Coherent Magnetic Oscillation in the Spin Ladder System α'-NaV_2O_5

H. Kamioka, S. Saito, M. Isobe, Y. Ueda, and T. Suemoto

Institute for Solid State Physics, University of Tokyo, Kashiwanoha 5-1-5, Kashiwa-shi, Chiba 277-8581, Japan

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We report the first observation of coherent magnetic excitations in a spin ladder system NaV_2O_5 by using femtosecond time-domain spectroscopy. A pronounced coherent oscillation is observed at 127 cm^{-1} (nearly twice the spin gap energy) and assigned to a two-magnon bound state, based on the temperature dependence of the intensity below the charge ordering phase transition at $T_C = 34$ K. This mode can be observable only when circularly polarized light is used as a pump or a probe beam, suggesting that it corresponds to a spin-flip excitation from the singlet ground state. A phonon mode strongly coupled to the spin state is also found at 303 cm^{-1}.

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The physical properties of low dimensional quantum spin systems have recently been studied by various experimental techniques with a great interest to explore the phenomena predicted in theoretical research on Heisenberg spin systems [1]. The sodium vanadate α'-NaV_2O_5, which was at the beginning thought to be the second example of the inorganic spin Peierls material, is a similar spin system but has a more complicated feature, that is, a spin ladder structure in the ground state. This compound exhibits a charge ordering phase transition accompanied by a spin dimerization and a lattice distortion at $T_C = 34$ K. In the charge ordered phase, the V ions change their charge valance [2] from uniform $V^{4.5+}$ to alternating V^{4+} and V^{5+}, and the spins attached to V^{4+} ions are believed to be dimerized with a zigzag configuration in the *ab* plane giving rise to the opening of spin energy gaps [3,4].

The dimerized spin system reveals unique magnetic excitation spectra caused by the spin exchange interaction, which consists generally of a triplet branch at the energy Δ, a corresponding two-particle continuum of spin excitations starting from 2Δ, and well-defined magnetic bound states [5]. The energy values of these excitations provide the essential information for assessing the validity of the theoretical models describing such quantum spin systems. In the case of NaV_2O_5, the spin gap energy Δ was observed through the measurements of the magnetic susceptibility [6], NMR [7], and neutron scattering [8]; however, the other expected excitations have not been observed by using these measurements.

On the other hand, the optical spectroscopy is known to provide powerful tools for studying the low energy excitation spectra near the zone center $\boldsymbol{q} = 0$, where we expect magnetic excitation levels. The optical conductivity spectrum in the infrared region revealed the opening of the energy gap around 130 cm^{-1}, and it was interpreted as the double spin-flip excitation [9]. In the Raman scattering measurements, the anomalous peaks were found around the low energy region by Kuroe *et al.* (at 62 and 128 cm^{-1}) [10] and Lemmens *et al.* (67 and 134 cm^{-1}). The difference of the peak positions might come from the Na deficiency according to the results of the measurements with such samples performed by the latter [11]. They have concluded that the peaks come from the magnetic origin, although the details of their assignment for these peaks were different. The former assigned the peaks to the spin-triplet states. The latter assigned the peaks to the spin-singlet states, not to the singlet-triplet excitations, because the selection rule for usual Raman scattering imposes a spin conservation through the light scattering process, and the peaks show neither a shift nor a broadening under magnetic field up to 7 T. Although some of the spin excitation states in NaV_2O_5 have been studied by using these spectroscopic techniques, a comprehensive understanding of these states has not been well established until now. The aim of this Letter is to report the new magnetic excitation coherently excited by circularly polarized femtosecond light pulses. Furthermore, we show the usefulness of the reflection probe time-domain spectroscopy in quantum spin systems. This will open a doorway to investigating the ultrafast dynamics of the magnetic excitations and coherent control of the magnetic ordering.

Single crystals of NaV_2O_5 were grown by a self-flux method [12], and the cleaved *a*-*b* surface was used for the time-domain reflectivity measurements. The sample was placed in a vacuum on a cold finger of a He gas flow cryostat and was excited by pulses from a mode-locked Ti:sapphire laser. The laser produced 25 fs pulses at a repetition rate of 76 MHz with a wavelength centered at 790 nm. The pulses were divided into a pump and a probe beam and focused on the sample surface by an achromatic lens into a spot with a diameter of 40 μm. The delay distance of the pump beam was modulated by a shaker at a frequency of 355 Hz for the phase sensitive detection, and then the ac component of the intensity of the reflected probe beam was detected as a function of the time delay between the pump and the probe pulses.

In order to improve further the signal to noise ratio, the reflective electro-optic sampling (REOS) technique [13] was also introduced for the measurement. The reflected probe beam was split into two orthogonal components $R_\perp$ and $R_\parallel$ with nearly the same magnitude by a polarized beam splitter and detected by p-i-n photodiodes. The

differential signal $\Delta R = R_\perp - R_\parallel$ was fed into a lock-in amplifier to pick up the dielectric modulation through the rotation of polarization for linear polarized light or the distortion of the circularly polarized light. This REOS measurement is usually used for detecting phonons other than totally symmetric modes in cubic semiconductors and trigonal semimetals, because of its selective sensitivity for low symmetric modes. However, this technique can probe all existing modes for NaV_2O_5 because it has approximately an orthorhombic symmetry. The time derivatives of the reflectivity change from REOS measurements, using the shaker method at 4.8 K $< T_C$ with 20 mW pump power, are plotted as a function of time delay in the inset of Fig. 1. The clear and oscillatory signal was obtained at positive time delay, because the ultrashort pulse gave a deep modulation of reflectivity and realized a good signal to noise ratio. The Fourier transform of the time-domain data is shown in Fig. 1. The spectrum shows that all the peaks correctly correspond to the ordinary phonon modes at 90.6, 181, 230, 303, 420, 450, and 531 cm^{-1}, already obtained from Raman scattering, respectively [14]. All the peak positions are in agreement with the Raman data within 3 cm^{-1}. This means that the time-domain reflectivity measurement enables us to observe directly the "coherent phonons" generated by an impulsive excitation. However, we could not observe any distinct change of the temperature dependence around the critical temperature T_C with this high pump power. Therefore, the following experiments have been done with a weaker pump power (5 mW) to avoid the heating and other high intensity effects on the sample.

The temperature dependence of the observed intensities for the 303 and 531 cm^{-1} peaks at this low pump power experiment is presented in Fig. 2. To remove the fluctuation due to the measurement conditions, the peak intensities are normalized by the intensity of the 420 cm^{-1} phonon peak which is nearly constant at all the temperatures. In this figure, we found that the intensity of the phonon mode 303 cm^{-1} increases linearly below T_C, while the phonon mode 531 cm^{-1} stays almost constant in the whole temperature range investigated. The temperature dependence of the Raman intensity reported in Ref. [14] is also plotted in this figure. The magnetic modes at 67 and 134 cm^{-1} show a linear increase of intensity below T_C, while the folded phonon mode 948 cm^{-1} has a totally different behavior, having a step-function-like change at T_C caused by the formation of a superlattice structure. This gradual increase of Raman intensity has been considered to be due to growth of the magnetic ordering, which is completely destroyed above T_C by the thermal fluctuation. The linear temperature dependence of the magnetic modes was also observed in the spin-Peierls system $CuGeO_3$ [15], and recognized as a common feature for magnetic modes. The linear dependence of the 303 cm^{-1} peak, which is seen in Fig. 2, could be acquired also by changing the laser intensity with a nominal temperature fixed at 4.8 K. From the correspondence between this power dependence and the curve shown in Fig. 2, the rate of heating by laser is estimated as 1.5 K/mW. Therefore, in 5 mW excitation, the gap between a nominal temperature and an actual temperature is suppressed within about 7.5 K.

The linear dependence observed in the present experiment closely resembles the behavior of the magnetic modes at 67 and 134 cm^{-1}. The only difference is the fact that it does have some intensity above T_C. Above T_C,

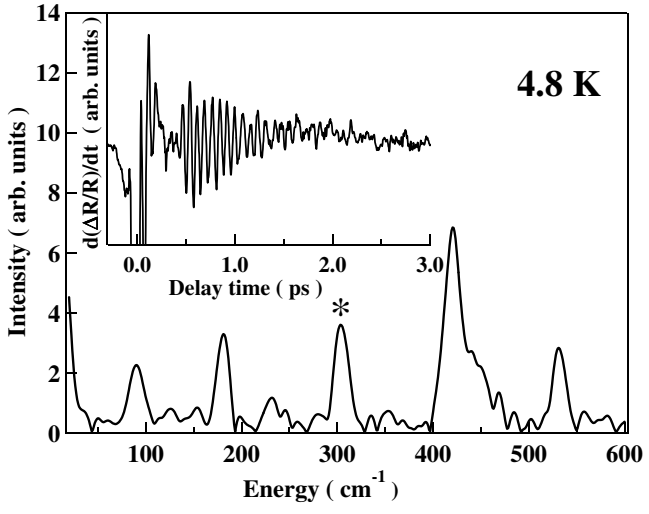

FIG. 1. The Fourier transform of the time-domain measurement data is shown for 4.8 K. The inset shows the time derivatives of the reflectivity change measured as a function of time delay.

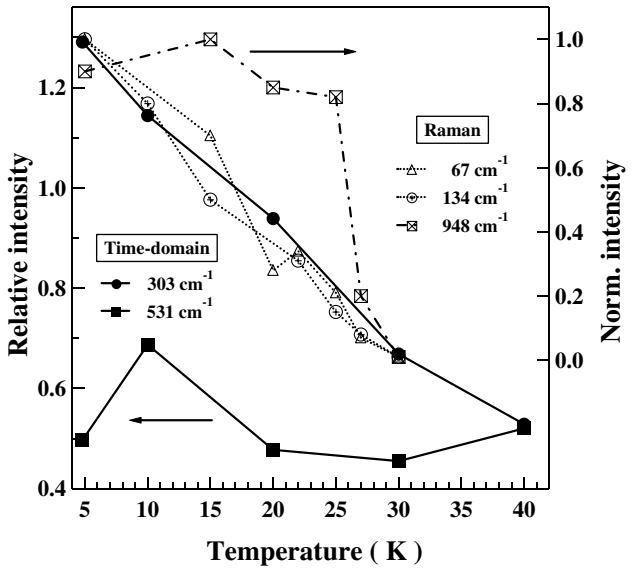

FIG. 2. The temperature dependence of the peak intensities of phonons obtained by our time-domain measurements. The solid lines and the symbols show the intensities relative to that of the 420 cm^{-1} peak. The dashed and dash-dotted lines show the normalized integrated intensities of the Raman modes observed below T_C, reported in Fig. 4 of Ref. [14].

this phonon mode is associated with the oscillation of the oxygen located at the rung of the vanadate ladder along the c axis from the numerical calculation based on the rigid ion model [16]. Below T_C, the vanadate spins are dimerized with the neighboring spin through the superexchange interaction relayed by the intermediate oxygen [4,17]; therefore, the anomalous temperature dependence of the 303 cm^{-1} phonon mode intensity suggests that the phonon mode is closely related to the phase transition via the superexchange interactions strongly affected by spin dimerization. Such an anomaly for phonon properties was also confirmed in the Raman scattering of superconductor $YBa_2Cu_3O_{7-\delta}$ [18], and the special phonon mode (B_{1g}, 340 cm^{-1}) was attributed to the change of the superexchange interaction between Cu spins through the oxygen. Besides this 303 cm^{-1} mode, no conspicuous change accompanied by the exotic phase transition in NaV_2O_5 was observed.

In the present report, we directed our attention to the fact that a circularly polarized light can transfer an angular momentum to a material through the spin-orbital interaction, and expected that the spin-flip modes would be detectable when a circularly polarized light are used as a probe or a pump beam in our time-domain measurements. The time derivative of reflectivity change with the circularly polarized probe at 10 K is shown in the inset of Fig. 3. A new beat structure is overlapped on the usual data sequence, which means that an additional mode appeared in this system. Actually, the Fourier spectrum reveals the appearance of the new pronounced peak located at 127 cm^{-1}. This peak could be also observed when we used a circularly polarized pump beam combined with a linear or circularly polarized probe beam. In Fig. 4 the intensities of the new peak are plotted as a function of temperature. It depends linearly on the temperature difference from T_C, just the same as the magnetic modes at 67 and 134 cm^{-1} in Raman measurement, while the phonon mode 531 cm^{-1} stays constant. This mode has an effective intensity only below T_C, unlike the 303 cm^{-1} phonon mode. From these facts, we conclude that the new mode is really ascribed to a spin excitation state. Furthermore, this is the first demonstration to observe the coherent spin oscillation (magnon) as far as the authors know.

The 127 cm^{-1} mode locates near the position of the magnetic state 134 cm^{-1}, but the deviation of this value from 134 cm^{-1} is considerably larger than the expected error, because the errors in phonon peaks are smaller than 3 cm^{-1} as mentioned earlier. Furthermore, the magnetic bound state 134 cm^{-1} with spin singlet would be observed with linear polarization. Based on these facts, it is concluded that this 127 cm^{-1} mode corresponds to a new oscillatory magnetic bound state with spin triplet. The magnetic states in the low dimensional spin systems have been predicted theoretically and discovered in some materials [19]. The theory assuming the nearest neighbor and next-nearest neighbor interactions predicts a triplet excitation above the lowest singlet excitation to the leading order approximation [5]. This is not consistent with our result, because the 127 cm^{-1} triplet was found below 134 cm^{-1}. In the recent theoretical analysis [20], which considers the higher order effects, predicts some additional triplet and singlet bound states between the second triplet and the two-particle continuum. The 134 cm^{-1} mode might be assigned to one of these singlet states.

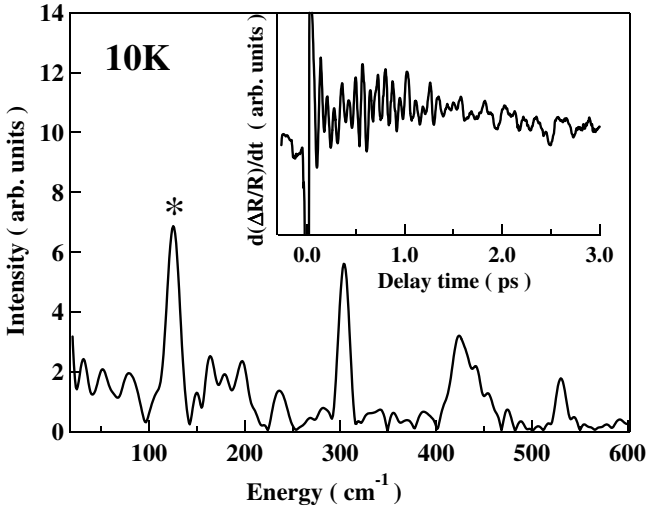

FIG. 3. The Fourier transform of the time-domain data taken with a circularly polarized probe at 10 K is shown. An additional new peak appears at 127 cm^{-1} in the spectrum. The inset shows the time derivatives of the reflectivity change measured as a function of time delay.

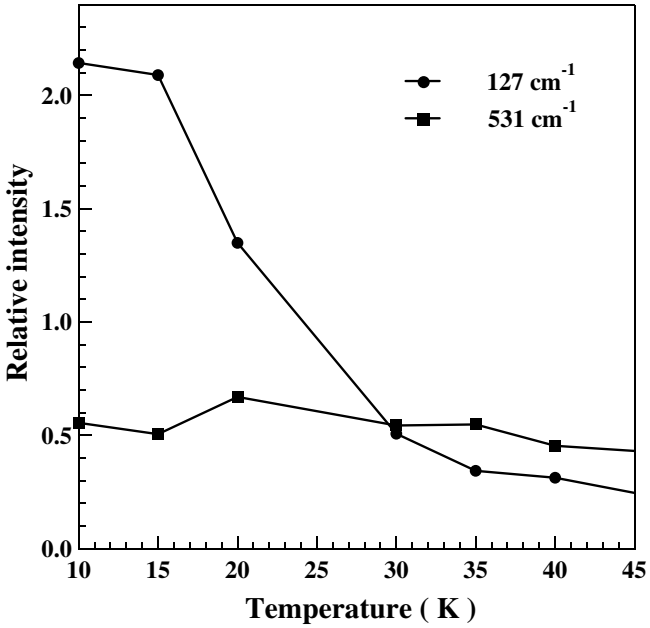

FIG. 4. The temperature dependence of the new mode at 127 cm^{-1} and the 531 cm^{-1} phonon mode relative to the 420 cm^{-1} phonon is shown.

The mechanism of detecting the elementary excitations by coherent excitation is not the same as Raman scattering. Sometimes the mode, nondetectable by Raman spectroscopy, can clearly be observed by this method, as seen in the case of certain phonon modes in Mo oxide [21]. Although several theoretical models have been proposed to explain the coherent phonon generation, the following two models are representative and applied to various materials. The first one is known as a DECP (displacive excitation of coherent phonons) model, which has been found to be valid for many semiconductors and semimetals [22]. This model assumes an excitation of vibration induced by an instantaneous change of the equilibrium atom position due to photogenerated carriers through the deformation potential interaction. The system starts to oscillate around the new equilibrium position, and the dynamical distortion of the lattice causes the change of the reflectivity. The second is based on impulsive stimulated Raman scattering, which attributes the generation mechanism of coherent phonons to the coherent Raman process. This model has been successfully applied to ferroelectric materials and some semiconductors [23]. According to the band calculation for NaV_2O_5 by Smolinski [24], the excitation photon energy 1.57 eV (790 nm) lies in the region of transitions from d_{xy}, the bottom of the $3d$ band, to the d_{yz} or d_{zx}. From the fact that the excitation for NaV_2O_5 is accompanied by the real transition and only the fully symmetric modes (A_1) are observed, it is suggested that the ordinary phonon modes (typically, 420 and 531 cm^{-1}) are caused by a DECP mechanism. On the other hand, the mechanisms for the generation and detection of the magnetic modes are obliged to be speculative because of the lack of sufficient information about this system. Nevertheless, we can assume the following scenario for the mechanisms based on our experimental results.

When a circularly polarized light is used as a pump beam, it can directly excite the triplet bound state accompanied by the change of the spin angular momentum. This magnon bound state will be generated as a sideband of the exciton corresponding to the d-d transition. The coherent nutation of this bound state will modulate the reflectance probed either by circularly or linearly polarized beam. In the case of a linearly polarized pump with a circularly polarized probe, two kinds of triplet excitations will be generated with phonon modes, because the linearly polarized light can be decomposed into two circularly polarized light beams with clockwise and counterclockwise rotations. Then one of these two would be selectively detected by a circularly polarized beam.

At the present time, it is difficult to decide the details of the excitation and detection process and which mechanism is mainly responsible for the coherent magnon observed in the low temperature phase of NaV_2O_5. However, the discovery of the new triplet mode between the spin gap and two-particle continuum clearly shows that the spin excitation spectrum of NaV_2O_5 should be treated by the theory including higher order spin-spin interaction as Trebst *et al.* [20] showed. Furthermore, the results of our measurements clearly demonstrate that the time-domain coherent excitation measurement with REOS configuration using circularly polarized light provides a new powerful method for investigating subtle spin excitation levels from the correlated electron systems.

In conclusion, we have applied the time-domain spectroscopy to a transition metal oxide NaV_2O_5 around the phase transition temperature T_C. Below T_C, we have found that the peak intensity of the 303 cm^{-1} coherent phonon mode depends linearly on the temperature as the magnetic mode does, indicating a strong coupling to the spin state. Furthermore, we demonstrated the ability of the time-domain spectroscopy with circularly polarized light to research the ultrafast spin dynamics in condensed matter, and found a new spin excitation level at 127 cm^{-1} in the low temperature phase of NaV_2O_5.

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