent agreement between the δC_p data and the Raman integrated intensity data indicates that the specific-heat anomaly of NH_4Br is closely associated with the behavior of the 56-cm^{-1} mode. In other words, agreement between the Raman and specific-heat data suggests that the earlier proposed mechanism³ for the 56-cm^{-1} mode is essentially correct.

The fact that the 56-cm^{-1} mode continues to exist above T_λ indicates that the short-range order persists in the disordered phase. Because of the difficulty associated with establishing a definite baseline for subtracting off the part of scattering due to complete disorder, the Raman intensity is not compared with the specific heat data above T_λ . In addition, one expects Eq. (2) to be invalid because $\rho(T)$ in the disordered phase is not small. Nevertheless, as is clearly shown in Fig. 2, although the short-range order exists above T_λ , the evolution of order in NH_4Br starts at about 260°K , which is considerably higher than T_λ ($= 235^\circ\text{K}$). The result of slow evolution of order below T_λ and of the existence of residual short-range order above T_λ is significantly different from the lambda transition in NH_4Cl , where it was found by the IR study that there is no residual order above T_λ .

One independent support for the slow evolution of order in NH_4Br is provided by the calculation of the entropy change from the specific-heat measurements reported in Ref. 8. The entropy change associated with the reorientation of the

NH_4^+ ions in the vicinity of λ transition is 0.74 eu, which is substantially less than the $R \ln 2 = 1.38$ eu for NH_4Cl . The result suggests that the change from complete disorder to complete order is spread out over a much wider temperature range than for the chloride and is consistent with the present low-frequency Raman data.

In conclusion, we point out that despite its close association with the λ transition, the low-frequency mode at 56 cm^{-1} is not, however, the "soft mode" for the order-disorder transition in its usual sense. While the peak frequency of this mode is insensitive to temperature (see Fig. 1), the spectral width is broadened considerably as the temperature is lowered below T_λ , along with the drastic decrease in scattering intensity. The anomalous broadening and the quantitative correlation of the temperature-weighted Raman intensity with the specific-heat data suggests that the mechanism of decaying short-range order below T_λ is correct. This mechanism, which has been shown to be responsible for both the specific-heat anomaly and the Raman scattering below T_λ , is likely also responsible for the correlated critical oscillations of NH_4^+ ions recently observed in the proton spin-lattice relaxation near the λ transition in NH_4Br .¹⁰

¹See, for example, *Proceedings of the Ninth Inter-*

national Conference on Low Temperature Physics, Columbus, Ohio, 1964, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yaqub (Plenum, New York, 1965), Pt. B, p. 1179.

²The λ transition in NH_4Br has been studied by NMR [see, for example, K. Shimomura, T. Kodama, and H. Negita, *J. Phys. Soc. Jap.* **27**, 255 (1969)], by ultrasonic velocity measurements [see, for example, C. W. Garland and C. F. Yarnell, *J. Chem. Phys.* **44**, 1112 (1966)], by IR absorption [E. L. Wagner and D. F. Hornig, *J. Chem. Phys.* **18**, 296 (1950); N. E. Schumaker and C. W. Garland, *J. Chem. Phys.* **53**, 392 (1970)], by neutron scattering [G. Venkataram *et al.*, *J. Phys. Chem. Solids* **2**, 1107 (1966)], and by Raman scattering [see, for example, C. H. Wang and P. A. Fleury, in *Light Scattering Spectra of Solids*, edited by G. B. Wright (Springer, New York, 1968), pp. 651-663; C. H. Perry and R. P. Lowdes, *J. Chem. Phys.* **51**, 3648 (1969)].

³Wang and Fleury, Ref. 2.

⁴A. M. Karo and J. R. Hardy, *Phys. Rev.* **160**, 702 (1967).

⁵C. H. Wang and R. B. Wright, to be published.

⁶Yu. M. Kagan and Ya. A. Iosilevskii, *Zh. Eksp. Teor. Fiz.* **45**, 819 (1963) [*Sov. Phys. JETP* **18**, 562 (1964)].

⁷K. Huang, *Statistical Mechanics* (Wiley, New York, 1963), pp. 341-346.

⁸M. Sorai, H. Suga, and S. Seki, *Bull. Chem. Soc. Jap.* **38**, 1125 (1965).

⁹C. W. Garland and N. E. Schumaker, *J. Phys. Chem. Solids* **28**, 799 (1967).

¹⁰A. R. Sharp and M. M. Pintar, in *Proceedings of the Sixteenth Colloque AMPERE, 1970* (North-Holland, Amsterdam, to be published).

Born-Oppenheimer Principle in Reverse: Electrons, Photons, and Plasmons in Solids—Singularities in Their Spectra*

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A novel application of the Born-Oppenheimer approximation is made which predicts the strength and nature of the singular threshold structure associated with plasmon satellites for a wide class of experiments involving the interactions of photons or fast electrons with solids.

I consider here the theory of plasmon singularities in a wide class of experiments in which a core electron is excited up into the continuum of unoccupied states. This excitation could be produced either by absorption of a photon or by a collision with a fast electron. It is measured either by detecting a change in the initial-state particle as in soft-x-ray absorption or high-energy-electron energy loss, or by detecting a final-state product as in x-ray photoemission,

soft-x-ray emission, or appearance-potential spectroscopy.¹ Typically the spectra from such experiments have plasmon satellites and possibly threshold singularities.²

In experiments such as x-ray emission and absorption, the plasmon satellites tend to be much weaker than one might expect after estimating the coupling constant. There is, however, a strong cancelation³ in second-order perturbation theory. In general, though, one knows that