Time-resolved Raman spectroscopy applied to the photo-induced phenomena in NaV$_2$O$_5$

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Abstract. Picosecond time resolved Raman scattering measurements were performed in a spin ladder system $\alpha'$-NaV$_2$O$_5$. We observed the decrease and recovery of the superstructure peak at 66 cm$^{-1}$ in the low temperature phase by photoexcitation. The transient local temperature of the sample by photoexcitation was obtained from the intensity ratio of the anti-Stokes and Stokes scattering. It is found that the highest temperature of 23 K induced by the optical pumping is far below the phase transition temperature of 34 K. The temporal changes of the Raman scattering intensities are ascribed to the decrease of the order parameter in the superlattice structure induced by optical pumping in the low temperature phase. We demonstrate a high potentiality of time-resolved Raman scattering spectroscopy for investigating the photo-induced phenomena.

1. Introduction
Photo-induced phase transition (PIPT) is a hot topic in the photo-induced phenomena recently [1-8], because it has some possibilities; we can manipulate the physical properties of materials by photons and create new phases that cannot be reached through the quasi-thermal-equilibrium path [1]. Some studies have been reported in charge transfer complexes [2], halogen bridged metal complexes [3], and perovskite type oxides [4-6]. The study of the dynamical process of PIPT is also important, which gives us information on the origin of PIPT and the non-thermal path for transition to new phase. However, there are rather small studies on the dynamics of PIPT. Up to now, most of investigations of PIPT dynamics have been based on the transient absorption or reflectance measurements, which probe the electronic transitions. Recently, the time-resolved X-ray diffraction, which can obtain the temporal information on the lattice system directly, has been developed and applied to TTF-chloranil [7]. However, the time-resolution was limited at about 100 ps. Another choice for obtaining information on the lattice system might be time resolved Raman spectroscopy, which have better time resolution from sub-picosecond to picosecond time range [9]. This method enables us to obtain fruitful information on not only lattice structure but also low energy electronic transition and spin ordering. Especially, the superlattice structures, which often change at the phase transitions, can be used to probe the phase. Furthermore, the transient local temperature within the laser spot can be measured by obtaining the intensity ratio of Stokes scattering and anti-Stokes scattering. The evaluation of the laser heating in studying PIPT is very important to distinguish between the thermal and non-thermal effects.

The sample we investigated was a spin ladder system $\alpha'$-NaV$_2$O$_5$, which shows a phase transition of charge ordering accompanying spin pairing at $T_c = 34$ K [10-13]. The main structure of $\alpha'$-NaV$_2$O$_5$
consists of V$_2$O$_5$ layers formed by corner-sharing distorted VO$_5$ pyramids and the Na ions are intercalated between these layers. The vanadium ions form ladder structures in each layer. The legs are running along the $b$-axis and the rungs along the $a$-axis are formed by two V ions bridged by an O ion. Neighboring ladders are linked via common edges of the pyramids to form a $a$-$b$ layers. In the high temperature phase (HTP), all V ions are charged equally (V$^{4.5+}$), while in the low temperature phase (LTP), charge separation occurs, resulting in V$^{4+}$ and V$^{5+}$ which form zigzag double chain arrangements along the $b$ axis [14]. The V$^{4+}$ ion has one $d$-electron, while the $d$-orbital of V$^{5+}$ ion is empty. The two V$^{4+}$ ions on the neighboring legs form a spin singlet. Reflecting the lattice distortion associated with this ordering, $2a \times 2b \times 4c$ superlattice structure appears [15]. The characteristics of this phase transition are of great interest, because the charge separation, charge ordering, spin pairing, and lattice distortion should occur cooperatively at $T_c$. Very recently, our group suggested that PIPT occurs from the LTP to a HTP-like phase by the transient reflectance measurements [8].

In this paper, we report on a dynamical investigation of photo-induced phenomena in α’-NaV$_2$O$_5$ using the time resolved Raman scattering measurement. The other aim is to demonstrate the usefulness of this method for investigating PIPT.

2. Experiment

Time-resolved Raman scattering measurements were performed in the quasi-backscattering geometry by using picosecond laser pulses. The used sample α’-NaV$_2$O$_5$ was grown from the melt, using the self-flux method [16]. The dimensions of the sample are typically about $1 \times 2 \times 0.3$ mm$^3$ in $a$, $b$ and $c$ axes, respectively, and the measurements were performed on the $a$-$b$ plane. The sample was set in the vacuum space of a He-flow cryostat. A mode locked Ti:sapphire laser provides the pulses with the pulse width of 1.5 ps, the central wavelength of 800 nm, and the repetition rate of 82 MHz. The output of this laser was divided into a pump beam of 800 nm used for excitation of the sample and a probe beam of a frequency-doubled 400 nm used for measuring the Raman spectra. The powers of the pump and probe beams are $2.0 \times 10^{-6}$ and $1.2 \times 10^{-6}$ J/cm$^2$, respectively, and the diameter of the pump beam is 150 µm. The polarizations of the pump and probe beams were parallel to $b$ and $a$ axes, respectively. The excitation of 800 nm corresponds to the tale of the absorption peak at 1.2 eV [17], and it is assigned to the transition of the charge transfer on-rung 3d(V)-2p(O)-3d(V) resonance [18] or d-d transition of V$^{4+}$ ions [19]. The $a$ axis-polarized Raman scattering spectra scattered from the sample surface were detected as a function of the delay time relative to the pump pulse using a triple spectrometer and a Liq. N$_2$ cooled CCD. The total spectral energy resolution of this setup was 10 cm$^{-1}$.

3. Experimental results and discussions

Figure 1 shows Raman spectra without pump beam in LTP at 4 K and in HTP at 34 K. The power of the probe beam is $2.8 \times 10^{-7}$ J/cm$^2$. The spectra in LTP have 5 peaks at 66, 91, 106, 134, and 183 cm$^{-1}$, while the spectra in HTP have only 2 peaks at 91 and 134 cm$^{-1}$, which are assigned to phonon modes marked by squares in Fig. 1 [12]. The three peaks at 66, 106, 134 cm$^{-1}$ marked by asterisks in Fig. 1 appear only in LTP, and these peaks are assigned to the folded phonon modes due to the superlattice structure [20,21] (or magnon modes by some reports [12,13]) in LTP. The broad peak around 100 cm$^{-1}$ is ascribed to the electronic Raman scattering related with the charge ordering [22]. The changes of the peaks due to the superlattice structure in LTP by photoexcitation are useful for investigating PIPT, because these peaks appear only in LTP and we can distinguish the phase by using these peaks. Especially, we focused on the peak at 66 cm$^{-1}$, as the intensity changes between in LTP and in HTP are largest among the superlattice structure modes in this sample.

We show the results of the time resolved Raman scattering spectroscopies between 0 and 20 ps in Fig. 2 (a). The enlargement around the peak at 66 cm$^{-1}$ in Fig. 2 (a) is shown in Fig. 2 (b). After the photoexcitation, the peaks at 66 and 106 cm$^{-1}$ are apparently smaller than those before photoexcitation.
and the intensities decrease with increasing delay time up to 20 ps, while the phonon peak at 183 cm$^{-1}$ shows almost no change in this measurement. The temporal evolution of the peak intensities at 66 cm$^{-1}$, which were obtained from a fitting by Gaussian function, was plotted in Fig 3. The intensity rapidly decreases after the photoexcitation, reaches a minimum value of 0.78 at 20 ps, and after then it recovers slowly. The temporal evolution of the peak intensity at 106 cm$^{-1}$ is very similar to that of 66 cm$^{-1}$. We obtained the decay and recovery times of 5 ps and 800 ps from double exponential function fitting, respectively. These values are close to the values obtained by the transient reflection measurement [8]. These results suggest that this decrease and recovery of the Raman intensity corresponds to the partial destruction and recovery of the superlattice structure by the optical excitations.

In order to take account of the change of the local temperature within the laser spot, we obtained the transient local temperature from intensity ratio of the anti-Stokes scattering and Stokes scattering in the same experimental layout. As seen in Fig. 4, the local temperature shows a highest temperature of 23 K at 20 ps and it decreases after then. The rising and decay time constant are 6 ps and 800 ps, respectively. These temperatures are still far below $T_\text{c}$ (= 34 K) and this indicates that the phase transition from LTP to HTP by the laser heating does not occur. The local temperature before the excitation by the pump pulse is 19 K and it is higher than 4 K, the temperature of the cryostat. This
temperature difference is explained by the thermal accumulation due to the photoexcitation. As the thermal diffusion is slow and the decay time of the local heating is longer than the laser repetition interval of 12 ns.

We investigated the effect of the increase of the local temperature in LTP. The temperature dependence of the intensity at 66 cm$^{-1}$ peak without pump beam was examined in detail. It is found that the intensity decreases nonlinearly with increasing temperature near 34 K, that is, the temperature dependence of the peak intensity near 4 K is very small but it increases with increasing temperature. We estimated the temporal change of the intensity of 66 cm$^{-1}$ peak by only thermal effect, which was calculated using by the temporal change of the local temperature in Fig. 4 and the peak intensity at each temperature in steady state. We compared the estimated intensity only by the thermal effect with the experimental result in Fig. 3, as shown in Fig. 5. In Fig. 5, the result of the transient reflectance at 20 K in Ref. 8 is also shown. These time profiles are very similar in terms of the decay time, the minimum value, and the delay time at the minimum value. These agreements suggest that the observed temporal changes of Raman spectra and transient reflectance are mainly ascribed to the change of the local temperature induced by optical pumping in LTP. In these experiments including the transient reflectance measurement, the pulses with a repetition rate of ~ 80 MHz were used for the optical sources, and the effect of the heat accumulation in the sample by the optical pumping cannot be

![Figure 3: Temporal evolution of the Raman intensities at 66 cm$^{-1}$ peak.](image)

![Figure 4: The local temperature within the laser spot obtained from the ratio of the Stokes and anti-Stokes scattering.](image)
ignored. Higher energy excitations using pulses with a lower repetition rate are more suitable for investigating PIPT, because it can reduce the effect of the heat accumulation. Now, we are undergoing on the measurement of the transient reflectance using a Ti:sapphire regenerative amplifier laser with the repetition rate of 1 kHz.

4. Summary
We performed picosecond time resolved Raman scattering spectroscopies in the low temperature phase $\alpha'$-NaV$_2$O$_5$. The peak intensity at 66 cm$^{-1}$ decreased after photoexcitation, reaches minimum of 0.78 at 20 ps, after then recovers gradually. The temporal changes of the transient local temperature at sample surface were observed by measuring the Stokes and anti-Stokes scattering. The temporal changes of the Raman scattering intensity are ascribed mainly to the decrease of the order parameter in the superlattice structure induced by the transient changes of the local temperature. We demonstrated that time resolved Raman spectroscopies are promising tool for investigating PIPT, because they can provide us valuable information about lattice, spin, electronic transition, and transient local temperature simultaneously in picoseconds time range.

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