Light Scattering in $Cd_2Nb_2O_7$ at Phase Transitions

N. N. KOLPAKOVA, G. A. SMOLENSKY, I. G. SINY, E. G. KUZMINOV, S. D. PROKHOROVA, V. D. MIKVABIA and I. E. MYLNIKOVA

A. F. Ioffe Physico-Technical Institute of the Academy of Sciences of the USSR, 194021 Leningrad, USSR

The Raman spectra of $Cd_2Nb_2O_7$ were measured over the tempereture range $10 \sim 500$ K. The results obtained are discussed in connection with the ferroelectric phase transitions in $Cd_2Nb_2O_7$. The possibility of the commensurate-incommensurate phase transition in these crystals is suggested. At room temperature the elastic constants of $Cd_2Nb_2O_7$ are reported.

It is known that Cd₂Nb₂O₇ undergoes successive phase transitions at $T_1 = 206$ K, $T_2 =$ 185 K and $T_3 = 85 \text{ K.}^{1-4}$ Below $T_2 \text{ Cd}_2 \text{Nb}_2 \text{O}_7$ is of ferroelectric phase.¹⁻³⁾ The dielectric measurements showed³⁾ that another polar phase appearing below 200 K preceded this phase. Yet crystal symmetry at the new phases and the character of the both ferroelectric transitions in Cd₂Nb₂O₇ remains to be discovered. In this paper, the lattice dynamics of $Cd_2Nb_2O_7$ crystals at phase transitions is investigated. The first results on Raman scattering measurements in these crystals were published in.⁵⁾ Moreover, in paraphase the infrared (IR) active mode which softens as T_2 is approached from above was observed.⁶⁾ Single crystals of $Cd_2Nb_2O_7$ were grown by the flux method.³⁾

The Raman spectra of Cd₂Nb₂O₇ were measured over the temperature range $10 \sim 500$ K in the frequency region $0 \sim 900$ cm.⁻¹ Figure 1 shows the spectra observed. At room temperature. The middle group consists of one mode of $E_{\rm g}$ species (314 cm⁻¹) and two modes of $T_{2\rm g}$ species (274 and 337 cm^{-1}). The third group (440 cm⁻¹) corresponds to the A_{1g} species and the first one $(0 \sim 240 \text{ cm}^{-1})$ seems to be a combination of A_{1g} , E_g and T_{2g} species. As the factor-group analysis for Cd2Nb2O7 crystals of the space group Fd3m has it, the A_{1g} , E_{g} and 4 T_{2g} species are Raman active.^{5,6)} Figure 1 shows the experimental number of modes to exceed that predicted by the analysis. Probably, at room temperature the space group of $Cd_2Nb_2O_7$ does not belong to Fd3m, which was recently revealed for other pyrochlore-type crystals as well.⁷⁾ It is the first-order Raman spectrum that is observed at room temperature. Within $200 \sim 500$ K the number of lines in the

spectrum is unchanged and this leads to believe the crystal to belong to the cubic system over this temperature range.

The phase transitions at T_1 , T_2 and T_3 cause considerable modifications of the basic spectrum: the lines of the spectrum are splitted and additional lines appear, with an anomalous temperature behaviour of both intensity and frequency shifts being observed for some of them. To illustrate these changes the spectrum at 10 K is presented in Fig. 1. Below T_1 the Raman spectrum as a whole is altered most considerably. The polarized Raman measurements are obscured by domains, the latter being detectable with a polarizing microscope rather well. This means that the crystal symmetry





below T_1 is lowered. Moreover, the inversion centre is lost the ferroelectric phase. Consequently, the IR active modes are expected to be also Raman active.

Since the low lying IR and Raman active modes are of great interest for lattice dynamic studies let us discuss the low frequency spectra in details. The IR soft-mode frequency is about 15 cm^{-1} at 200 K.⁶⁾ Fig. 2(a) shows that below T_1 the wing of the Rayleigh line is very broad and extends to about 20 cm^{-1} . The temperature alteration of it within $10-20 \text{ cm}^{-1}$ leads to suppose that the mode corresponding to the IR soft mode is present in the spectra. This mode softens as T_2 is approached from above, Below T_2 the frequency of this mode increases again (Fig. 2(b), (c)). At 170 K the mode is well-defind at 12 cm^{-1} as a shoulder of the Rayleigh line and at 145 K its frequency is about 40 cm^{-1} . Within 100-185 K the frequency versus temperature dependence of the soft mode (Fig. 3) is described as $\omega_s = 1.46 (185 - T)^{0.47}$, in a good approximation. The presence of soft modes both above and below T_2 enables to classify the ferroelectric phase transition at T_2 as a proper one.

Below T_1 the Raman scattering intensity increases in the region 2–10 cm⁻¹ as well, which seems to be due to the fact that an additional low-frequency mode has appeared (Fig. 2(a), (c)). Its frequency increases very slowly as the temperature goes down and is about 5 cm⁻¹ at 145 K. This mode is probably unaffected by the



Fig. 2. Raman spectra in the frequency region $0 \sim 25$ cm⁻¹ below phase transitions at T_1 and T_2 (spectral resolution ± 1 cm⁻³)



Fig. 3. Frequency shift and linewidth versus temperature of the soft mode appearing below T_2 .

phase transition at T_2 . It is present in the spectra down to T_3 and disappears below T_3 . So, this mode is supposed to soften on approaching T_1 from below. Since above T_1 no Raman or IR active soft modes of low frequency were detected Cd₂Nb₂O₇ is considered to be of improper ferroelectric type below T_1 .

Below T_3 in the spectra two low frequency modes with an anomalous temperature behaviour exist. The results are shown in Figs. 4 and 5. As the temperature increases the 41 cm⁻¹-mode at 10 K is found to soften. At about 30 K the 21 cm^{-1} -mode appears. The interaction between the two modes leads to level repulsion and intensity transfer somewhere between 65-75 K. As the temperature goes up again the mode of lower frequency softens toward T_3 whereas the mode of higher frequency is stabilized near 24 cm^{-1} . The similar temperature behaviour of low frequency modes has been reported in some ferroelectrics⁸⁻¹⁰ at the commensurate-incommensurate phase transitions. On the basis of this analogy it may be supposed that $Cd_2Nb_2O_7$ suffers the commensurate-incommensurate phase transition at T_3 . In this case somewhere between 65-75 K (Fig. 5) another phase transition (incommensurate-commensurate one) is expected to take place. The soft mode below T_3 should correspond to the amplitude mode in the incommensurate phase. It should be noticed that below about 65 K additional lines appear in the spectra (for example, the 65 cm^{-1} -mode at 10 K, its intensity decreasing fast as the temN. N. KOLPAKOVA, G. A. SMOLENSKY, I. G. SINY, E. G. KUZMINOV, S. D. PROKHOROVA, V. D. MIKVABIA and I. E. MYLNIKOVA



Fig. 4. Raman spectra in the region $0 \sim 50$ cm⁻¹ below phase transition at T_3 . The spectrum at 76 K is reduced 1.5 times as compared to the spectra at the other temperatures. Spectral resolution \pm 1.5 cm⁻¹.



Fig. 5. Frequency shifts versus temperature of two modes appearing below T_3 .

perature increases). Perhaps, at the latter transition (incommensurate-commensurate phase) the crystal symmetry is lowered once again.

For elastic property measurements we used two differently oriented samples: with (111), (110), $(1\overline{1}1)$ planes and with (111), (110), (112)planes. In the first case light scattering by longitudinal and pure shear modes is studied, and in the second one by a transverse mode degenerated in the (111) plane. The refractive indices n=2.33 has been measured for $\lambda =$ 4880 Å and the density ϱ is equal to 6.90 gcm⁻³ according to our measurements. The following values of elastic costants for the cubic phase were obtained: $c_{11} = 3.31$, $c_{12} = 1.26$ and c_{44} = 1.03 (in 10^{10} Nm⁻²). Photoelastic constants were estimated by comparison of the phonon intensity in $Cd_2Nb_2O_7$ and in $Gd_2(MoO_4)_3$ where photoelastic constants are known:¹¹⁾ p_{44} $= 0.030, p_{11} - p_{12} = 0.057.$

References

- 1) F. Jona, G. Shirane and R. Pepinsky: Phys. Rev. 98 (1955) 903.
- A. de Bretteville and R. Oman: Bull. Am. Phys. Soc. 2) Ser. II, 4 (1959) 62.
- 3) G. E. Golovshchikova, V. A. Isupov and I. E. Mylnikova: FTT 13 (1971) 2349; V. A. Isupov, G. I. Golovshchikova and I. E. Mylnikova : Ferroelectrics 8 (1974) 507.
- 4) A. Pietraszko and L. A. Shuvalov: Abstracts of the Fourth International Meeting on Ferroelectricity, Leningrad, USSR, September, 1977.
- R. V. Pisarev, I. G. Sinii, E. G. Kusminov and I. E. 5) Mylnikova: Izv. Akad. Nauk SSSR, Ser. Fiz. 41 (1977) 588.
- 6) Ju. M. Poplavko, A. S. Knjazev, V. G. Tsykalov and L. P. Pereverzeva: Ferroelectrics 21 (1978) 399; Ju. M. Poplavko, A. S. Knjazev, V. I. Zaharov, V. G. Tsykalov and V. V. Alekseev: FTT 16 (1974) 713.
- 7) J. Pannetier: Solid State Commun. 34 (1980) 405.
- M. Wada, A. Sawada and Y. Ishibashi: J. Phys. Soc. 8) Jpn. 47 (1979) 1185.
- M. Takashige, T. Nakamura, M. Udagawa, S. 9) Kojima, S. Hirotsu and S. Sawada: J. Phys. Soc. Jpn. 48 (1980) 150.
- 10) S. Kojima, M. Takashige, T. Nakamura, K. Ohi, H. Kakinuma: Solid State Commun. 31 (1979) 755.
- 11) J. Sapriel and R. Vacher : J. Appl. Phys. 4 (1977) 1191.

34