Magnetic bound states in the quarter-filled ladder system α'-NaV_2O_5

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Raman scattering in the quarter-filled spin ladder system α'-NaV_2O_5 shows in the dimerized singlet ground state ($T \leqslant T_{SP} = 35$ K) an unexpected sequence of three magnetic bound states. Our results suggest that the recently proposed mapping onto an effective spin chain for $T > T_{SP}$ has to be given up in favor of the full topology and exchange paths of a ladder in the dimerized phase for $T < T_{SP}$. As the new ground state we propose a dynamic superposition of energetically nearly degenerate dimer configurations on the ladder. [S0163-1829(98)03646-7]

Low-dimensional quantum spin systems such as spin chains, ladders, or plaquettes received considerable attention from both theoretical and experimental points of view due to their manifold of unconventional spin excitation spectra. Of particular interest is the so-called spin-Peierls transition. The degeneracy of the ground state of an isotropic one-dimensional (1D) spin-1/2 system is lifted due to the coupling to the lattice, leading to a dimerized singlet ground state and the opening of a singlet-triplet gap.

The magnetic excitation spectrum of a dimerized spin chain consists of a triplet branch at Δ_{01}, a corresponding two-particle continuum of triplet excitations starting at $2\Delta_{01}$, and well defined magnetic bound states.[1–3] The latter consist of strongly interacting triplet excitations with a high energy cutoff at $2\Delta_{01}$. The existence of a singlet bound state at $\sqrt{3}\Delta_{01}$ is predicted by a 1D model with frustrated next-nearest-neighbor interaction $J_2 = 0.24 J_1$, acting as a binding potential. A further triplet bound state should appear for higher values of J_2.[2] A study of magnetic bound states in quantum spin systems therefore gives valuable insight into the low-energy spin excitations which govern the physics of these systems.

Half-filled spin ladder systems attracted enormous interest recently due to the surprising changes of the ground state and excitation spectrum interpolating between one- and two-dimensional quantum spin systems.[4] For even-leg ladders the doping by holes is found to lead to superconductivity. On the other hand, for the quarter-filled ladder system as the corresponding diluted system the ground state and spin excitation spectrum have not been well understood until now. However, it is expected that they show a similar rich excitation scheme as the half-filled system.[5]

The inorganic compound α'-NaV_2O_5 with double chains of edge-sharing distorted tetragonal VO_5 and a spin-Peierls-like transition[6,7] at $T_{SP} = 35$ K has been interpreted as a quarter-filled spin ladder system.[8] Recent x-ray diffraction data at room temperature are in favor of a centrosymmetric (D_{2h}^{13}) structure with only one type of V site of average valence +4.5. The spins are therefore attached to a V-O-V molecular orbital on the rungs.[8–10] The exchange interaction across the rung is by a factor of 5 larger compared to that along the legs.[8] Hence the ladder can be described by an effective spin chain.

The formation of a singlet ground state in α'-NaV_2O_5 below T_{SP} is observed as a drop in the magnetic susceptibility.[6,7] The observation of superlattice peaks in x-ray scattering proves a lattice dimerization with a doubling of the unit cell along the a and b axis and a quadrupling along the c axis.[11] The singlet-triplet gap was estimated using magnetic susceptibility: $\Delta_{01} = 85$ K,[7] NMR: 98 K,[12] ESR: 92 K,[13] and neutron scattering: 115 K.[11] Anomalous behavior of the spin-Peierls-like transition is evidenced by drastic deviations from the weak coupling regime, e.g., a large value of the reduced gap $2\Delta_{01}/k_B T_{SP} = 4.8$-6.6 K.[7,11–13] Moreover, hints for dynamic two-dimensional spin correlations are observed in neutron scattering.[11]

In this paper we will present an experimental investigation of the spin excitation spectrum of dimerized spin ladders in α'-NaV_2O_5 yielding evidence for magnetic bound states. Raman scattering as a powerful experimental technique allows us to probe dimerization-induced modes and the relevant exchange paths by applying polarization selection rules. Three modes appearing for $T < T_{SP}$ are identified by the selection rules and the temperature dependence of their intensity and linewidth as magnetic bound states. They originate from a lifting of the degeneracy of the ground state, which is thought to be a dynamic superposition of energetically degenerate dimer configurations along the rungs, legs, and diagonals of the ladders.

The scattering geometries available for our phonon Raman experiments on α'-NaV_2O_5 with our crystals, i.e., with the polarization of the incident and scattered phonons parallel to the directions (aa), (bb), (cc), and (ab) one expects 15 A_1 modes and 7 B_1 modes for the previously assumed noncentrosymmetric structure (C_{2v}^7),[14,15] whereas experimentally we observed only 8 and 3 modes,[16] respectively, in

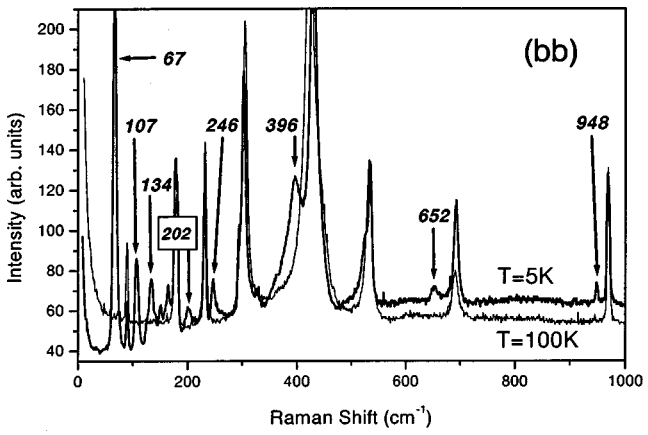

FIG. 1. Raman spectra of α'-NaV_2O_5 at 100 (thin line) and 5 K (bold line) with incident and scattered light parallel to the ladder direction (bb polarization).

agreement with the factor group analysis for the centrosymmetric structure (D_{2h}^{13}). In addition, infrared absorption data[17,18] did not show any phonons coinciding with our Raman-active phonon modes. Therefore the centrosymmetric D_{2h}^{13} structure should be favored. Hence there are no two inequivalent V sites which would give rise to the weakly coupled pairs of V^{4+} and V^{5+} chains as proposed by Isobe *et al.*[6]

In Fig. 1 we compare the Raman scattering intensity with incident and scattered light polarization parallel to the legs of the ladders (b axis) for temperatures above (100 K) and below ($T=5$ K) T_{SP}. At high temperature several phonons are observed ranging from 90 to 1000 cm^{-1} assigned as A_{1g} modes. In contrast to $CuGeO_3$ no spinon continuum is observed with polarization parallel to the chains. This is in agreement with previous results that a considerable frustration is required to observe a spinon continuum in light scattering experiments.[19] In α'-NaV_2O_5 the frustration is supposed to be weak.[8,10] A broad phonon at 422 cm^{-1} [$\approx J$ (Refs. 6,7)] hardens in energy unusually strong by 2.5% upon lowering temperature below $T=T_{SP}$. This demonstrates a non-negligible spin-phonon coupling in this system.

Several additional modes are detected in the dimerized phase in bb polarization. The frequencies of these excitations are 67, 107, 134, 151, 165, 202, 246, 294 (shoulder), 396, 527 (shoulder), 652 (remnant from aa polarization), and 948 cm^{-1}. In addition, for frequencies below 120 cm^{-1} an overall drop of the background intensity is observed. This is a typical phenomenon for the occurrence of an energy gap. The value of this gap can be determined experimentally to be about 120–125 cm^{-1}. If we attribute this gap to be the onset of the two-particle continuum of triplet excitations $2\Delta_{01}$, we obtain $\Delta_{01}\approx 60$–62 cm^{-1}, in good accordance with the value determined from susceptibility data.[7]

For the discrimination between phonon modes arising because of the existence of a superstructure and possible magnetic bound states in Raman spectroscopy some criteria have been developed in the case of $CuGeO_3$.[20] In this frustrated spin chain compound one singlet bound state is observed only for incident and scattered light parallel to the chain direction. These polarization selection rules are consistent

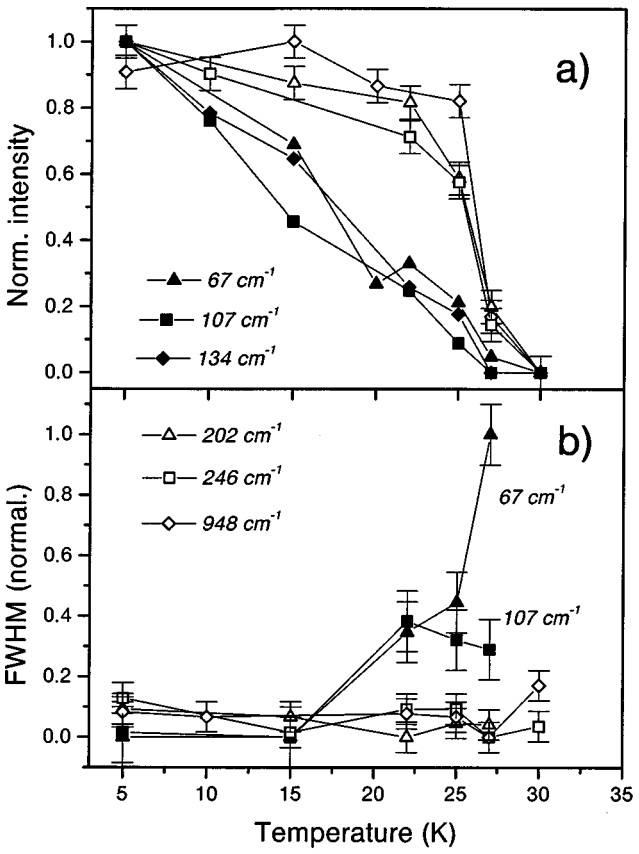

FIG. 2. (a) Integrated intensity of the additional modes observed below T_{SP} and (b) normalized halfwidth (full width at half maximum) of the additional modes as function of temperature.

with the spin conserving nature of the exchange light scattering mechanism ($\Delta s=0$) with a Hamiltonian which is identical to the Heisenberg exchange Hamiltonian. This process allows no off-diagonal scattering matrix element (in crossed polarizations) as observed for one magnon excitations in 2D or 3D antiferromagnets. As the singlet bound state responds very sensitively by defects and thermal fluctuations its scattering intensity as function of temperature reaches its maximum intensity at lower temperatures compared with the dimerization induced phonon modes.[20] On the other hand, phonon related bound state phenomena observed, e.g., in rare-earth chalcogenides showed different properties concerning their selection rules and frequencies.[21]

The temperature dependence of scattering intensity, frequency shift, and linewidth for various modes observed in the quarter-filled ladder system α'-NaV_2O_5 leads us to an unambiguous distinction between the three modes with energies close to $2\Delta_{01}$ (67, 107, and 134 cm^{-1}) and the other dimerization induced modes at higher energies. Before pointing this out we have to exclude that the 67-cm^{-1} mode is a singlet-triplet excitation (one magnon or spin-flip scattering). This would only be allowed if magnetic light scattering were dominated by spin-orbit coupling. In light scattering experiments in a static magnetic field of up to 7 T neither a shift nor a broadening of this mode was observed. Therefore a one-magnon scattering process can be excluded and hence spin-orbit coupling plays a negligible role in the present context.

Figure 2(a) shows the intensity of several modes at low

temperatures ($T<T_{SP}$) normalized to the adjacent most intense ones. Clearly one can distinguish between the modes at 67, 107, and 134 cm^{-1} on the one hand, and the modes at, e.g., 202, 246, and 948 cm^{-1} on the other hand. The second group follows the behavior expected for a second order type phase transition, i.e., the intensity increases quite sharply upon cooling and then saturates towards low temperatures. The first group of modes obviously increases in intensity upon cooling much more gradually and shows no saturation towards lower temperatures. A similar temperature dependence of the intensity was found for the singlet bound state at 30 cm^{-1} in $CuGeO_3$.[20]

Figure 2(b) gives further support for this interpretation. The change of linewidth normalized to the strongest change (67-cm^{-1} mode) is shown as function of temperature. While the three modes at 202, 246, and 948 cm^{-1} do not show any broadening upon approaching the phase transition temperature from below, a behavior typical for simple zone boundary folded phonons, the two modes at 67 and 107 cm^{-1} become remarkably broader. This effect is also accompanied by a small softening of their frequency. The mode at 134 cm^{-1} has been omitted in this analysis due to a strongly changing background. Nevertheless, the tendency is the same.

Further insight can be gained from the comparison with a formerly investigated single crystal of α'-NaV_2O_5 in Ref. 16 with a slightly broader transition width. The temperature dependence of the intensity of the additional modes at 64, 103, and 130 cm^{-1} shows a similar distinction from the other dimerization-induced modes. However, their frequencies are lower by about 4 cm^{-1} and their absolute intensities are reduced compared to the single crystals used in the present investigation. The energy of all other modes is independent of sample quality. As shown in substitution experiments in $CuGeO_3$ (Ref. 20) magnetic bound states in quantum spin systems are extremely sensitive to any defect or thermal fluctuation. Hence from an experimental point of view we have presented reliable evidence that the three modes at 67, 107, and 134 cm^{-1} are related to the singlet-triplet gap and therefore indeed magnetic bound states.

Spin chain models, which neglect magnetic or magnetoelastic interchain coupling successfully explain the excitation spectrum of $CuGeO_3$ with one singlet bound state.[1,2] Affleck[3] proposed a different physical picture which allows for more than one bound state. Due to a linear confining potential mediated via interchain coupling magnetic bound states of soliton-antisoliton pairs arise. If the slope of this confining potential is not too strong, there would be a chance for more than one bound state below the two particle continuum. However, this would imply a more pronounced one dimensionality in α'-NaV_2O_5 compared to $CuGeO_3$.

The experimental data in the dimerized phase do not confirm this. Figure 3 shows the polarization dependence of the low-energy excitation spectrum. It can be clearly stated that the intensity of the 67-cm^{-1} mode is not restricted to bb-polarization parallel to the legs. It appears in the aa (i.e., perpendicular to the ladder) and ab polarizations, as well. Also the 134-cm^{-1} mode and the onset of a continuum at 120 cm^{-1} are observed in all three polarization configurations. So the one dimensionality concerning the polarization selection rules is obviously not pronounced. On the other hand, the mode at 107 cm^{-1} fulfills the selection rules expected for a singlet bound state in a dimerized chain. It only appears in bb polarization along the ladder direction. Also its energy, as pointed out above, corresponds to the energy of the singlet bound state mode in $CuGeO_3$, i.e., $\sqrt{3}\Delta_{01} = \sqrt{3}$ (60–62 cm^{-1}).

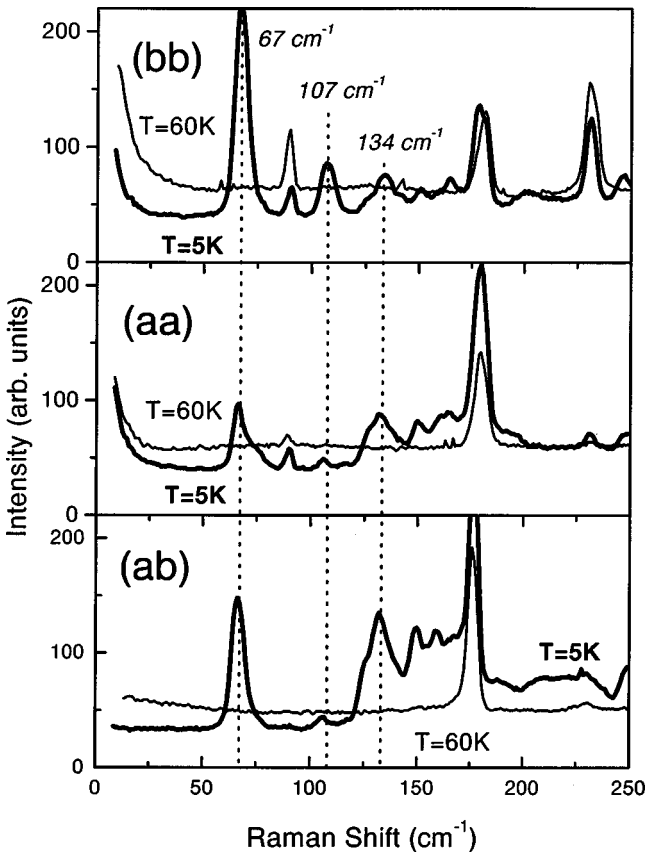

FIG. 3. Raman spectra of α'-NaV_2O_5 for three scattering configurations in the ab plane of the single crystal.

This leads us to the following interpretation of our experiments based on α'-NaV_2O_5 as a quarter-filled ladder: It is not surprising that this compound can have a spin-Peierls transition into a dimerized ground state assuming an effective spin chain model. To understand the full excitation spectrum this point of view obviously is not enough. As more bound states exist than allowed in models based on dimerized chains we consider the possible exchange paths of the quarter-filled ladder to construct further possible dimer states. These might occur along the rung (a axis), and the ladder legs (b axis) and its diagonals. To obtain the observed superlattice structure and allowing only weak interaction between ladders the possible dimers are restricted to a square of adjacent sites. Figure 4 shows a representation of these possible states. The energies of a- and b-axis dimers should be nearly degenerate leading to a system of several competing ground states. Hopping processes between these states will form a quantum superposition which splits the dimer energy levels by Δ_{el} and leads to a lowering of the lowest eigenstate. This dynamic configuration is allowed as long as the energy of phonons $\hbar\omega_{ph}$ with a dominant spin-phonon coupling that induce the dimerization, fulfill $\hbar\omega_{ph} \gg \Delta_{el}$. This picture is comparable with the dynamic Jahn-Teller effect or the RVB model.

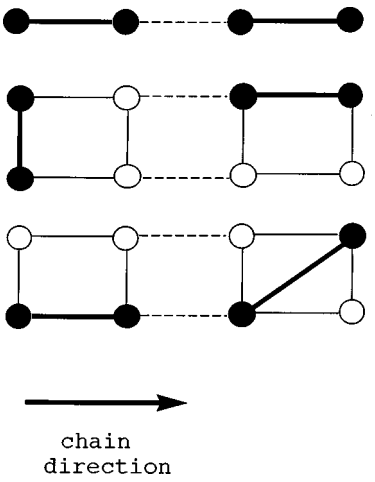

FIG. 4. Possible dimer configurations of a dimerized chain (first horizontal row) and a quarter-filled ladder (second and third row). Possible microscopic resonating dimer configurations are given. The induced lattice superstructure is compatible with the observed lattice doubling in α'-NaV_2O_5.

In this way the breakdown of the selection rules observed in light scattering as well as the unexpected low energy of the bound state at 67 cm^{-1} is described qualitatively. A quantitative discussion will have to explain the exact energies of the singlet modes as well as those of the modes in the triplet channel. Therefore neutron scattering data are of crucial importance. In recent experiments of Yosihama[11] a triplet mode with a steep dispersion along the b^* axis (ladder direction) splits into two branches along the a^* axis. Its maximum splitting of 34 K ($=23.5$ cm^{-1}) gives a new low-energy scale and may be understood as a bonding-antibonding band of the dimers on adjacent plaquettes. This additional scale is much smaller than the charge transfer gap $\Delta_{CT}=0.7$ eV of the V-O-V orbital, the lowest excited state in the spin chain models of Refs. 8,10. As a rough estimate the energy separation between the first and the second singlet bound state (40 cm^{-1}) observed in Raman scattering experiments should be comparable with twice the maximum splitting of the triplet dispersion along the a^* axis. The factor of 2 results from the binding of two triplet states to a singlet bound state.

Using light scattering in α'-NaV_2O_5, magnetic singlet bound states were identified. These states consist of triplet excitations that are bound with respect to the ''free'' two-particle continuum of states above $2\Delta_{01}$. While the mode at 107 cm^{-1} fits both in energy and selection rules to a singlet bound state in a dimerized spin-1/2 Heisenberg chain, the other two bound states do not fit to such a simple picture. Instead, we propose the origin of the singlet modes at 67 and 134 cm^{-1} as due to a superposition of several nearly degenerate dimer configurations on the quarter-filled ladder. We therefore give evidence that, in contrast to the homogeneous high-temperature phase, the dimerized phase of α'-NaV_2O_5 cannot be understood on the basis of a dimerized spin chain. Instead, it is necessary to consider the topology and enlarged exchange degrees of freedom of a ladder.

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