Raman scattering from magnetic excitations in the spin-ladder compounds CaV_2O_5 and MgV_2O_5

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We present the Raman-scattering spectra of CaV_2O_5 and MgV_2O_5. The magnetic contribution in the Raman spectra of CaV_2O_5 is found in the form of a strong asymmetric line, centered at $2\Delta_S$, with a tail on the high-energy side. Our analysis of its spectral shape shows that the magnetic ordering in CaV_2O_5 can be described using a $S=1/2$ two-leg ladder Heisenberg antiferromagnetic model with $J_\parallel/J_\perp \sim 0.1$, and a small interladder exchange. The spin-gap and exchange constant are estimated to be $\Delta_s \sim 400\ \mathrm{cm}^{-1}$ (570 K) and $J_\perp \sim 640$ K. No magnon bound states are found. In contrast to CaV_2O_5 the existence of the spin gap is not confirmed in MgV_2O_5, since we found no feature in the spectra which could be associated with the onset of the two-magnon continuum. Instead, we observe two-magnon excitation at $340\ \mathrm{cm}^{-1}$, presumably related to the top of the two-magnon branch.

I. INTRODUCTION

The spin-1/2 ladder systems, which are the intermediate situation between one-dimensional (1D) and two-dimensional Heisenberg antiferromagnet (HA), show fascinating quantum effects such as dramatic dependence of the ground state on the width of the ladder (the width of the ladder is defined as a number of coupled chains).[1] Namely, ladders made of even number of legs have spin-liquid ground state with an exponential decay of the spin-spin correlations produced by the finite spin gap. Among them, the two-leg ladder is the first member of the family, with a largest spin gap of about 0.5 J (assuming the same coupling constant along the legs and the rungs).

Realizations of the ladders are recognized in Sr-Cu-O structures,[2] and recently in AV_2O_5, $A=$Ca, Mg (two-leg ladder).[3] According to their crystal structures, vanadium oxides are quasi-2D layered materials, with spin-1/2 vanadium ions which form two-leg ladders coupled in the trellis lattice. The spin gap is observed in CaV_2O_5 to be around 600 K,[4,5] and the magnetic susceptibility measurements[5] demonstrated almost perfect agreement with spin-1/2 two-leg ladder HA model. On the other hand, there is only contradicting evidence for the existence of the spin-gap in MgV_2O_5.[6,7]

The excitation spectrum of the ladder has been analyzed by a variety of the mathematical techniques. However, it was recently shown that the two-magnon bound state (we will use word magnon although classical magnons do not exist in quantum systems), besides usual triplet (gap mode) and two-magnon continuum, may appear in the excitation spectra.[8] Such a bound state is also predicted for the dimerized quantum spin chain[9] and indeed observed in $CuGeO_3$,[10] using a Raman-scattering technique. These singlet-singlet transitions (the $30\ \mathrm{cm}^{-1}$ mode in the Raman spectra of $CuGeO_3$ is believed to be the transition between ground state and the two-magnon bound state which are both singlets) are allowed and take place via exchange scattering mechanism.[11] On the contrary, the Raman scattering process on spin-gap excitations (one-magnon scattering) takes place via spin-orbit interaction,[11] and it is usually negligible due to quenched orbital momentum in the transition metal ions. It is therefore, desirable to study Raman scattering in magnetic ladder materials such as CaV_2O_5 and MgV_2O_5, since these experiments provide information about the spin dynamics and the type of magnetic order. In this paper, we present a study of the spin dynamics in CaV_2O_5 and MgV_2O_5 using Raman scattering technique. We analyze the origin of the magnetic modes in the spectra and discuss the difference between magnetic ordering in these two compounds.

II. EXPERIMENT

The measurements were performed on polycrystalline samples, prepared as described in Ref. 3. As an excitation source we used the 514.5 nm line of an Ar^+ ion laser. An average power of 5 mW was focused with microscope optics on the surfaces of the pellets. The temperature was controlled with a liquid helium micro-Raman cryostat (CryoVac, Vacuubrand GMBH). The spectra were measured in backscattering geometry using a DILOR triple monochromator equipped with a CCD camera.

III. RAMAN SPECTRA OF CaV_2O_5

CaV_2O_5 has an orthorhombic unit cell, space group *Pmmn*,[5] with a crystalline structure formed by layers of VO_5 square pyramids. The Ca ions are situated between these layers, see Fig. 1. The pyramids are mutually connected via common edges and corners making characteristic V zigzag chains along the *b* axis. All vanadium atoms are in 4+ va-

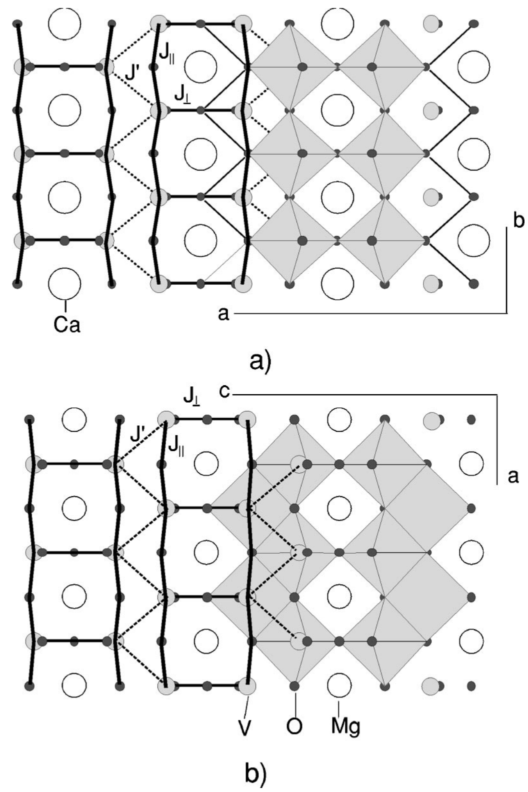

FIG. 1. Schematic representation of the (a) CaV_2O_5 and (b) MgV_2O_5 crystal structures. The thick and dashed lines represent the superexchange pathways.

lence state thus carrying the spin=1/2. Effectively, this structure can be regarded as composed from spin-1/2 two-leg ladders connected with each other in the trellis lattice.

CaV_2O_5 is isostructural with NaV_2O_5. Therefore, the same irreducible representations correspond to the vibrational modes of CaV_2O_5 and NaV_2O_5:[12]

$$\Gamma_{\rm opt}=8A_g(aa,bb,cc)+3B_{1g}(ab)+8B_{2g}(ac)+5B_{3g}(bc)$$
$$+7B_{1u}(\mathbf{E}||\mathbf{c})+4B_{2u}(\mathbf{E}||\mathbf{b})+7B_{3u}(\mathbf{E}||\mathbf{a}).$$

The room-temperature Raman spectra of CaV_2O_5 are presented in Fig. 2. Comparing the phonon averaged intensities, of *HH*, *HV* and *VV* scattering configurations, with the polarized Raman scattering spectra of NaV_2O_5 single crystals we assign the phonon modes of CaV_2O_5. The phonon frequencies of CaV_2O_5 are found to be close to those in NaV_2O_5, as expected from similarity between lattice constants and interatomic distances in these two oxides. The low-temperature spectra of CaV_2O_5 are shown in Fig. 3. In addition to phonons we found a strong asymmetric line at 795 cm^{-1} (1137 K) with a tail towards higher energies. This line decreases in intensity and broadens by increasing the temperature, together with the intensity decrease of the associated continuum, see the left inset in Fig. 3. Moreover, its energy is in the range of $2\Delta_s$, estimated from the spin-gap measurements, thus suggesting its magnetic origin. Below, we will show by detailed discussion of the experimental results that this is indeed the case, i.e., that 795 m^{-1} feature corresponds to the onset of the two-magnon continuum at $2\Delta_s$.

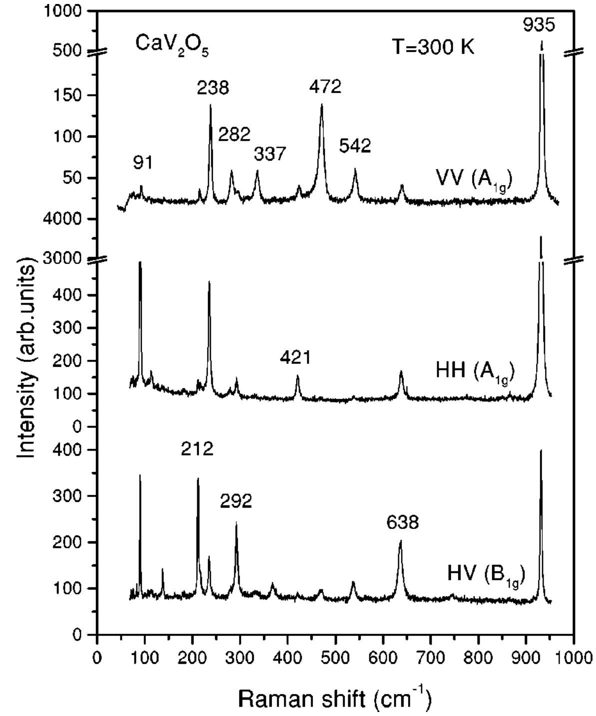

FIG. 2. Raman spectra of CaV_2O_5 at room temperature in three different polarized configurations.

The magnetic susceptibility measurements[6] show a broad maximum around 400 K, with a decrease towards zero at low temperatures, thus reflecting the low dimensionality of the magnetic interaction, the singlet ground state and the finite spin gap. The spin gap is found to be around 660 K using electron spin resonance[5] and at around 500 K using nuclear magnetic resonance[4] experiments. Since the magnon dispersion is not reported in the literature, the exchange couplings are estimated by comparison of the calculated and measured temperature dependencies of the susceptibility. The Monte Carlo simulations[13,14] showed that the magnetic properties of CaV_2O_5 can be indeed described using a coupled ladder

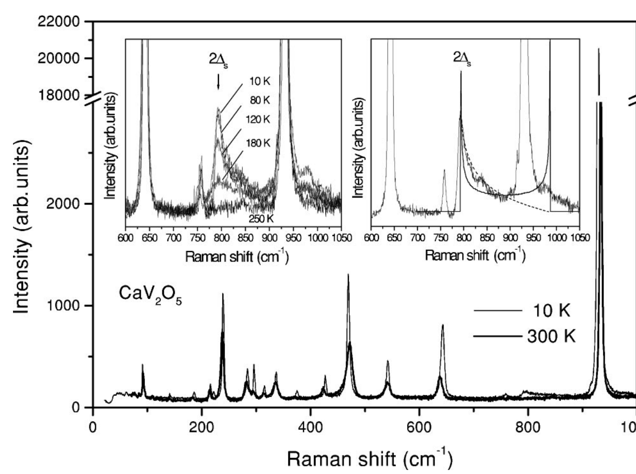

FIG. 3. Raman spectra of CaV_2O_5 at room temperature (thick line) and at $T=10$ K (thin line). Left inset: The temperature dependence of the onset of the magnetic continuum at 795 cm^{-1}. Right inset: The $T=10$ K Raman spectra compared with DOS calculation and exact diagonalization result for the spin-ladder model, see text.

spin-1/2 *HA* model (trellis lattice) with in-rung exchange ($J_\perp \sim 600$ K) five times or even an order of magnitude larger then the exchange along the legs. The interladder exchange is found to be negligible.

Thus we start analyzing our Raman spectra using Heisenberg Hamiltonian for the ladder model:

$$H = J_\perp \sum_{i,j \text{ rungs}} \mathbf{S}_i \cdot \mathbf{S}_j + J_\parallel \sum_{i,j \text{ legs}} \mathbf{S}_i \cdot \mathbf{S}_j , \tag{1}$$

where the $\mathbf{S}_i$ represents a spin-1/2 operator at site i of the ladder. The properties of the magnetic excitations in the Heisenberg ladder have been obtained using perturbation method in the strong coupling limit.[15] In this limit $J_\perp > J_\parallel$ the lowest spin-triplet dispersion is[15]

$$\omega(k) = J_\perp + J_\parallel \cos(k) + \frac{3}{4}\frac{J_\parallel^2}{J_\perp} + \cdots .$$

The minimum and the maximum energies of the triplet are at $k=\pi$ ($\omega \sim J_\perp - J_\parallel$) and at $k=0$ ($\omega \sim J_\perp + J_\parallel$). Thus the gap is $\Delta_s \sim J_\perp - J_\parallel$, and the total width of the branch $\sim 2J_\parallel$. Therefore, from the measurements of the energy onset and the width of the two-magnon continuum we could uniquely obtain the values of the exchange integrals $J_\perp$ and $J_\parallel$.

As we have already mentioned, the two-magnon excitations in the Raman spectra can be observed through the exchange-scattering process. Then, the well defined peak around $2\Delta_s$ is expected in the Raman spectra of the ladder, due to the singularities of the one-dimensional density of (two-magnon) states (DOS),[16] or due to the appearance of the magnon bound state.[8] In the first case the peak position is exactly $2\Delta_s$ while in the second case the peak can be found at $2\Delta_s - \delta$, δ being the magnon binding energy. We believe that the 795 cm^{-1} line in CaV_2O_5 Raman spectra does not correspond to a magnon bound state due to the following reasons.

(1) The frustration in this material is expected to be small,[14] and the binding energy is then estimated to be small.[8]

(2) The intensity of the 795 cm^{-1} line saturates at temperatures below 80 K. In the case of the bound state the linear dependence of its intensity as a function of the temperature is believed to be the fingerprint of it, without saturation up to very low temperatures.[17]

Thus, we assign the onset of the magnon continuum to $2\Delta_s = 795$ cm^{-1} and obtain the spin-gap in CaV_2O_5 to be $\Delta_s = 398$ cm^{-1} (570 K). Moreover, the width of the continuum is estimated to be around 200 cm^{-1}, see left inset of Fig. 3. The shape of the magnon continuum in the spectra is compared with classical noninteracting two-magnon spin-wave calculation (DOS), $I \sim \Sigma_k \delta[E - 2\omega(k)]$, and with numerical simulations of the spin-ladder model[16] using exact diagonalization technique. These spectra are presented in the right inset of Fig. 3. As expected, the DOS (full curve), obtained using $J_\perp \sim 640$ K and $J_\parallel \sim 70$ K, failed to explain the nonobservation of the van Hove singularity, associated with the top of the two-magnon branch. It is well known, that in the ideal one-dimensional systems magnons do not behave classically but form a continuum of excitations.[18] This effect is clearly seen in exact diagonalization result (dashed curve, in the right inset of Fig. 3) obtained with $J_\parallel / J_\perp \sim 0.1$ in Ref. 16. However, a discrepancy between the theory and the experiment is still found around 1000 cm^{-1}. The possible explanation may lie in the fact that the exact diagonalization result,[16] has been obtained strictly for the two-magnon scattering process, thus neglecting higher-order magnon contributions. Also, we have to note that the inclusion of the higher-order magnon processes would produce the scattering intensity above the two-magnon high-energy cutoff but it will still fail to explain the weak broad peak observed in the spectra around 980 cm^{-1}. We suggest that such a shape of the two-magnon continuum may come from the next-nearest-neighbor interactions, which were not taken into consideration in the numerical simulations.

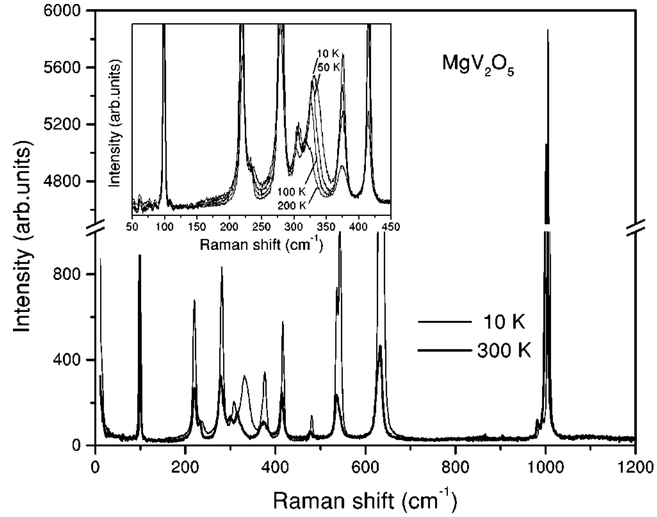

FIG. 4. Raman spectra of MgV_2O_5 at room temperature (thick line) and at $T = 10$ K (thin line). Inset: Raman spectra at various temperatures in the 50 to 450 cm^{-1} frequency range.

IV. RAMAN SPECTRA OF MgV_2O_5

MgV_2O_5 has an orthorhombic unit cell, space group *Cmcm*,[19] with a similar V-O layered structure as in CaV_2O_5. The structure can be described as a linkage of VO_5 pyramids, with apical oxygens along the *b* axis. The V zigzag chains run along the *a* axis. The factor group analysis (FGA)[20] gives

$$\Gamma_{\text{opt}} = 8A_g(aa,bb,cc) + 5B_{1g}(ab) + 5B_{2g}(ac) + 6B_{3g}(bc) + 7B_{1u}(\mathbf{E}||\mathbf{c}) + 7B_{2u}(\mathbf{E}||\mathbf{b}) + 4B_{3u}(\mathbf{E}||\mathbf{a}).$$

The room temperature and the $T = 10$ K Raman spectra of MgV_2O_5 are shown in Fig. 4. In addition to phonon excitations, which we will not discuss here, we observe the continuumlike asymmetric mode around 340 cm^{-1}. This structure shows large intensity and frequency dependence as a function of the temperature. The temperature dependence of the spectra in the frequency range from 50 to 450 cm^{-1} is shown in the inset of Fig. 4. The continuum clearly extends from 150 to 350 cm^{-1} with a spectral weight cutoff around 350 cm^{-1}. This mode shifts to lower energies, as well, and decreases in intensity by increasing temperature. Such a form of the spectra and its temperature dependence suggests the two-magnon origin of the continuum, with a peak at 340 cm^{-1} corresponding presumably to zone boundary magnons.

On the other hand, no feature is found in the vicinity of $2\Delta_s \sim 21$ cm^{-1} (30 K) – 32 cm^{-1} (45 K),[6,7] so the existence of the spin gap is not confirmed by our results. However, we have to note that this energy range is close to the frequency limit (10 cm^{-1}) of our experiment.

The existence of the large zone boundary magnon spectral weight in the Raman spectra, reflects strong deviation of the magnetic ordering in MgV_2O_5 from the 1D two-leg-ladder type observed in CaV_2O_5. In principle, such a deviation may be a consequence of the two effects.

(1) There is a spin gap in MgV_2O_5 (according to our measurements it must be less than 10 cm^{-1}) and the values of the exchange constants along legs and rungs are either very close to each other, or the rung exchange is much smaller than the leg exchange (the latter case corresponds to homogenous Heisenberg antiferromagnetic chain with a large frustration).

(2) There is no spin-gap and magnetic ordering is quasi-2D.

For the first case, since the existence (and the value) of the gap is still an open question and since all measurements are performed on polycrystalline samples, it is hard to make any estimation of the exchange integrals. On the other side, if we assume 2D magnetic ordering, the effective exchange constant can be estimated from the position of the two-magnon peak using relation $E_{\text{two-magnon}} = 2.7\,J$. In this case we obtain $J = 125$ cm^{-1} (180 K), which is close to the energy $J_\parallel = 144$ K obtained in Ref. 14. However, this formula is strictly valid only for 2D square lattice with the isotropic exchange, which is clearly not the case in MgV_2O_5 even though the exchange couplings (along legs and rungs) are found to be all of the same order.[14] Because of that, we believe that neither one of the above mentioned models are applicable to MgV_2O_5, since this compound belongs to the class of strongly frustrated trellis lattices. Unfortunately, the existence of the spin-gap and the type of magnetic ordering in this type of lattice are not yet known.[21]

V. CONCLUSION

In conclusion, we present the Raman-scattering spectra of CaV_2O_5 and MgV_2O_5. In CaV_2O_5 we found the onset of the two-magnon continuum at the energy $2\Delta_s \sim 795$ cm^{-1} in the form of the strong asymmetric line with a tail on the high-energy side. From the analysis of its spectral shape, we argue that the magnetic ordering in CaV_2O_5 can be described using a $S = 1/2$ two-leg ladder Heisenberg antiferromagnetic model with $J_\parallel / J_\perp \sim 0.1$, and a small interladder exchange. The spin gap and exchange constant are estimated to be $\Delta_s \sim 400$ cm^{-1} (570 K) and $J_\perp \sim 640$ K. No magnon bound states are found. In contrast to CaV_2O_5 the existence of the spin gap is not confirmed in MgV_2O_5. Instead, we observe a strong two-magnon excitation at about 340 cm^{-1} corresponding presumably to zone boundary magnons. These results reflect strong deviation of the magnetic ordering in MgV_2O_5 from the 1D two-leg-ladder type observed in CaV_2O_5.

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