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Raman study on symmetry analysis in NdGaO₃

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Abstract

Raman scattering spectra of NdGaO₃ have been studied between 21 K and room temperature. Well resolved 18 phonons were observed and assigned to the irreducible representation of the *Pbnm* space group. In addition to the phonon modes, we have observed electronic transitions between the crystal-field split levels of the Nd³⁺ ion (⁴I_{9/2}) at lower temperatures. At temperatures higher than approximately 50 K, we have observed luminescence concerning the transition from the ²K_{15/2} or ²G_{9/2} state to the ground state ⁴I_{9/2} of the Nd³⁺ ion. No phase transition has been observed in this crystal below room temperature.

1. Introduction

Neodymium gallate, NdGaO₃, with a perovskite structure is widely used as a substrate in making a thin film of high-*T_c* superconductors (HTS) [1]. The lattice constant and coefficient of its thermal expansion match HTS materials such as YBa₂Cu₃O₇ and enable us to prepare an ideal superconductor thin film. In particular, it was believed to be stable over a wide temperature range without pronounced discontinuity. Savytskii *et al* [2], however, found a thermal anomaly near 200 K in the temperature dependence of the thermal expansion coefficient, the dielectric loss angle and the magnetic susceptibility. Vasylechko *et al* [3] investigated the crystal structure at 100 and 293 K, and they found that both structures differ considerably in the character of the thermal motions of cations in NdGaO₃. There is increasing interest in this crystal structure over the range of low temperature to room temperature.

In spite of the numerous studies performed, the crystal structure of NdGaO₃ is still a matter of some controversy. In a previous work, the crystallographic structure of NdGaO₃ was proposed to be the centrosymmetric orthorhombic group *Pbnm* (D_{2h}¹⁶) at room temperature by Geller [4] using x-ray powder photography. However, Brusset *et al* [5] determined NdGaO₃ to be the non-centrosymmetric group *Pbn*2₁ (C_{2v}⁹) by x-ray diffraction using a single crystal. Later studies based on neutron diffraction have confirmed the non-centrosymmetric

structure [6, 7]. On the other hand, x-ray powder diffraction [8] and Raman scattering [9] suggested the centrosymmetric structure. Recently Marti *et al* [10] refined their neutron data and found similar reliability factors using the centrosymmetric orthorhombic group $Pbnm$.

The Raman scattering method, which is sensitive to crystal symmetry, is a powerful technique to measure the structural anomaly. The irreducible representation Γ for the $Pbnm$ space group of the Raman-active modes at the zone centre can be decomposed as follows by a factor group analysis [11]:

$$\Gamma(Pbnm) = 7A_{1g} + 7B_{1g} + 5B_{2g} + 5B_{3g}. \quad (1)$$

For the $Pbn2_1$ space group it is [12]

$$\Gamma(Pbn2_1) = 14A_1 + 15A_2 + 14B_1 + 14B_2. \quad (2)$$

Until the recent x-ray and neutron diffraction studies, it was difficult to demonstrate the experimental differences of both space groups clearly. However, the Raman scattering method will make clear which space groups $NdGaO_3$ belongs to, as shown by equations (1) and (2). Savytskii *et al* [9] and Sanjuan *et al* [13] measured polarized Raman spectra for $NdGaO_3$ at room temperature, and the symmetry was determined on the basis of the space group $Pbnm$. However, the measurement of polarized Raman scattering has not been carried out yet in the temperature range near 200 K. In this study, a polarized Raman scattering experiment using single-crystal $NdGaO_3$ has been carried out from a low temperature of 21 K to room temperature to clarify the crystal symmetry.

2. Experimental

A single crystal of $NdGaO_3$ was transparent with a greenish brown tinge and its purity was better than 99.995% (prepared by FIT Co.). It was cut into a rectangular shape oriented along the a , b and c axes ($7 \times 6 \times 8$ mm³ in size) and its surface was optically polished. The c axis was parallel to the longest direction.

Polarized Raman spectra were measured from about 21 K to room temperature in a right-angle scattering geometry. The excitation source was a 4880 Å line of an Ar⁺ ion laser at a power level of 100–200 mW. Most measurements were made at 100 mW power level to avoid local heating of the sample. The scattered light was analysed by a double monochromator (CT-1000D, JASCO Co.) having a spectral resolution of about 2 cm⁻¹. The sample was mounted inside a closed-cycle He-gas refrigerator (U102AW, DAIKIN Co.). Temperatures were measured with a gold–iron–chromel thermocouple and controlled by a temperature controller (DB1000, CHINO Co.). The wavenumber was calibrated with a plasma line of the Ar⁺ ion tube. The accuracy of the wavenumber was about 1 cm⁻¹.

Specific features of the absorption spectra of the Nd³⁺ ions have complex fine structures towards changes in the Nd³⁺ ion environment [14]. UV–visible spectroscopy provides information on the electronic structure. The transmission spectra around the 4880 Å line were measured in the temperature range of 9.1–294.8 K with a CARY4 spectrophotometer (Varian Co.) equipped with a liquid helium cryostat (CF-1204, Oxford Instruments Co.).

3. Results

3.1. $Z(YY)X$ and $X(ZZ)Y$ — $7A_{1g}$ modes ($Pbnm$) or $14A_1$ modes ($Pbn2_1$)

Figures 1 and 2 show the polarized Raman spectra measured in a right-angle scattering geometry with $Z(YY)X$ and $X(ZZ)Y$ arrangements parallel to the crystallographic axes. According to the phonon scattering selection rules, it is expected that curves in figures 1 and 2

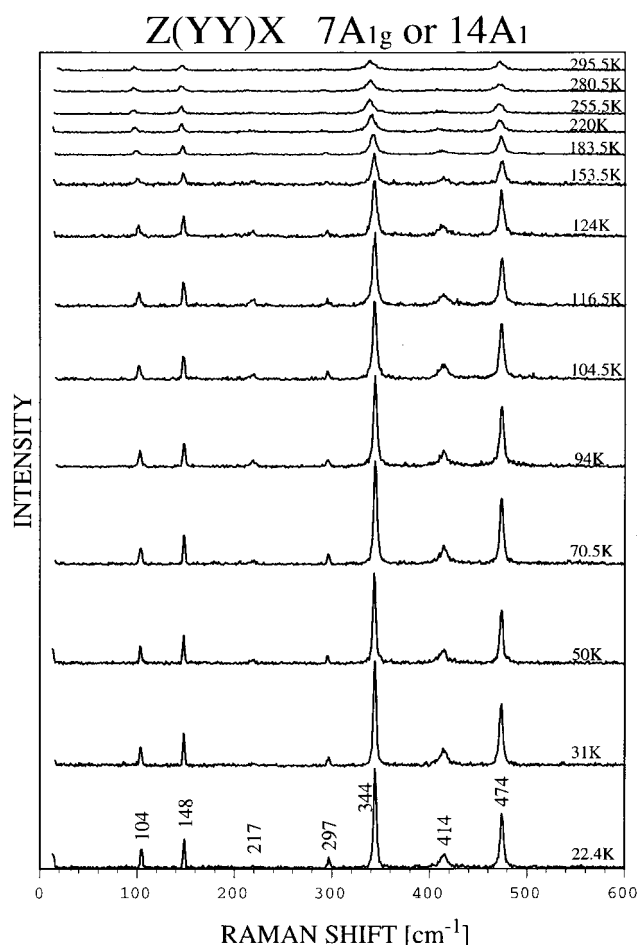


Figure 1. Raman spectra of NdGaO₃ at different temperatures in the Z(Y \bar{Y})X scattering configuration. The laser wavelength for all spectra is 488.0 nm.

will be an irreducible component of the A_{1g} symmetry in the *Pbnm* space group or the A₁ symmetry in the *Pbn2₁* space group. It can be seen that bands at 104, 148, 217, 297, 344, 414 and 474 cm⁻¹ are observed. Additionally, bands around 60 and 171 cm⁻¹ arise in the temperature range 100–200 K, as marked with an arrow in figure 2.

3.2. Z(X \bar{Y})X—7B_{1g} modes (*Pbnm*) or 15A₂ modes (*Pbn2₁*)

Figure 3 shows the Z(X \bar{Y})X polarization spectra, which demonstrated bands at 89, 155, 183, 219, 365 and 453 cm⁻¹. The intensity of the band at 183 cm⁻¹ is too weak to measure above 100 K, as shown in figure 3(b).

3.3. Z(XZ)X—5B_{2g} modes (*Pbnm*) or 14B₁ modes (*Pbn2₁*)

Figure 4 shows the Z(XZ)X polarization spectra, which demonstrated bands at 91, 146, 336, 412 and 466 cm⁻¹. As mentioned for X(ZZ)Y, bands around 60 and 171 cm⁻¹ appear in the temperature range 100–200 K as marked with an arrow in figure 4(a). Moreover, a weak band

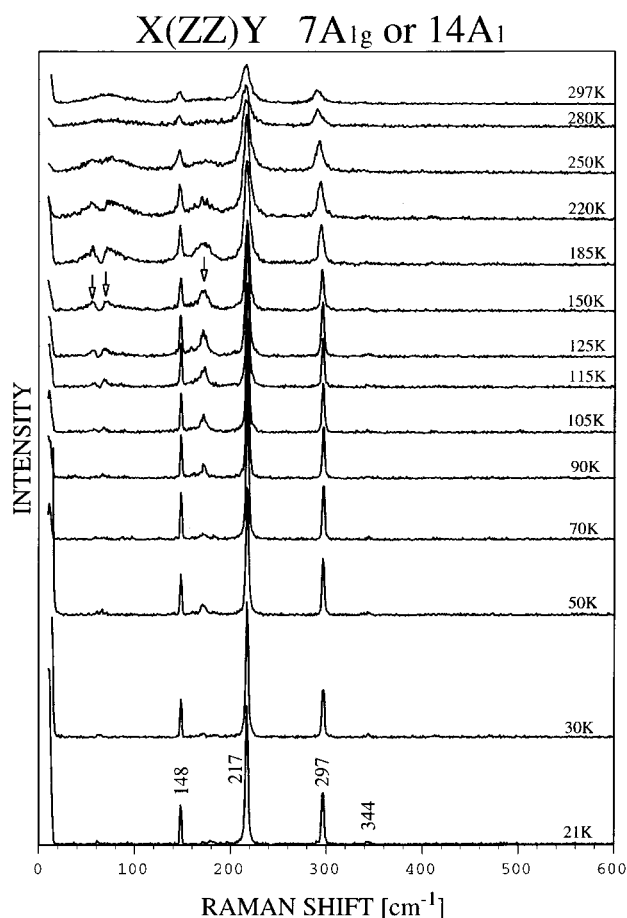


Figure 2. Raman spectra of NdGaO_3 at different temperatures in the $X(ZZ)Y$ scattering configuration.

at 425 cm^{-1} can be seen in the low temperature region in figure 4(b). At higher temperatures above 100 K, the 425 cm^{-1} band can hardly be observed as well as the 183 cm^{-1} band in the (XY) polarized configuration.

3.4. $Z(YZ)X$ — $5B_{3g}$ modes ($Pbnm$) or $14B_2$ modes ($Pbn2_1$)

Figure 5 shows the $Z(YZ)X$ polarization spectra, with observed bands at 90, 171, 183, 206 and 355 cm^{-1} . The bands around 60 cm^{-1} were also observed in the temperature range from 100–200 K, though the intensities were very weak as marked with an arrow in figure 5(b).

Bands with the following three types of temperature dependence were observed.

- (1) Those that can hardly be observed at room temperature due to the strong temperature dependence: (XY) 89 and 183 cm^{-1} , (XZ) 91 and 425 cm^{-1} , (YZ) 90 and 183 cm^{-1} .
- (2) Those that clearly appear at 100–200 K without being observed at the lowest temperature, and then decrease as the temperature increased: (ZZ) 59, 66 and 171 cm^{-1} , (XZ) 59, 65 and 171 cm^{-1} , (YZ) 58 and 66 cm^{-1} .
- (3) Those that can be observed with broadening monotonically over the whole temperature range.

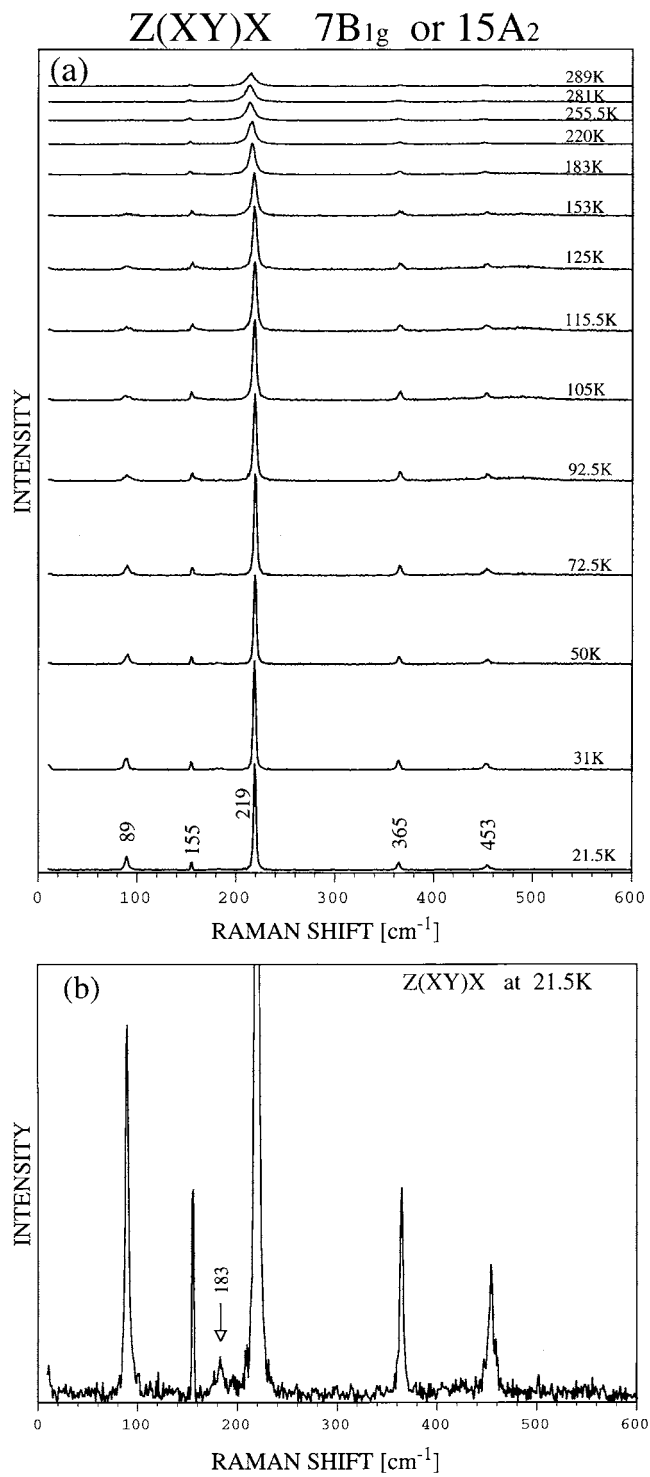


Figure 3. Raman spectra of NdGaO₃ (a) at different temperatures and (b) at 21.5 K in the Z(XY)X scattering configuration.

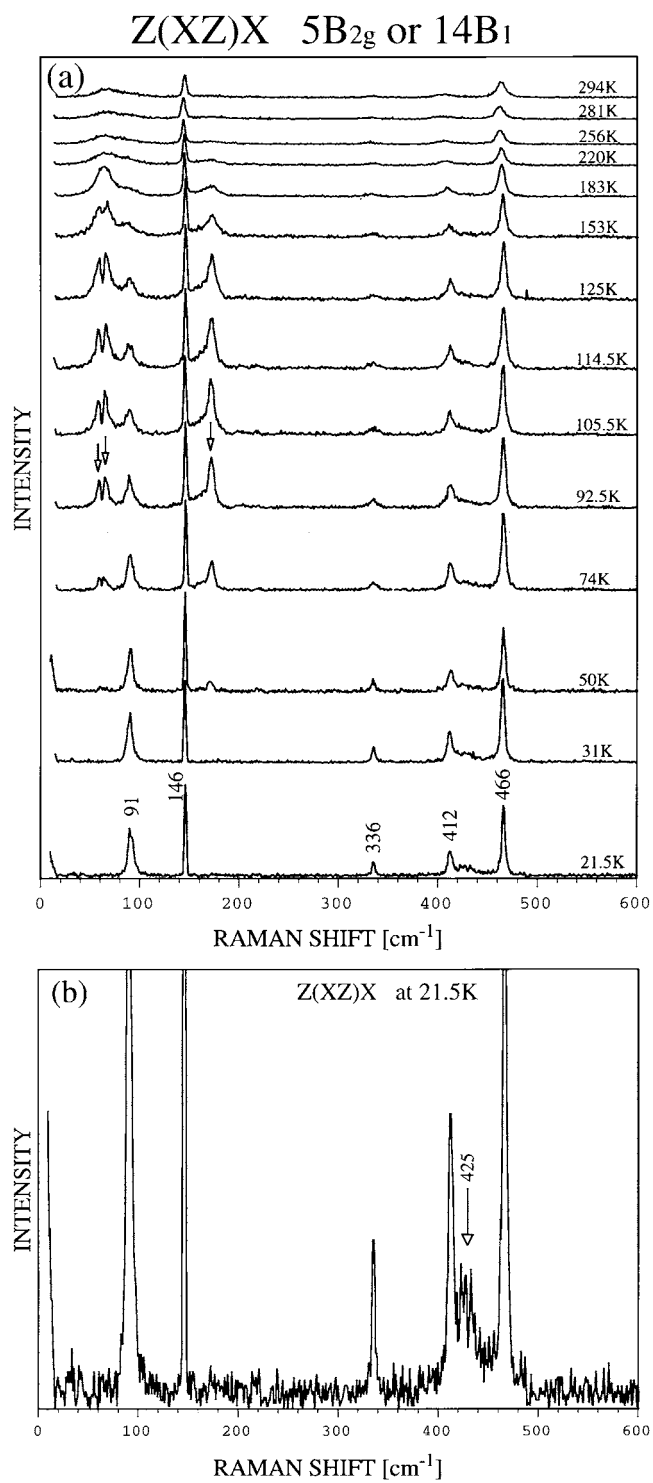


Figure 4. Raman spectra of NdGaO₃ (a) at different temperatures and (b) at 21.5 K in the Z(XZ)X scattering configuration.

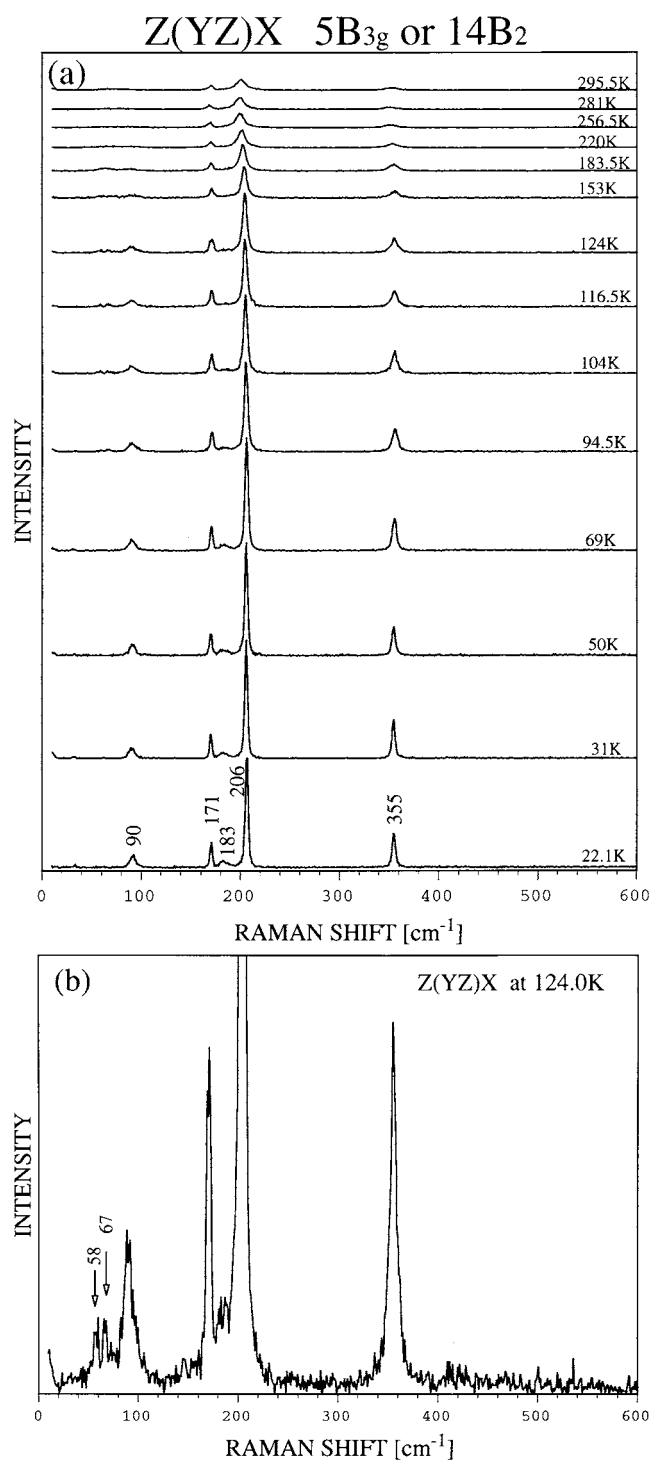


Figure 5. Raman spectra of NdGaO₃ (a) at different temperatures and (b) at 124.0 K in the Z(YZ)X scattering configuration.

4. Discussions

4.1. The bands with temperature dependence (1)

The vibrational nature of transitions excited in a crystal by the ordinary Raman effect is not essential, and a similar effect could be observed for transitions between electronic states with energies E_i and E_f by absorption of a photon of energy $\hbar\omega_0$ and emission of one with energy $\hbar\omega_1$, where $\hbar(\omega_0 - \omega) = E_i - E_f$ [15]. Raman scattering from the electronic states has been found to be a useful method for determining the low-lying electronic energy states of rare-earth ions in various complexes [16–18]. Using the neutron scattering technique, Podlesnyak *et al* [6] investigated the crystal-field split levels of the ground-state J multiplet $^4I_{9/2}$ of the Nd^{3+} ions ($4f^3$) in NdGaO_3 . The ten-fold degeneracy of the ground-state $^4I_{9/2}$ of the Nd^{3+} ions is split by the crystal field into five Kramers doublets. They determined that the energies of all possible excitations from the lowest Stark level to the other Stark levels are 92, 181, 425 and 548 cm^{-1} [6]. Our bands obtained at 89 and 183 cm^{-1} in the (XY) spectrum, at 91 and 425 cm^{-1} in the (XZ) spectrum and at 90 and 183 cm^{-1} in the (YZ) spectrum exhibit strong temperature broadening as the temperature increased. Therefore we identified these bands as the electronic f – f transition of the Nd^{3+} ions.

4.2. The bands with temperature dependence (2)

Extraordinary bands around 60 and 171 cm^{-1} in the (ZZ) , (XZ) and (YZ) polarized configurations were clearly observed in the temperature range 100–200 K. In order to examine the temperature dependence of the scattering intensities, these Raman spectra were decomposed using the Lorentz functions. Figure 6 shows one example of the decomposed XZ polarized spectra at 114.5 K. The intensities of the bands around 60 and 171 cm^{-1} were normalized using the first-order Raman band at 146 cm^{-1} . Figure 7(a) shows the temperature dependence of the relative intensity of the sum of the two bands at 59 and 66 cm^{-1} , since the two bands around 60 cm^{-1} could not be separated above 183 K, as shown in figure 4. It takes a maximum value near 200 K. Table 1 summarized the temperature dependence of Raman scattering efficiencies for one- and two-phonon processes. The ratio of the scattering efficiencies should become constant, as a function of temperature, when the two components are based on first-order Raman scattering. On the other hand, a ratio of the second-order scattering efficiency to the first-order one should be increased monotonically with temperature in proportion to the Bose–Einstein function ν . There is no discrepancy to discuss the sum of the two bands for examining those characters: (1) if both are first order, the normalized values will be constant with temperature, (2) if one is first order and the other is second order or both are second order, the normalized values will be increased with temperature, depending on the second-order character. The present temperature dependence in figure 7(a) proves that the bands around 60 cm^{-1} have neither first nor second-order Raman scattering character. On the other hand, figure 7(b) shows that the relative intensity of the band at 171 cm^{-1} normalized by 146 cm^{-1} was intense near 100 K with maximum value. Thus, the band at 171 cm^{-1} is also concluded to be neither first- nor second-order Raman scattering.

Figures 8(a)–(c) show the Raman spectra of the (ZZ) , (XZ) and (YZ) polarized configurations in the -250 – 250 cm^{-1} frequency range, respectively. Several weak bands observed on the anti-Stokes side could be convincingly shown to be first order and electronic Raman transitions. The other extraordinary bands around 60 and 171 cm^{-1} were not observed on the anti-Stokes side of the (ZZ) and (XZ) polarized configurations (figures 8(a) and (b)). It would be possible that these extraordinary bands concerned luminescence. The band at 171 cm^{-1} in the (YZ) polarized configuration can be seen on the anti-Stokes side in figure 8(c),

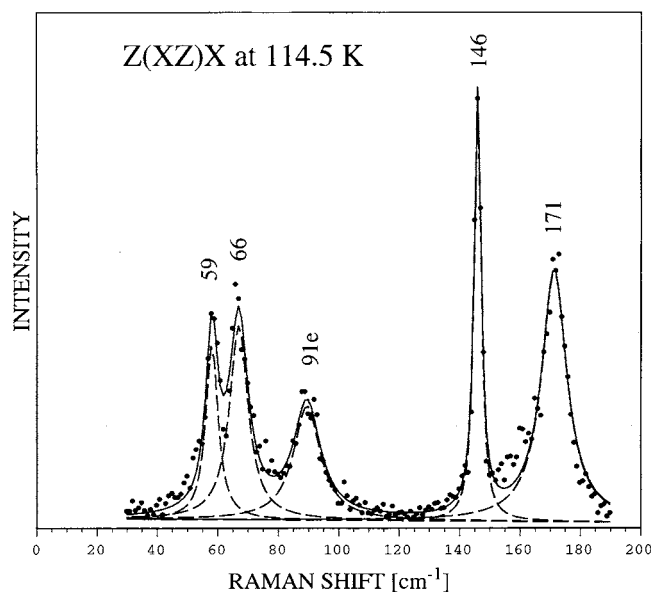


Figure 6. Comparison of an experimental spectrum at 114.5 K in $Z(XZ)X$ (full circle) with a calculated one (full curve) using Lorentz functions (broken curve). The electronic Raman band is labelled by 'e'.

Table 1. Temperature dependence of Raman scattering factors. ($\nu_j = [1 - \exp(-\hbar\omega_{jq}/k_B T)]^{-1}$).

Transition process		Stokes-Raman scattering efficiency
One-phonon		$\nu_j + 1$
Two-phonon	Overtone band	$\nu_j^2 + 3\nu_j + 2$
	Sum band	$1 + \nu_j\nu_k + \nu_j + \nu_k$
	Difference band	$\nu_j\nu_k + \nu_k$

indicating a phonon mode. In order to investigate the electronic structures around an incident 488 nm laser line, the temperature dependence of the absorption spectra was measured. Figures 9(a) and (b) show a temperature dependence of the absorption spectra for the electric polarized vector E parallel to the c -crystallographic axis (Z) and perpendicular to the c axis (Z), respectively. According to the energy-level diagram of the Nd³⁺ ion [14], one expects to find transitions to levels of the $^4I_{9/2}$ and $^2K_{15/2}$ states in that region. Transitions from the lowest level of the ground state $^4I_{9/2}$ to the $^2K_{15/2}$ state are observed between 477.5 and 478.5 nm at 10.2 K (marked with A). The absorption spectra taken at higher temperatures exhibit additional peaks (marked with B, C, D, E), which correspond to transitions of another crystal-field level. Schematic electron transitions of Nd³⁺ are described in figure 9(a). In the $E \parallel Z$ polarization, it can be seen that weak bands are observed at 486.0 and 489.6 nm (marked with *). Though we cannot perform an accurate assignment on these bands, it would be a transition to the higher energy level belonging to the $^2K_{15/2}$ or $^2G_{9/2}$ states, which may have the polarization property in the Z direction. The extraordinary band around 60 cm⁻¹ seems to be attributed to luminescence between the 488.0 nm laser line and the band at 489.6 nm, having a difference energy of about 67 cm⁻¹, and it seems to split the intensity due to its self-absorption. It is consistent with observing only in the (ZZ), (XZ) and (YZ) configurations as including the

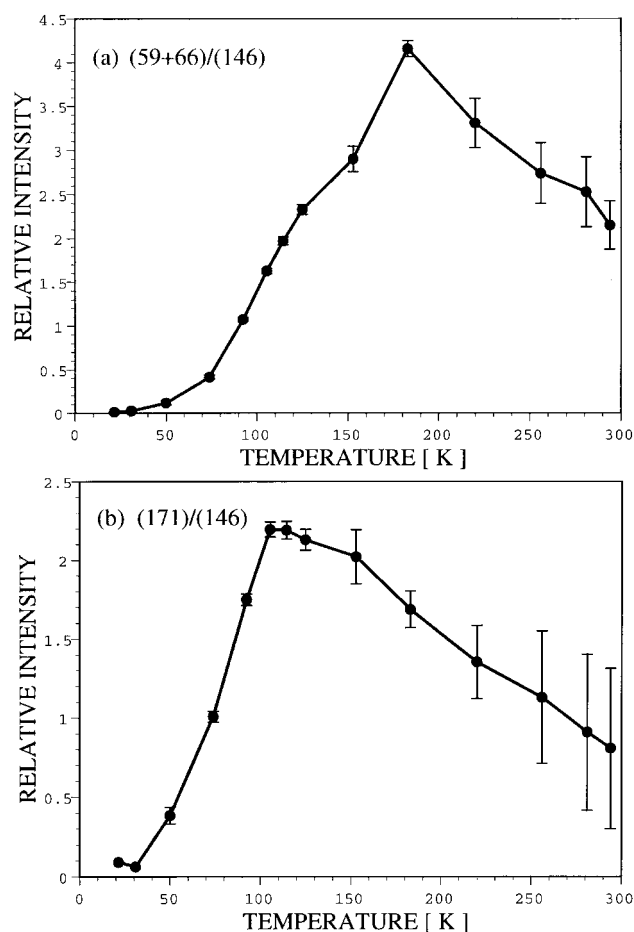


Figure 7. Temperature dependence of the relative intensities for (a) the band around 60 cm^{-1} and (b) at 171 cm^{-1} .

Z component. Moreover, figure 10 shows the temperature dependence of the optical density for the absorption band at 489.6 nm . It can be seen that the absorption increases drastically with an increase in temperature from $\sim 100\text{ K}$. The temperature dependence of the intensity of the 60 cm^{-1} band is directly correlated with that of the absorption band at 489.6 nm in the lower temperature region, and above 200 K it can be broadening due to the strong effect of temperature. Though a clear absorption which corresponded to the band at 171 cm^{-1} was not determined, we concluded that it would consist of an origin equal to the band around 60 cm^{-1} .

4.3. Comparison with previous studies

The observed mode frequencies are summarized in table 2. The measurement of polarized Raman spectra has also been made by Savytskii *et al* [9] and Sanjuan *et al* [13] at room temperature. Crystal axes defined by Savytskii *et al* [9] are consistent with our study. From the relative intensity for each band, Sanjuan *et al* [13] may have taken the reverse X and Y crystal axes to us. Their (XZ) and (YZ) polarized configurations may correspond to the (YZ) and (XZ) configurations in our study, respectively. These previous studies are

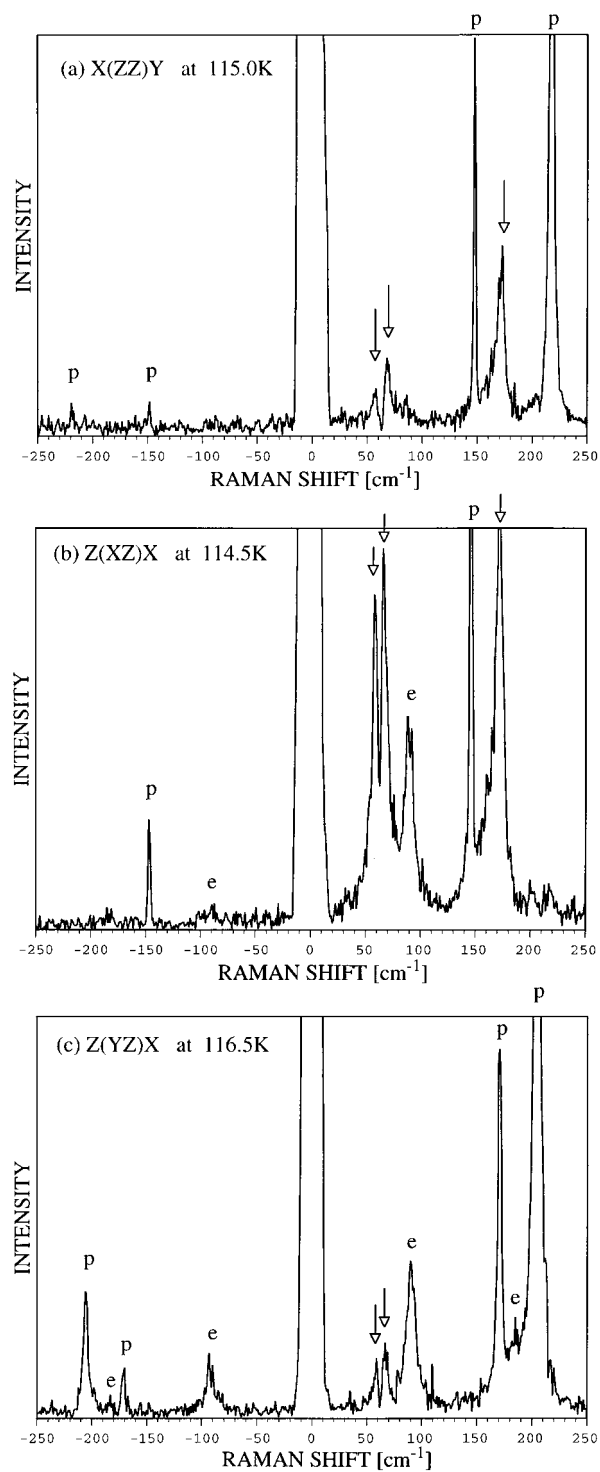


Figure 8. Raman spectra in (a) $X(ZZ)Y$, (b) $Z(XZ)X$ and (c) $Z(YZ)X$ at the frequency range between -250 and 250 cm^{-1} . The labels ' p ' and ' e ' indicate the vibronic and electronic Raman transitions, respectively.

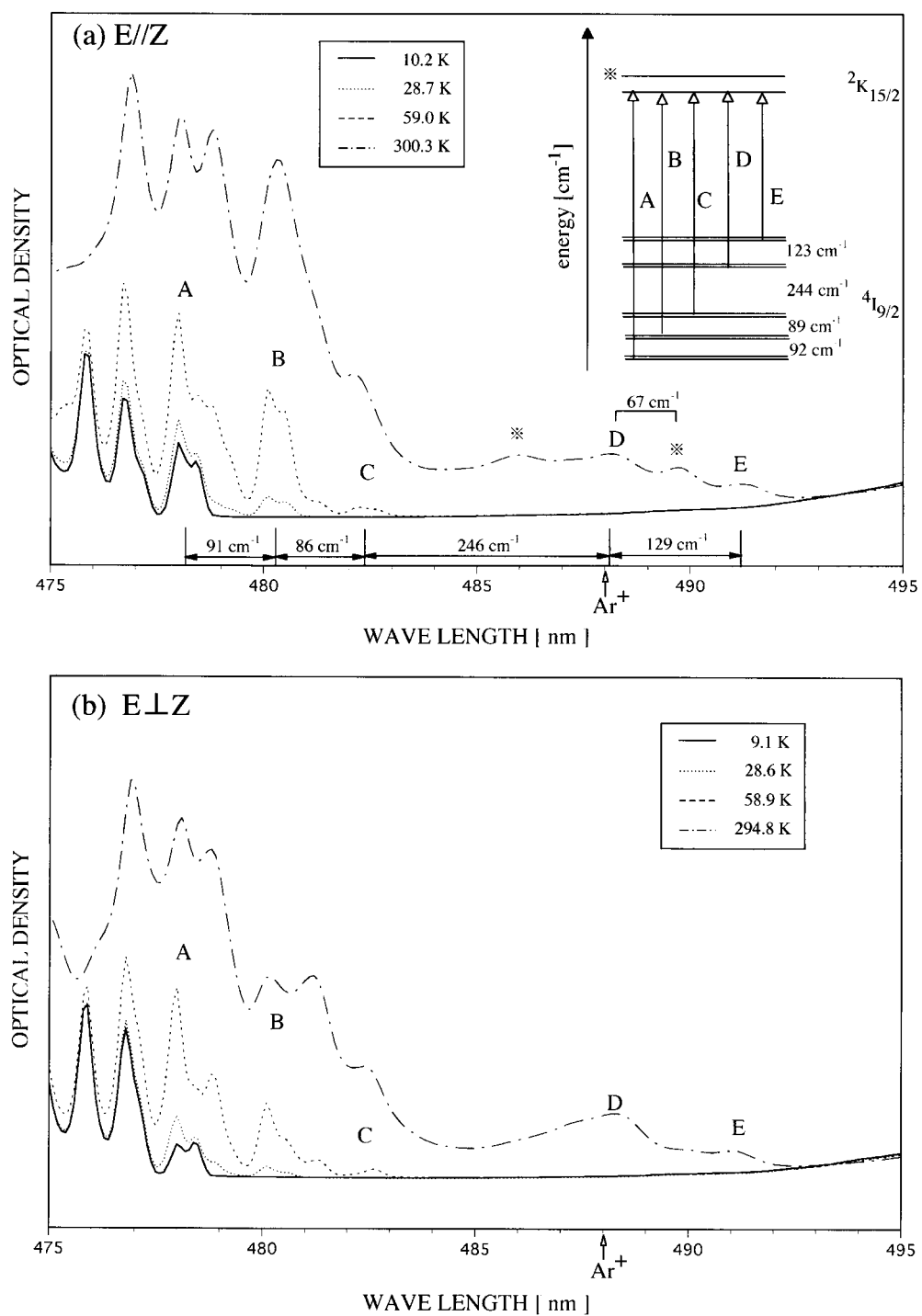


Figure 9. The absorption spectra of Nd^{3+} in $NdGaO_3$ at several temperatures with a energy diagram: (a) $E // Z$ and (b) $E \perp Z$. Numbers on the right in a energy diagram give the splitting energy of the $4I_{9/2}$ manifold of Nd^{3+} [6].

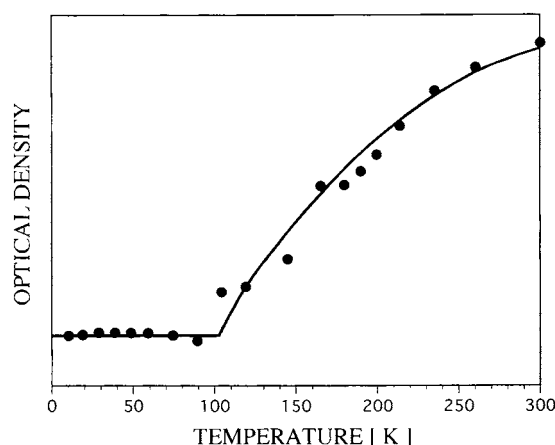


Figure 10. Temperature dependence of the optical density for the absorption band at 489.6 nm labelled with \ast in figure 9(a). The full curve is a guide for the eye.

also referred to in table 2. Our observed frequencies at room temperature almost agree with the values of Savytskii *et al* [9] and Sanjuan *et al* [13]. As discussed above, the numerals in the square or underlined denote the luminescence or electronic Raman spectra, respectively.

In the A_g or A_1 modes with (YY) and (ZZ) polarized configurations, 96, 145, 215, 289, 339 and 470 cm^{-1} bands were observed in all studies at room temperature. Savytskii *et al* [9] observed an additional band around 25 cm^{-1} . As shown in figure 1, the band cannot be observed even at low temperature in our study. A weak band at 414 cm^{-1} can be observed only at lower temperatures because of the weak scattering intensity. It is concluded that seven well resolved phonon modes, including the band at 414 cm^{-1} , were observed in the present study, with six bands being consistent with the two previous studies.

In the B_{1g} or A_2 modes with the (XY) polarized configuration, bands at 110 and 448 cm^{-1} differ between observed bands of Savytskii *et al* [9] and Sanjuan *et al* [13]. The low temperature measurements enable us to identify the four phonon modes (153, 214, 363, 449 cm^{-1}) unambiguously, which are consistent with the values obtained by Sanjuan *et al* [13]. The band at 110 cm^{-1} by Savytskii *et al* [9] may be considered to be a residual missing mode. However, we think that the band is not the XY -polarized phonon mode, because the band could not be observed even at the lowest temperature.

Savytskii *et al* [9] and Sanjuan *et al* [13] have seen a band around 460 cm^{-1} in the B_{2g} or B_1 modes with the XZ polarized configuration and the B_{3g} or B_2 modes with the YZ polarized configuration. As shown in figures 4 and 5, the band at 466 cm^{-1} only appears in the XZ polarized configuration. Their results are ascribed to leakage of the modes. Moreover, the phonon modes at 334 and 405 cm^{-1} were new and clearly found in the present measurement in the XZ polarized configuration. The four phonon modes (144, 213, 334, 405 cm^{-1}) were present in the XZ configuration. In the YZ configuration, the three phonon modes (168, 199, 351 cm^{-1}) were present.

The phonon modes of NdGaO₃ were made clear in table 2 by measuring at lower temperatures. It is possible to assign the present phonon modes to both the space groups $Pbnm$ and $Pbn2_1$, as given by equations (1) and (2). However, the number of observed phonon modes is significantly different from the number expected for $Pbn2_1$. In the case of $Pbnm$, the number of Raman active modes in each irreducible representation is close to the

Table 2. Symmetry assignment, polarization and frequency of NdGaO₃ Raman bands observed at about 21 K and room temperature [9, 13].

<i>Pbnm</i>	<i>Pbn2₁</i>	Polarization	Number of observed bands	
Present study				Wavenumber of the observed bands (cm ⁻¹) at about 21 K
7A _{1g}	14A ₁	YY, ZZ	7	104, 148, 217, 297, 344, 414, 474
7B _{1g}	15A ₂	XY	6	89, 155, 183, 219, 365, 453
5B _{2g}	14B ₁	XZ	6	91, 146, 336, 412, 425, 466
5B _{3g}	14B ₂	YZ	5	90, 171, 183, 206, 355
Present study				Wavenumber of the observed bands (cm ⁻¹) at room temperature
7A _{1g}	14A ₁	YY, ZZ	7	68, 96, 145, 215, 289, 339, 470
7B _{1g}	15A ₂	XY	4	153, 214, 363, 449
5B _{2g}	14B ₁	XZ	5	67, 144, 334, 405, 463
5B _{3g}	14B ₂	YZ	4	71, 168, 199, 351
Savytskii <i>et al</i> [9]				Wavenumber of the observed bands (cm ⁻¹) at room temperature
7A _{1g}	14A ₁	XX, YY, ZZ	7	25, 96, 145, 215, 290, 337, 470
7B _{1g}	15A ₂	YX	4	110, 151, 213, 362
5B _{2g}	14B ₁	XZ	3	92, 144, 461
5B _{3g}	14B ₂	ZY	6	93, 145, 170, 200, 351, 462
Sanjuan <i>et al</i> [13]				Wavenumber of the observed bands (cm ⁻¹) at room temperature
7A _{1g}	14A ₁	XX, YY, ZZ	6	95, 144, 214, 289, 336, 469
7B _{1g}	15A ₂	XY	4	151, 212.5, 361.5, 448
5B _{2g}	14B ₁	XZ(→ YZ)	4	168, 199, 349, 461
5B _{3g}	14B ₂	YZ(→ XZ)	3	142, 199, 459

□: Luminescence, ___: electronic Raman spectra.

number expected for *Pbnm* and does not exceed it. It is concluded that a NdGaO₃ crystal has the space group *Pbnm*. No softening or no discrete changes, which suggest the structural phase transition or the anomaly of the physical property of NdGaO₃ near 200 K [2], were measured by the present Raman spectroscopy. However, the electronic excitation from the level ⁴I_{9/2} of Nd³⁺ seems to have a close relation to the anomaly of the physical properties near 200 K [2], as the luminescence appears in the temperature range 100–200 K.

5. Conclusion

The temperature dependence of polarized Raman scattering was carried out using a NdGaO₃ single crystal in order to make clear the symmetry group and investigate a structural anomaly around 200 K. Well resolved 18 phonon modes were observed and interpreted as the space group *Pbnm*. The 7 phonon modes from 7A_{1g}, the 4 phonon modes from 7B_{1g}, the 4 phonon modes from 5B_{2g} and the 3 phonon modes from 5B_{3g} were determined.

At lower temperatures electronic Raman scattering was investigated at 90, 183 and 425 cm⁻¹, which were identified as the electronic transitions between the Stark levels of the ground state ⁴I_{9/2} of the Nd³⁺. In the case of the 488 nm excitation source, luminescence from the higher energy level belonging to the ²K_{15/2} or ²G_{9/2} to the ground state ⁴I_{9/2} were generated at around 60 and 171 cm⁻¹ for higher temperatures.

No structural phase transition has been observed in this crystal in the temperature range from 21 K to room temperature.

Acknowledgments

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