

Interaction of pseudospins and the density spectrum of libration states in an NH_4Cl crystal

M. V. Belousov and V. D. Petrikov

Institute of Physics, A. A. Zhdanov Leningrad State University

(Submitted 23 June 1981)

Pis'ma Zh. Eksp. Teor. Fiz. **34**, No. 4, 183–185 (20 August 1981)

The bandwidth (T_6) of one-phonon libration states has been determined from the Raman scattering (RS) spectra of two-phonon transitions. The static octupole moment of an ammonium ion has been calculated for the first time in the multipole-multipole interaction model of T_6 ; this has made it possible to estimate the interaction energy of pseudospins and the phase-transition temperature.

PACS numbers: 63.20.Dj, 78.30.Gt

Ammonium-halide crystals are the classical subject for studying Ising phase transitions (PT). In these crystals the ammonium ion can assume two orientations, which are customarily described by the pseudospin. According to theoretical concepts,^{1–3} the interaction of pseudospins is determined by the octupole moment I_3 of an ammonium ion. However, a calculation of the vibrational spectrum of ND_4Cl , which was made in Ref. 4 using neutron-scattering data,⁵ showed that the charges on the deuterium atoms, and hence the value of I_3 , are close to zero. This follows from the fact that no dispersion of the libration vibration $\omega_6(\mathbf{k})$ was detected in Ref. 5. This result contradicts the existing concepts of PT in ammonium halides and, as noted in Ref. 4, requires a more precise determination.

We have investigated the RS spectra of the two-phonon transitions $\omega_6 + \omega_6$; this allowed us to obtain precise data on the width of the $\omega_6(\mathbf{k})$ band and to determine for the first time the static octupole moment of the ammonium ion.

We have investigated experimentally the RS spectra of the δ phase of an NH_4Cl_4 crystal at $T = 80$ K. The spectra were excited by an argon laser ($\lambda_0 = 514.5$ nm and a power of 1 W) and were recorded by a Spex-Ramalog 6 in the storage mode with the aid of a "Scamp" minicomputer. The contribution of stray polarization spectra was subtracted out.

The shape of the obtained $\omega_6 + \omega_6$ spectra of E (Fig. 1a) and F_2 (Fig. 1b) symmetry show that they are two-particle transitions. Consequently, the anharmonic shift in this case is small (≈ -14 cm^{-1} for the E and F_2 transitions according to an indirect estimate²) compared to the width of the two-particle spectrum (110 cm^{-1} for E and 75 cm^{-1} for F_2 transitions) and does not lead to the formation of a bound (single-particle) state. We note that the small anharmonic interaction of the vibrations (AIV) does not shift the limits of the two-phonon spectrum, but it does influence its shape significantly.^{6–8}

According to the selection rules,⁹ only the overtone transitions $\omega_{6i}(\mathbf{k}) + \omega_{6i}(-\mathbf{k})$, where $i = 1, 2$, and 3 is the number of the branch, are allowed for the symmetrical

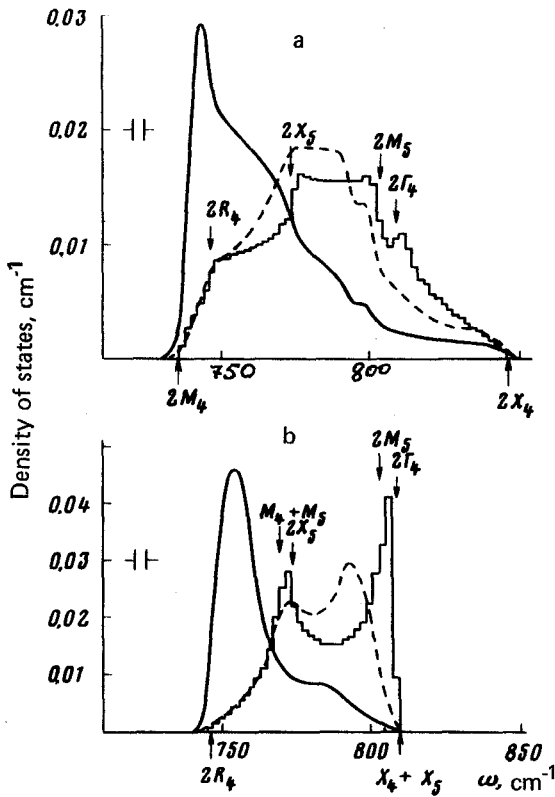


FIG. 1. Spectra of the density of $\omega_6(\mathbf{k}) + \omega_6(-\mathbf{k})$ states. (a) E symmetry and (b) F_2 symmetry in the NH_4Cl crystal. The solid curves represent the experimental RS spectra and the dashed curves denote the spectra obtained from the experimental spectra after taking AIV into account; the histograms were calculated using 8×10^6 points from the dispersion $\omega_6(\mathbf{k})$. The arrows indicate the calculated frequencies of the transitions at the symmetrical points of the Brillouin zone. All spectra were normalized to a unit area. The calculated spectrum of E symmetry (a) coincides with the density spectrum of single-phonon states expanded by a factor of two along the frequency scale.

points of the Brillouin zone in the spectrum of E symmetry. Therefore, we can predict that the density spectrum of unperturbed AIV $\omega_6 + \omega_6(E)$ states is identical to the density of single-phonon ω_6 states that has been expanded by a factor of 2 along the frequency scale. In the multipole-multipole interaction approximation the dispersion $\omega_6(\mathbf{k})$ is determined by the derivative of the static octupole moment I_3 with respect to the rotation angle ϕ . Consequently, by determining from the spectrum of $\omega_6 + \omega_6(E)$ transitions the width T_6 of the spectrum of single phonon states, we can find $\partial I_3 / \partial \phi$ and calculate the quantity I_3 . The equations needed to calculate $\omega_6(\mathbf{k})$ were taken from Ref. 10. As a result of the calculation, we obtained the following relationship between T_6 (cm^{-1}) and I_3 ($\text{C} \cdot \text{m}^3$):

$$T_6 = 5,05 \times 10^{52} \frac{I_3^2}{\omega_6 M a^7} .$$

Here ω_6 is the midfrequency (cm^{-1}), a is the lattice constant (nm), and M is the moment of inertia of the ion ($\text{kg} \cdot \text{m}^2$). The obtained relationship is valid for the δ phase as well as the γ phase of ammonium-halide crystals. In the calculation we ignored the polarizability of the ions, which leads to an indirect interaction, since it is small at the frequency ω_6 . In addition, an indirect ω_6 interaction via dipole-active vibrations is allowed only for phonons of M_5 and X_5 symmetry and has no effect on the frequencies of the zone limits, which correspond to phonons of M_4 and X_4 symmetry (see Fig. 1a).

The cutoff frequencies and the value of T_6 used for the calculation were taken from the $\omega_6 + \omega_6(E)$ spectrum (Fig. 1a). The good agreement obtained between the calculated and experimental cutoff frequencies of the $\omega_6 + \omega_6(F_2)$ spectrum (Fig. 1b) confirms the correctness of the model used. Histograms of the density of two-phonon states of E symmetry [$\omega_{6i}(\mathbf{k}) + \omega_{6i}(-\mathbf{k})$] and of F_2 symmetry [$\omega_{6i}(\mathbf{k}) + \omega_{6j}(-\mathbf{k})$, where $i \neq j$] were calculated from the dispersion $\omega_6(\mathbf{k})$; this made it possible to perform an additional test of the model and to estimate the AIV constants. To do this, we reconstructed the densities of $\omega_6 + \omega_6(E)$ and $\omega_6 + \omega_6(F_2)$ states, which were unperturbed by AIV, from the experimental RS spectra. The calculation was made in the point-interaction model of quasiparticles.⁶⁻⁸ The curves obtained with the AIV constants $\Delta_{66}^E = -17 \text{ cm}^{-1}$ and $\Delta_{66}^{F_2} = -20 \text{ cm}^{-1}$ are represented by the dashed lines in Fig. 1 and, as one can see, they agree satisfactorily with the calculated histograms (the discrepancy in the region of $2M_5$ transitions is presumably caused by the indirect interaction).

The value obtained by us for the octupole moment of an ammonium ion is $J_3 = 1.6 \times 10^{-49} \text{ C} \cdot \text{m}^3$; this corresponds to an effective charge of 0.29 of the elementary charge of hydrogen. The simplest estimate of the pseudospin interaction energy in a rigid (unpolarized) lattice gives $J = 6(J_3^2/a^7) = 56 \text{ cm}^{-1}$. Hence, the temperature of the PT, calculated for a simple cubic Ising lattice in accordance with Ref. 11, is $T_c = J/0.22 \cdot k_B = 360 \text{ K}$. Considering the approximate nature of the estimate of T_c , we must regard its agreement with the true value of $T_c = 243 \text{ K}$ to be satisfactory.

1. Y. Yamada, M. Mori, and Y. Noda, *J. Phys. Soc. Jap.* **32**, 1565 (1972).
2. A. Huller and J. W. Kane, *J. Chem. Phys.* **61**, 3599 (1974).
3. V. G. Vaks and V. E. Schneider, *Phys. Status Solidi A* **35**, 61 (1976).
4. E. Cowley, *Phys. Rev.* **B3**, 2743 (1971).
5. H. C. Teh and B. N. Brockhouse, *Phys. Rev.* **B3**, 2733 (1971).
6. E. I. Rashba, *Zh. Eksp. Teor. Fiz.* **50**, 1064 (1966) [*Sov. Phys.-JETP* **23**, 708 (1966)].
7. V. M. Agranovich, *Fiz. Tverd. Tela.* **12**, 562 (1970) [*Sov. Phys.-Solid State* **12**, 430 (1970-71)].
8. M. V. Belousov, D. E. Pogarev, and A. A. Shlutin, *Fiz. Tverd. Tela* **18**, 521 (1976) [*Sov. Phys.-Solid State* **18**, 300 (1976)].
9. A. L. Shuvalov and V. S. Gorelik, Preprint FIAN, No. 3, 1979.
10. N. Neto *et al.*, *Chem. Phys.* **29**, 167 (1978).
11. M. E. Fisher, *Rep. Prog. Phys.* **30**, 615 (1967).

Translated by Eugene R. Heath

Edited by S. J. Amoretty