

Effect of Pressure on the Magnetic Phase Transition in α' - NaV_2O_5

The spin-Peierls (SP) transition in its simplest form may occur in antiferromagnetically coupled $S=1/2$ Heisenberg or XY chains if magnetoelastic coupling causes a spin-lattice dimerization which induces a gap opens in the magnetic excitation spectrum. The gap separates the diamagnetic groundstate from a continuum of excited states. The SP transition traditionally it has gained renewed interest triggered by the discovery of a low-temperature phase transition in CuGeO_3 which showed the signatures of a SP transition below 14 K.

Lately, the compound α' - NaV_2O_5 was suggested to represent the second inorganic SP system. A magnetic phase transition occurs in α' - NaV_2O_5 at $T_C \approx 34$ K below which the spin susceptibility $\chi^{\text{spin}} \rightarrow 0$ as $T \rightarrow 0$. A gap of about 10 meV develops and a lattice distortion appears. Based on the original crystal structure determination, $S = 1/2$ chains in α' - NaV_2O_5 were supposed to originate from V^{4+} ions being arranged in chains along the b axis. This structure model was strongly guided by the assumption of a charge disproportionation and the formation of two different V moieties viz. V^{4+} and V^{5+} in a non-centrosymmetric crystal structure. Redeterminations of the crystal structure at room temperature rather indicated α' - NaV_2O_5 to crystallize in a centrosymmetric structure. The new structure model retains the general arrangement of the atoms but finds all V atoms to be identical with an average oxidation state of +4.5. A local density approximation analysis proposed the electrons to be distributed in molecular type wavefunctions across a V–O–V rung of V–O ladders which run along the b direction. In consequence the notion of a quarter filled ladder system has been introduced for α' - NaV_2O_5 which renders a natural explanation for the insulating character of α' - NaV_2O_5 .

The nature of the state below the phase transition originally proposed by to be a conventional SP state is currently strongly disputed. The detection of two inequivalent V sites by NMR is interpreted as due to charge disproportionation associated to the formation of the singlet magnetic ground state. In contrast to CuGeO_3 , charge degrees of freedom therefore appear to be an essential feature of the phase transition in α' - NaV_2O_5 .

Here we report about of a high pressure (< 1 GPa) Raman scattering and magnetization investigation of the transition temperature of α' - NaV_2O_5 . By applying pressure the transition temperature of α' - NaV_2O_5 decreases, in contrast to CuGeO_3 for which a remarkable increase with pressure has been detected. We discuss our findings with respect to the results of a recent high-pressure x-ray crystal structure investigation which reveals a pronounced anisotropy of the compressibilities and with respect to theoretical predictions for the pressure dependence of the transition temperature in SP systems.

Figure 1(a) shows Raman spectra of α' - NaV_2O_5 in the temperature range of 5–18 K at a pressure of 0.55 GPa. The transition to the low-temperature phase manifests itself in the Raman spectra by the appearance of additional peaks due to the folding of the Brillouin zone and changes to the magnetic excitation spectrum. In our configuration, Raman modes intrinsic to the low-temperature phase could be observed at 657 and 950 cm^{-1} . From the temperature dependence of the intensity of the 950- cm^{-1} peak [inset Fig. 1(b)], T_C at a given pressure could be deduced. Figure 1(b) displays T_C versus pressure P . The zero-pressure value of T_C determined by this method is a few degrees lower compared to accurate determinations from specific heat or magnetic susceptibility measurements which yield $T_C = 33.2(2)$ K. This deviation is mostly due to heating of the sample by the incident laser beam. The heating effect should, however, hardly affect the pressure dependence of T_C . Figure 1(b) shows T_C as a function of pressure. The transition temperature decreases rapidly with increasing pressure at a rate of -15(5) K/GPa. No signature of a phase transition was detected at pressures above 1.2 GPa and temperatures down to 5 K. This finding indicates a suppression of the phase transition at relatively low pressures. In this respect, α' - NaV_2O_5 behaves similar to most organic SP compounds.

T_C can be determined more accurately from the sharp drop in the magnetic susceptibility below the transition. Figure 2 displays a set of magnetic susceptibilities of α' - NaV_2O_5 for various pressures. The magnetization of the empty cell has been subtracted. The high signal-to-noise ratio allows a reliable determination of the T_C from the peak temperature of the quantity $d(\chi_{\text{mol}} \cdot T)/dT$ (inset Fig. 2(a)). There was no indication of hysteresis when cycling the pressure in the range up to 1 GPa and back to ambient pressure. T_C decreases with increasing pressure as is shown in Fig. 2(b). This result confirms the observation

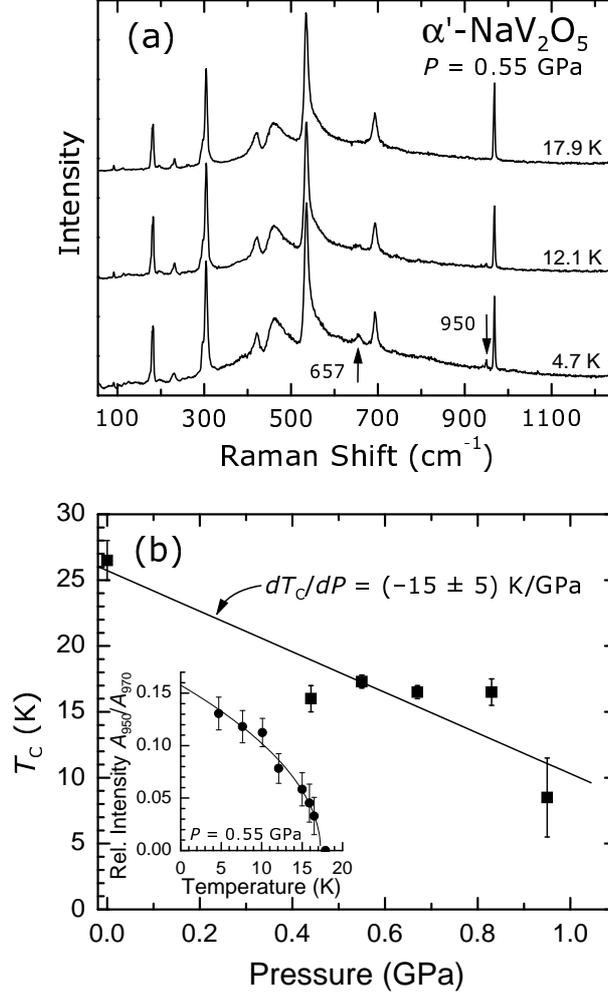


Figure 1: (a) Raman spectra of α' - NaV_2O_5 at 0.55 GPa for temperatures of 4.7–17.9 K. (b) Transition temperature of α' - NaV_2O_5 versus pressure as deduced from the intensity measurements of the Raman peak at 950 cm^{-1} (see inset).

of the Raman scattering experiments and proves the decrease of the transition temperature with increasing pressure. The average linear pressure coefficient for T_C is $-10(1) \text{ K/GPa}$, somewhat lower than observed in the Raman scattering results but within mutual error. From the magnetization experiments the pressure dependence appears to be nonlinear with a negative curvature. A fit to a parabolic decrease $T_C[\text{K}] = 34.0 - 6.1(2.6)P - 6.0(3.7)P^2$, where pressure P is in GPa, fits the data with an improved χ^2 parameter, however, in view of the error bars this presumption requires further experimental confirmation.

The phenomenology of the magnetic transition on α' - NaV_2O_5 closely resembles that of a SP transition in quasi-one-dimensional spin systems. The variation of T_C with pressure in organic SP systems has been studied by Bray. Using the expressions for T_C as derived by Pytte and Cross and Fisher a decrease of T_C with pressure is predicted as has, for instance, been observed for the organic SP system TTF-CuBDT.

An increase of T_C with pressure, as experimentally realized e.g. in (MEM)-(TCNQ) $_2$, has theoretically been explained by Lepine by taking into consideration an anharmonic coupling of the (anharmonic) SP soft mode to the average lattice strain along the chains. Depending on the sign of the coupling energy between the soft mode and the lattice strain along the chain, T_C can either decrease or increase with pressure.

The above scenario, which is based on an essentially one-dimensional picture and intrachain interactions only, does not readily apply to α' - NaV_2O_5 . Recent crystal structure determinations under pressure

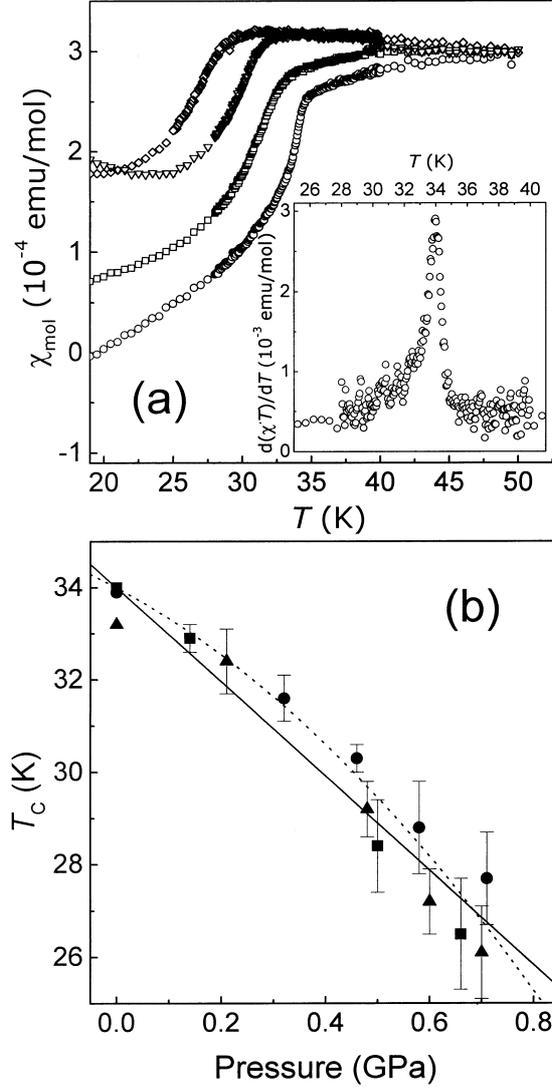


Figure 2: (a) Magnetic susceptibility of α' - NaV_2O_5 measured at different external pressures, 0, 0.32, 0.46 and 0.71 GPa, from right to left, respectively. The inset displays the temperature derivative of $\chi_{mol} \cdot T$ with χ_{mol} taken at ambient pressure (b) Pressure dependence of the SP transition temperature T_{SP} of α' - NaV_2O_5 . The full line represents a fit of a linear decrease ($T_C[\text{K}] = 34.0 - 10.2(7) \cdot P$ [GPa]) to all data, the dotted line a fit with a parabola (see text). Different symbols refer to samples taken from different batches.

show that α' - NaV_2O_5 is rather incompressible along the chain axis (b) as well as perpendicular to the chains in the a -axis direction and most of the overall volume change is due to the large compressibility along the c -axis. The enhanced interlayer interaction affects in particular the apex oxygen atoms of the VO_5 units, as evidenced, for instance, by the pronounced softening of the out-of-plane vibrations of these oxygen atoms with increasing pressure. It therefore appears plausible that it is the enhanced interlayer coupling under pressure which plays a major role in determining the pressure dependence of T_C . On the one hand, the large reduction of the c -axis clearly affects the intralayer *elastic* properties as is indicated by the unusual pressure dependence of the a and b lattice parameters. These show negative compressibility at pressures above 4 GPa and near ambient pressure, respectively. Secondly, in view of the suggested charge disproportionation associated with the magnetic transition in α' - NaV_2O_5 , there may also be an additional more subtle *electronic* aspect specific to the transition in α' - NaV_2O_5 , namely an increase in the screening of Coulomb interactions with increasing pressure. To our knowledge, microscopic theoretical models proposed so far for α' - NaV_2O_5 deal with intrachain or intralayer couplings only and do not take into account the interlayer interactions.

In summary, from magnetization as well as Raman measurements the magnetic transition temperature in α' - NaV_2O_5 is found to be strongly pressure dependent. It decreases with pressure at an average rate of -10 K/GPa. In this respect the behavior of α' - NaV_2O_5 differs from that of CuGeO_3 which shows a pronounced increase of T_{SP} under pressure. Based on the evolution of structural parameters under pressure and anomalous pressure effects on lattice vibrational modes we argue that enhanced interlayer interactions are likely to play a major role in the suppression of the transition in α' - NaV_2O_5 under pressure.

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