

Optical Spectra and Phase Transition in $\text{AgNa}(\text{NO}_2)_2$

Riso KATO and Masanori HANGYO

Department of Physics, Faculty of Science,
Kyoto University, Kyoto, 606

Triplet absorption, luminescence, IR absorption and Raman scattering in $\text{AgNa}(\text{NO}_2)_2$ have been studied in relation to the phase transition in the crystal. Four components of the Raman spectrum due to the ν_2 -vibrations of NO_2^- ions observed in the ferroelectric phase are assigned to the non-equivalent NO_2^- ions in the crystal by referring to the luminescence and IR spectra. The temperature dependences of the intensities of the triplet absorption and Raman scattering show similar anomalies near T_c . These behavior is discussed by taking account of the reorientation of the NO_2^- ions in the crystal.

Silver sodium nitrite, $\text{AgNa}(\text{NO}_2)_2$, is known to be ferroelectric below the transition temperature $T_c = 38^\circ\text{C}$.^{1,2)} It undergoes an order-disorder type phase transition due to the reorientation of the NO_2^- ions in the crystal. At sufficiently low temperatures, NO_2^- ions are believed to be ordered along the b -axis of the crystal as shown by the solid curves in Fig. 1. According to the structural analysis by K. Ishida and T. Mitsui,³⁾ the NO_2^- ions at site-I change their directions toward the opposite sides more frequently than those at site-II do, when the temperature is raised and approaches to T_c . In this article, the temperature dependences of the triplet absorption and Raman scattering as well as the luminescence and IR absorption at LHeT are studied in relation to the phase transition in the crystal.

Triplet absorption

The crystal shows an optical absorption in 400 ~ 520 nm region due to the electronic transition $^1A_1 \rightarrow ^3B_1$ in NO_2^- (called as triplet absorption). The triplet absorption in $\text{AgNa}(\text{NO}_2)_2$ shows remarkable differences in

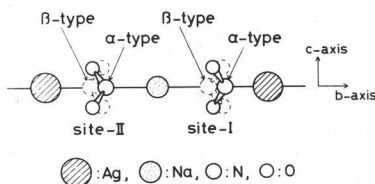


Fig. 1. Schematic arrangement of the constituent ions along the b -axis in $\text{AgNa}(\text{NO}_2)_2$.

contrast with that in NaNO_2 . The transition is usually spin-forbidden, so the intensity is very weak in NaNO_2 and almost constant for the change of temperature. In $\text{AgNa}(\text{NO}_2)_2$, the absorption of the $E//b$ polarization is about 300 times stronger than that in NaNO_2 . This enhancement is caused by the presence of the Ag^+ ion located near the NO_2^- ion. The 3B_1 state is mixed with closely lying singlet states, particularly with the electron transfer state associated with Ag^+ ion, $^1A_1[\text{NO}_2^-(\sigma) \rightarrow \text{Ag}^+(5s)]$, by spin-orbit interaction resulting in the enhancement of the triplet absorption of the $E//b$ polarization.⁴⁾ When the temperature is raised and approaches to T_c , the $E//b$ absorption in $\text{AgNa}(\text{NO}_2)_2$ decreases remarkably as shown in Fig. 2. The temperature dependence of the intensity of the triplet absorption is shown in Fig. 3. Above T_c , the $E//b$ intensity is reduced to about 30% of that at sufficiently low temperatures. The electron transfer transition (transfer

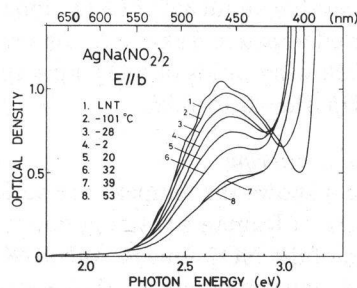


Fig. 2. Temperature variation of the $E//b$ spectrum of the triplet absorption in $\text{AgNa}(\text{NO}_2)_2$.

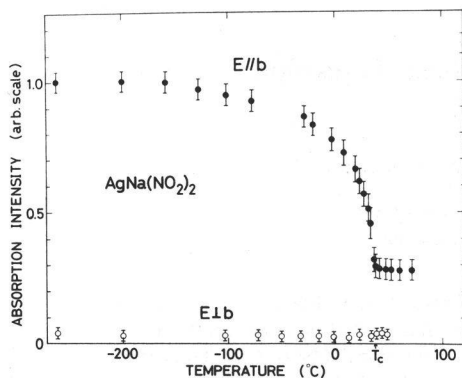


Fig. 3. Temperature dependence of the integrated intensities of the triplet absorption in $\text{AgNa}(\text{NO}_2)_2$. Closed circles show the $E//b$ intensities and open circles show the $E \perp b$.

of σ electron localized near the nitrogen atom of NO_2^- to Ag^+ (5s) is much stronger for NO_2^- -I α and -II β than NO_2^- -II α and -I β , because the nitrogen atoms of the former are facing and closer to Ag^+ ions. Then, the $^3\text{B}_1$ state in NO_2^- -I α and -II β is mixed much more with the electron transfer state than in NO_2^- -II α and -I β . Thus, it is likely that NO_2^- -I α and -II β receive the enhancement of the triplet absorption due to Ag^+ ion preferentially (designated as $\text{NO}_2^-_{\text{Ag}}$). The transition energy of the electron transfer from NO_2^- to Na^+ is much larger (≥ 8 eV), so the mixing of the state into the $^3\text{B}_1$ state is very small. At sufficiently low temperatures, all NO_2^- ions align along the b -axis, then NO_2^- -I α contributes mainly to the triplet absorption of $E//b$ polarization. With increasing temperature, NO_2^- ions at site-I and -II change their directions with different probabilities³⁾ resulting in the decrease of the NO_2^- ions which receive the Ag-enhancement. Above T_c , NO_2^- -I α and -II β become equivalent and the population of the sum of both ions are then estimated to be about 30% of that of NO_2^- -I α at low temperatures. This means that about 85% of NO_2^- ions at site-I are inverted from α to β above T_c . As a result, we get the following ratios of NO_2^- ions above T_c ; I α :I β =II β :II α =0.15:0.85.

Raman scattering

Figure 4 shows the temperature variation of the spectra of Raman scattering due to the ν_2 -vibration of the NO_2^- ions in $\text{AgNa}(\text{NO}_2)_2$. At sufficiently low temperatures, the spectrum consists of two components at 832 and 858 cm^{-1} . The IR absorption spectrum of the crystal at

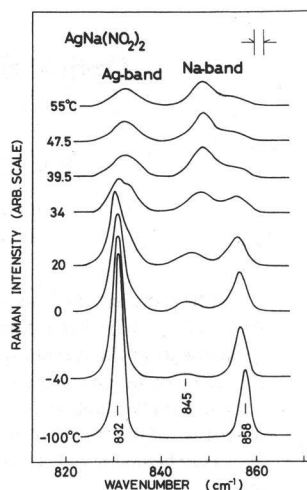


Fig. 4. Temperature variation of the ν_2 -spectrum of Raman scattering observed in near $b(cc)a$ configuration excited with 6328 Å line of He-Ne laser.

LHeT also shows corresponding two peaks at 829 and 856 cm^{-1} . The luminescence corresponding to the transition $^3\text{B}_1 \rightarrow ^1\text{A}_1$ shows series of vibronic lines with spacing of about 831 cm^{-1} , of which frequency corresponds to that of the ν_2 -vibration of NO_2^- ion. These are summarized in Table I. At low temperatures, the populations of NO_2^- -I β and -II β are negligible and the non-equivalent NO_2^- -I α and -II α are supposed to have slightly different frequencies of ν_2 -vibration. These frequencies will correspond to ~ 832 and ~ 858 cm^{-1} observed in Raman and IR spectra. Since the luminescence is also enhanced by the presence of Ag^+ ions, NO_2^- -I α is supposed to contribute to the luminescence mainly. Thus, the frequency of 831 cm^{-1} observed in the luminescence spectrum is ascribed to the ν_2 -vibration of NO_2^- -I α . Then, the component at 832 cm^{-1} in the Raman spectrum is assigned to NO_2^- -I α as well. The

Table I. Frequencies and intensity ratios of the two components of the ν_2 -spectra of Raman scattering, IR absorption and triplet luminescence at liquid helium temperature.

	ν_2 -frequencies (cm^{-1})	Intensity ratio
Raman	$832 \pm 3, 858 \pm 3$	2.9:1
IR	$829 \pm 2, 856 \pm 2$	$\sim 1:1$
Luminescence	$831 \pm 2, -$	(Ag-enhancement)

component at 858 cm^{-1} is accordingly assigned to NO_2^- -II α . With increasing temperature, the third component becomes appreciable at 845 cm^{-1} above -40°C and increases its intensity. Above T_c , it merges with 858 cm^{-1} component and becomes a broad band. This component is likely ascribed to the ν_2 -vibration of NO_2^- -I β , because NO_2^- -I β becomes equivalent to NO_2^- -II α above T_c . The weak shoulder which is appreciable on the high energy tail of 832 cm^{-1} component in $0\sim 35^\circ\text{C}$ region is ascribed to that of NO_2^- -II β based on the similar consideration. The intensity ratio of 832 and 858 cm^{-1} components at low temperatures is about 2.9:1. This means that the scattering efficiency of NO_2^- -I α is larger than that of NO_2^- -II α . The low lying electron transfer state associated with Ag^+ ion has a large oscillator strength and contributes to the Raman scattering as an intermediate state and gives rise to the enhancement of the scattering efficiency of NO_2^- -I α . Similarly, the scattering efficiency of NO_2^- -II β will receive the Ag-enhancement. Taking account of this fact and the informations from the absorption and luminescence spectra, we designate the 832 cm^{-1} component including its high energy shoulder as "Ag-band," since they are ascribed to $\text{NO}_{2,\text{Ag}}^-$ ions. On the other hand, 858 and 845 cm^{-1} components are designated as "Na-band," since they are ascribed to NO_2^- -II α and -I β (designated as $\text{NO}_{2,\text{Na}}^-$) which are facing to Na^+ ions. Then, the temperature dependences of the intensities of Ag- and Na-bands are expected to reflect those of the populations of $\text{NO}_{2,\text{Ag}}^-$ and $\text{NO}_{2,\text{Na}}^-$ ions. Indeed, the intensity of the Ag-band decreases in parallel with that of the triplet absorption, as seen in Fig. 5. On the other hand, the intensity of the Na-band increases with temperature so as to compensate the decrease of the Ag-band. When the corrections are made for the scattering efficiencies of Ag- and Na-bands, the sum of the intensities of both bands is almost constant over the temperature range of the experiment.

In conclusion, the temperature dependences of the triplet absorption and Raman scattering give the consistent results and the population ratios of NO_2^- ions above T_c are estimated to be $\text{I}\alpha:\text{I}\beta:\text{II}\beta:\text{II}\alpha \approx 0.15:0.85$. The populations of the $\text{NO}_{2,\text{Ag}}^-$ ion are 1, ~ 0.7 and ~ 0.3 at low temperatures, 20 and 50°C , respectively. These are summarized in Table II, where the results of

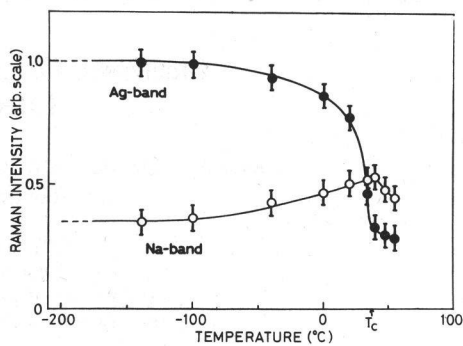
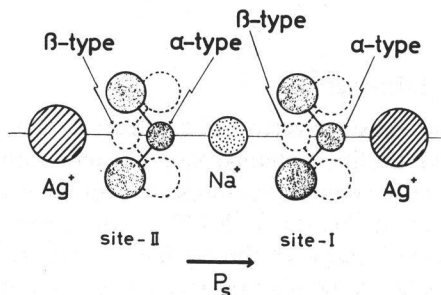


Fig. 5. Temperature dependence of the integrated intensities of the Ag- and Na-bands.

Table II. Populations of the $\text{NO}_{2,\text{Ag}}^-$ ion at low temperatures, 20 and 50°C , derived from Raman scattering, triplet absorption and X-ray studies.



	Triplet Absorption	Raman (Ag-band)	X-ray (Ishida et al)
LNT	1.0	1.0	(1.0) $\begin{cases} \text{I}\alpha:\text{I}\beta = 1.0:0 \\ \text{II}\alpha:\text{II}\beta = 1.0:0 \end{cases}$
20°C	~ 0.7	~ 0.75	0.7 $\begin{cases} \text{I}\alpha:\text{I}\beta = 0.4:0.6 \\ \text{II}\alpha:\text{II}\beta = 0.7:0.3 \end{cases}$
50°C	~ 0.3	~ 0.35	0.6 $\begin{cases} \text{I}\alpha:\text{I}\beta = 0.3:0.7 \\ \text{II}\alpha:\text{II}\beta = 0.7:0.3 \end{cases}$

X-ray study by K. Ishida *et al.*³⁾ are shown as well for comparison. It should be noted that the present results are consistent with the temperature dependence of P_s reported by K. Gesi²⁾ and are well interpreted by the theory given by S. Watarai and T. Matsubara.⁵⁾

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