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Ultrafast dynamics of photoinduced phenomena in the spin ladder system NaV$_2$O$_5$

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Abstract. Recent developments in the study of ultrafast dynamics are reviewed concerning the spin ladder system, $\alpha'$-NaV$_2$O$_5$, which is known to have a charge order phase transition accompanying spin dimerization at 34 K. The low energy excitations specific to the low temperature phase is observed by coherent excitation method and their origins are discussed, comparing with the Raman and infrared absorption data. Photoinduced phenomena are studied by transient reflectance and time-resolved Raman spectroscopy and the thermal and non-thermal effects are distinguished by their response time.

1. Introduction

The low dimensional spin systems have been receiving continued interest of solid state physicists, because the theories predict variety of interesting properties such as the spin ordering described by Heisenberg model, magnetic excitations and phase transitions characteristic to one-dimensional systems.

The $\alpha'$-NaV$_2$O$_5$ is known as a 2-dimensional spin ladder system, which has a magnetic phase transition accompanying charge ordering at $T_c=34$ K [1]. The main structure of $\alpha'$-Na-V$_2$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 and have average $+4.5$ charge in the high temperature phase (HTP). In contrast, the charge separates into V$^{+4}$ and V$^{+5}$ with a zigzag configuration in low temperature phase (LTP) as shown in Figure.1 (a). The stability of the zigzag configuration has been supported by theory [2]. The spins on the neighboring V$^{+4}$ ions make pairs to form spin singlets as shown by the dashed oval in figure 1 (a), resulting in a decrease of the magnetic susceptibility below $T_c$. This phase transition is accompanied by a lattice distortion with a 2a$\times$2b$\times$4c superlattice structure. The simultaneous occurrence of the spin dimerization and the lattice distortion is reminiscent of the spin-Peierls transition. Therefore, this transition is referred to as spin-Peierls-like phase transition.

The zigzag chains formed on the ladder are expected to behave like a one-dimensional spin system. The spin dimerization gives rise to the opening of a spin energy gap, which has been observed at 68 and 75 cm$^{-1}$ by NMR[3-5] and at 80 cm$^{-1}$ by neutron scattering [6]. The magnetic excitations have been investigated extensively by various methods especially by light scattering [7-9], but the interpretation has not been settled. Their origins and the interactions with phonons are important issues to be clarified.
The excited electronic states and their dynamics, especially the cooperative phenomena including destruction of charge order and spin pairing, are also the interesting subjects. However, this material has not been subjected to ultrafast spectroscopy up to now, as far as we know. In this report, recent developments in investigation of the dynamical behavior in this material are reviewed.

2. Coherent excitations

Figure 1 (a) Ladder structure of spins on the V⁴⁺ sites in the low temperature phase. (b) Coherent oscillation signal taken in a REOS configuration with delay-time modulation technique under excitation of circular polarized light at 5 K. The slowly varying component was subtracted. The time origin is around 0.25 ps.

Figure 2 (a) Temperature dependence of the Fourier power spectra of the oscillation signals. (b) Temperature dependence of the 125 cm⁻¹ mode intensity (dots) and IR modes (solid curves) reported in reference 14.
The low energy excitations i.e., phonons and magnetic excitations, have been studied mainly by infrared and Raman spectroscopy. In the Raman scattering measurements, anomalous peaks were found at 62 and 128 cm\(^{-1}\) by Kuroe et al.[7] and at 67 and 134 cm\(^{-1}\) by Lemmens et al. [8] and they were assigned to magnetic origins. Especially, the peak around 67 cm\(^{-1}\) has been discussed in relation with the single-triplet excitation, because the energy is close to the gap energy. However, the energy of this mode was independent of the magnetic field up to 7 T [9], which suggested that this mode cannot be assigned to a simple singlet-triplet excitation [10]. There is an idea to assign the 134 cm\(^{-1}\) mode to two-magnon excitation [11], but the value seems too high, when the renormalization due to magnon-magnon scattering is taken into account [10]. The interpretation of these and many other modes are controversial up to now.

To get further insight, we performed pump and probe reflectance measurements with 10 fs pulses from a mode-locked Ti: sapphire laser (\(\lambda=800\)nm, 75 MHz repetition). The single crystals of \(\alpha'\)-NaV\(_2\)O\(_5\) were grown by M. Isobe et al. [12] with a self-flux method and the cleaved a-b surface was used for reflectance measurements. The sample placed in the vacuum space of a cryostat was excited

| Lemmens\(^a\) | Raman | Fischer\(^b\) | Konstantinovic\(^c\) | IR | Popova\(^d\) | Coherent Excitation | Kamioka\(^g\) | This work\(^h\) |
|-------|-------|--------|-----------------|----|--------|-------------------|--------|--------|
| 67    | 67    | 66     | 70.0 (67.5)     | 91.2| 91     | -                 | 91     | 91     |
| -     | -     | 86     | -               | -   | -      | 111.7             | -      | -      |
| 107   | 107   | 106    | 107 (106), 101.4, 101.7 | -  | 102    | -                 | -      | -      |
| -     | -     | -      | 124.7, 125.6, 126.8, 127.6 | 127 | 125    | -                 | -      | -      |
| 134   | 134   | 132    | 133.1 (131.6)   | -   | -      | -                 | -      | -      |
| -     | -     | -      | 140.0           | -   | -      | -                 | -      | -      |
| 151   | 151   | 148    | 145.0, 145.7, 147.9, 148.2 | 157.2 | -  | -      | -                 | 163   |
| -     | -     | 158    | -               | -   | -      | 181               | 181   | -      |
| 165   | 164   | 165    | -               | -   | -      | -                 | -      | -      |
| -     | -     | 183    | 199.0, 199.5    | 234.2| 230    | 230               | -      | 202   |
| 202   | 202   | -      | -               | 244 | -      | -                 | -      | -      |
| -     | -     | 230    | 256             | -   | -      | -                 | -      | -      |
| 246   | 246   | -      | -               | 305 | 303    | 303               | -      | -      |
| -     | -     | 305    | -               | 314 | -      | -                 | -      | -      |
| 325   | -     | -      | 324.6, 327.4    | -   | -      | -                 | -      | -      |
| 332   | -     | -      | -               | -   | -      | -                 | -      | -      |
| 396   | -     | -      | -               | -   | -      | -                 | -      | -      |
| -     | -     | 410.3, 410.4 | -    | 420     | 422             | -      | -      |
| -     | -     | 422    | -               | -   | -      | -                 | -      | -      |

\(^a\)Reported in reference 8.
\(^b\)Low temperature data from reference 9.
\(^c\)From reference 13 (except e and f).
\(^d\)From reference 14. Values in parentheses refer to another sample.
\(^g\)From table IV of reference 14.
\(^h\)Values at 27K read from figure 3 of reference 13.
\(^i\)At 5K. Pump: 1 mW (circular), probe: 1 mW. The peaks found in more than two scans.
by circularly polarized light and the reflection of the probe light was measured in a REOS (reflective electro-optic sampling) configuration. The delay-time of the pump pulse was modulated by a shaker and the polarization rotation of the probe light was detected by a lock-in amplifier. A typical time-domain signal taken at 5 K is shown in figure 1 (b), where the oscillatory component after subtracting the slowly varying component is shown. The Fourier transform spectra of the time-domain signals at various temperatures are shown in figure 2 (a). The low and high frequency sides are suppressed due to the finite amplitude of the shaker. The frequencies of the peaks found more than twice in the measured spectra are listed in the last column of table 1. As indicated in the fifth column of the table, the peaks at 102, 163 and 202 cm\(^{-1}\) were not found in our previous measurement with a lower time-resolution [15]. The noisy aspect of the spectrum at 22.5 K (figure 2(a)) is ascribed to superposition of a large background signal, which will be discussed in the next section. It is clearly seen from figure 2 (a) that many of the modes lose their intensity, as the temperature goes up toward \(T_c\). Among these, the most interesting is the 125 cm\(^{-1}\) (127 cm\(^{-1}\)) mode, that was found in LTP by Konstantinovic \textit{et al.} (Raman) [13], Popova \textit{et al.} (IR) [14] and us [15] independently at nearly the same time. In the Raman spectrum, the 126 cm\(^{-1}\) peak appears on the tail of much stronger peak at 132 cm\(^{-1}\) [13], while the 132 cm\(^{-1}\) peak is absent and the 125 cm\(^{-1}\) peak appears as the most prominent peak in our spectrum. From the Na deficiency dependence, Konstatinovic have suggested that the 66, 86, 106 and 126 cm\(^{-1}\) modes have magnetic origin. Introduction of Na deficiency will destroy the magnetic order, but it is unlikely that small amount (3%) of such defects would bring about such a large modification of the phonon spectrum, they mentioned. On the other hand, Popova asserted that the modes around 70 (67.5), 107, 125 and 133 cm\(^{-1}\) originate in folded phonons, based on detailed analysis of the temperature dependence of their intensity and splitting observed in high-resolution IR spectra. As seen from table 1, many peaks have similar frequencies in Raman and IR measurements, indicating that these modes are both Raman and IR active. Judging from the very close values of frequency, the 125 cm\(^{-1}\) mode found in our experiment corresponds to the 124.7, 125.6, 126.8 and 127.6 cm\(^{-1}\) modes in IR spectra.

3. Transient reflectance and Raman spectroscopy: thermal effect

The non-oscillating component of the transient reflectance signal has large amplitude, and can be measured as a simple reflectance modulation. Figure 3 (a) and (b) show the response of the reflectance change, where the background components independent of the delay time (discussed later) are subtracted and the net changes of \(\Delta R/R\) are shown [16]. At room temperature (figure 3 (a)), the signal is negative in polarity with a sharp rise and has a lifetime about 500 fs. This response is assigned to the bleaching of the electronic transition due to band filling and/or depletion of the initial state population. Below \(T_c\), the response is two orders of magnitude larger and shows rather slow rise and a very long lifetime as shown in figure 3 (b). The build-up time constant is 3 ps at 4 K or 4 ps at 20 K, while the decay constant is about 400 ps at 4 K and increases up to 1500 ps at higher temperature. The temperature dependence of the maximum amplitude together with the magnitude of the
The thermal effect due to the laser irradiation is twofold. One is the transient heating, which is expected within a time shorter than the time constant of cooling due to thermal conduction across the excited volume. In this case the rise of temperature is estimated as $Q/C(T)v$, where $Q$ is the heat energy deposited by one pulse, $C(T)$ is the temperature dependent specific heat and $v$ is the excited volume. Another effect is the quasi-static heating governed by thermal conduction. It is given by $F/(\kappa \frac{dT}{dx})$, where $F$ is the fluence of the pumping light, $\kappa$ is the thermal conduction coefficient, and $dT/dx$ is the temperature gradient between the surface and the backside of the sample glued on the holder. The background component, which does not depend on the delay time, is caused by the quasi-static heating. If the temperature increase is small, the reflectance change will be proportional to $dR/dT$. As the reflectance has temperature dependence similar to curve (b) in figure 2 [17], the response will have a peak slightly below $T_c$, where $|dR/dT|$ reaches maximum. Thus the curve with open squares in figure 3 (c) can be understood qualitatively.

**Figure 3** Transient response of the reflectance at room temperature (a) and at low temperatures (b) in the $E_{\text{pump}}/a$ and $E_{\text{probe}}/b$ configuration. The beam powers were 2 mW and 0.5 mW, for pump and probe, respectively. (c) shows the temperature dependence of the transient response (dots) and background component (open squares) in the reflectance. (from reference 16)

**Figure 4** Time evolution of the Stokes Raman intensity of the 66 cm$^{-1}$ mode (a) and the local temperature determined from the ratio of Stokes and anti-Stokes lines of the 66 cm$^{-1}$ mode (b).
As the transient increase of temperature is hard to estimate, we performed time-resolved Raman measurement with a time-resolution of 2.5 ps, using a picosecond mode-locked Ti-sapphire laser. The fundamental beam at 800nm (30 mW) was used as the pump and its second order harmonics as the probe. Figure 4 (a) is the time evolution of the Stokes intensity of the 66 cm$^{-1}$ mode, which is characteristic to LTP, and (b) is the transient local temperature determined from the ratio of this peak and the anti-Stokes counterpart. After arrival of the pumping pulse, the temperature gradually increases from 19 to 23 K, but is always below $T_c$ at a typical excitation fluence in our measurements.

As the temperature dependence of the 66 cm$^{-1}$ peak is similar to the curve (b) in figure 2 and the build-up time constants of figure 4 (a) and (b) are close each other, the decrease of the 66 cm$^{-1}$ mode intensity is ascribed mainly to the increase of temperature within LTP. The similar time constant of the build-up of the reflectance can also be assigned to the transient increase of the temperature.

Finally, the temperature dependence of the transient response (solid circles in figure 3 (c)) can be understood as follows. If $Q$ is small and $C(T)$ is independent of temperature, the transient change of $R$ would be proportional to $dR/dT$ just like the quasi-static effect. However, $C(T)$ tends to zero following $C(T) \propto T^3$ at low temperature and $C(T)$ increases steeply near $T_c$ [18] because of the 1st order nature of the phase transition. Furthermore, $Q$ is not small. In this case, the reflectance change will be almost constant at lower temperatures and suppressed at higher temperatures close to $T_c$. This can qualitatively explain the difference of the temperature dependence curves in figure 3 (b). Our understanding at this stage is only qualitative and the polarization dependence of the decay profile reported in [16] has not been interpreted.

Nevertheless, we can tentatively conclude:

1) The transient response in the reflectance and intensity of the 66 cm$^{-1}$ mode under low excitation intensity (below 100 pJ/pulse) reflects mainly the change of the electronic and lattice properties induced by heating within LTP.
2) The thermal effect has a build-up time of 5–6 ps around 20 K, which reflects the time required for release of energy from the excited electronic states.
3) The local temperature of the excited volume decays in about 1 ns at 4 K.

4. Transient reflectance under high fluence: non-thermal effect

We studied the photoinduced phenomena with higher excitation intensity by using amplified pulses ($\lambda$=800 nm) at a repetition rate of 1 kHz. At the lowest power 0.1 mW, the reflectance decreases with a time constant 3 ps characteristic to the thermal effect and the overall time response is similar to those observed under low power excitation shown in figure 3 (b). In increasing the pump power, a fast rising component with an opposite polarity appears and an oscillating component is superposed at higher excitation intensity. By using white light continuum from a sapphire plate as a probe, we confirmed that the period of oscillation is approximately proportional to the wavelength of the probe light in the medium. This oscillation is ascribed to the interference of the probe light reflected at the surface and at the wave front of the impulsive acoustic wave propagating into the sample. All time response curves measured at different wavelengths, polarization and temperature were decomposed into four components i.e., a slowly rising (negative) component, a fast rising component, a damped oscillation and a short spike. The last one, that is not discernible in figure 5, is ascribed to electronic origin as figure 3 (a). The fast rising component is assigned to a non-thermal effect, because the rising time is less than 150 fs, which is far shorter than that of the thermal effect. Pure electronic effect is also unlikely to be responsible, because the lifetime is longer than 1 ns. The temperature dependence of the magnitude of the reflectance change in two polarization configurations is shown in figure 5 (b). In a-b polarization, the response decreases in increasing temperature. However, the inflection point does not agree with $T_c$, which is indicated by a dashed line. Therefore, this non-thermal effect is not directly related to the phase transition at 34 K. Change in the valence of the vanadium ions is likely to be responsible for this phenomenon.
5. Summary
The dynamical behavior of the photoinduced phenomena in \( \alpha' \)-NaV\(_2\)O\(_5\) was studied by pump and probe reflectance measurements and time-resolved Raman spectroscopy. In time-domain oscillation signals, a new mode was found at 125 (127) cm\(^{-1}\) and was suggested to originate from a mode related to charge and magnetic order, comparing with IR and Raman spectra reported in literature. A transient reflectance change with a slow rising time (3–4 ps) is found under low excitation density and ascribed to thermal effect. A fast rising component found at high intensity excitation was ascribed to a non-thermal effect.

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