

ELECTRONIC AND MAGNETIC PHASE TRANSITIONS IN QUASI ONE-DIMENSIONAL β - $\text{Na}_{1/3}\text{V}_2\text{O}_5$ UNDER PRESSURE*

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The pressure dependence of the phase transitions in the quasi one-dimensional vanadium oxide β - $\text{Na}_{1/3}\text{V}_2\text{O}_5$ has been studied by magnetic susceptibility and electrical resistivity measurements. Under pressure the metal-insulator (MI) transition at $T_{\text{MI}} = 130$ K shifts to lower, the magnetic transition at $T_{\text{N}} = 24$ K to higher temperatures. This behavior is discussed in terms of increasing interchain coupling.

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1. Introduction

Among the strongly anisotropic sodium vanadates $\text{Na}_x\text{V}_2\text{O}_5$ the quasi one-dimensional (1D) β - $\text{Na}_{1/3}\text{V}_2\text{O}_5$ is the only metallic compound. It exhibits a metal-insulator (MI) transition as a function of temperature at $T_{\text{MI}} = 130$ K [1]. The monoclinic structure comprises three inequivalent vanadium sites [2,3]. Two of the sites (V1, V2) have an octahedral and one (V3) a square pyramidal oxygen coordination. The latter site is assumed to be close to a V^{5+} (d^0) occupation, leaving one electron, donated by the sodium ions, to be distributed among four V ions on the V1 and/or V2 sites. Below T_{MI} different electron configurations in a charge ordered state have been discussed [4–7]. Resistivity measurements above T_{MI} show metallic behavior along the b axis, while semiconducting behavior is observed perpendicular to b. At $T_{\text{N}} = 24$ K a magnetic transition occurs [1], which has been shown by NMR measurements to be long range in nature [4]. From EPR and magnetization measurements [7–9] it was concluded, that the ordered state is a canted antiferromagnet, with the ferromagnetic component

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aligned along the b axis. External pressure is expected to increase inter-chain interactions and therefore can yield information about the effect of dimensionality on the phase transitions in this compound.

2. Experimental results

Needle like single crystals of a typical size of $4 \times 0.4 \times 0.2$ mm³ were grown by a flux method. The resistivity was measured using a standard four-probe DC-technique. AC-susceptibility measurements were performed using a mutual inductance bridge in which several crystals were aligned with the b axis parallel to the magnetic field. Quasi hydrostatic pressure experiments were carried out in a self clamped CuBe piston-cylinder cell. Anomalies in the electrical resistivity at 240 K and 222 K signal ordering on the Na sublattice. While these transitions appear to be independent of pressure, the MI transition shifts to lower temperatures at a rate of 28 K/GPa. The onset of the magnetically ordered state at T_N is indicated by a cusp in the AC-susceptibility, which shifts to higher temperatures at a rate of 5 K/GPa with increasing pressure. Fig. 1 summarizes the pressure dependencies of the phase transitions. $T_{MI}(p)$ was investigated for two different samples (open and filled symbols in Fig. 1(left)) both showing the same pressure dependence.

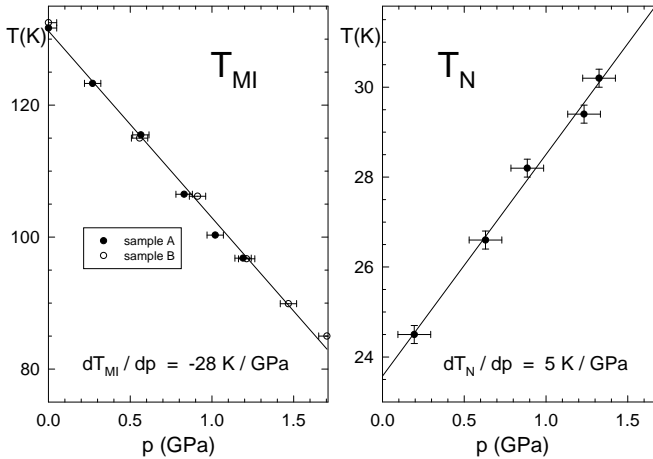


Fig. 1. Pressure dependencies of the MI transition (left) and the magnetic transition (right) as determined by resistivity and susceptibility measurements, respectively.

NEXAFS measurements in the total electron yield (TEY) mode were performed on the O 1s edge under ultra high vacuum at the U41-1/PGM beamline at the BESSY 2 storage ring using a crystal of the same batch as for the resistance measurements. A clean surface was prepared by cleaving the crystal inside the vacuum chamber. NEXAFS spectra of the O 1s edge

are presented in Fig. 2. It is expected from the quasi 1D structure that the hybridization between V $3d$ and O $2p$ states is highly anisotropic. This is reflected by the strong anisotropy of the spectra as the sample is rotated around the crystallographic a axis from a geometry with the polarization vector \vec{E} of the X-rays parallel to the 1D b axis ($\varphi = 0^\circ$) to one with \vec{E} perpendicular to the b axis (Fig. 2a). No changes in the spectra are observed on cooling the sample below the Na-ordering temperature and further below the MIT (Fig. 2b), indicating only subtle changes of the electronic structure at these transitions.

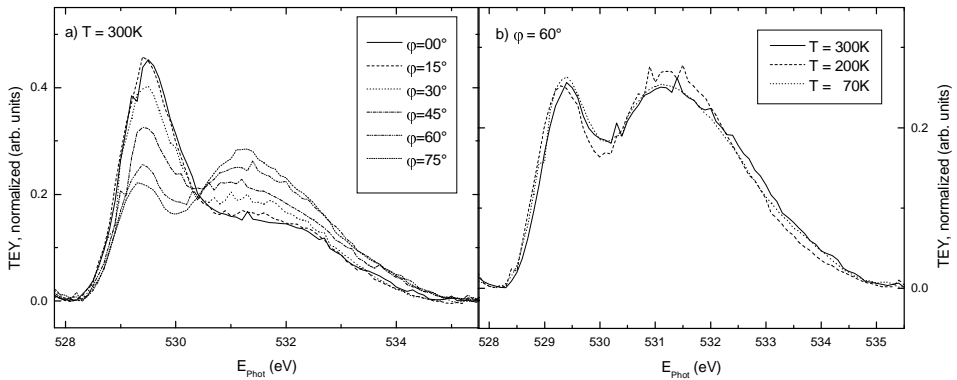


Fig. 2. NEXAFS spectra of the O $1s$ edge of $\text{Na}_{1/3}\text{V}_2\text{O}_5$ as a function of angle φ between the polarization vector of the incident X-rays and the crystallographic b axis (a) and as function of temperature T (b).

3. Discussion

The phase transitions at $T_{\text{MI}} = 130$ K and $T_{\text{N}} = 24$ K show a pronounced pressure dependence and clear signatures in the magnetic susceptibility, indicating that the V ions are involved in the respective transition. According to NMR measurements [4] the $3d$ -electrons occupy the V1 and V2 sites above T_{MI} . The expected quasi 1D nature of the resulting electronic structure is confirmed by our band structure calculations based on density functional theory, which show a pronounced dispersion parallel, but a very small dispersion perpendicular to the b axis. The partial density of states (DOS) further predicts a dominant occupation of the V2 sites compared to V1 and almost no occupation of the V3 sites. The 1D nature of the electronic structure and its concomitant Fermi surface nesting will leave $\text{Na}_{1/3}\text{V}_2\text{O}_5$ susceptible to a Peierls like transition. The pressure dependence of the MIT-transition is indeed consistent with such a scenario: application of pressure will increase the coupling between vanadium chains and, at the same time, the lattice stiffness. The increase of interchain interaction will increase the

3*d*-band dispersion perpendicular to the chains and, concomitantly, reduce the nested portion of the Fermi surface and, consequently, T_{MI} decreases. An increased lattice stiffness will decrease T_{MI} further. Increased interchain interaction will suppress fluctuations characteristic of the quasi 1D system and shift the magnetic transition to higher temperatures consistent with the observed pressure dependence of T_{N} .

To explain that a Peierls like transition results in an insulating state one has to involve both charge order and electronic correlations. Below the Na ordering the doubling of the unit cell in *b* direction and the concomitant band splitting will lead to 1/4 filled bands. The NMR results [4] suggest a charge ordering below T_{MI} with the 3*d*-electrons either completely on V1 or V2 sites. Our band structure calculations would favor the V2 sites. In a local picture this can be realized by a dimerization of V2 sites, resulting in a bonding-nonbonding splitting. The resulting half filled band situation could lead to an insulating state due to on-site Coulomb interactions. The fact that the NEXAFS spectra show no changes at T_{MI} suggests only subtle if any changes in the electronic structure on a local scale.

Clearly more investigations of the electronic structure and the lattice distortions at the MI-transition have to be carried out to obtain a better understanding of the insulating state and the distribution of the *d*-electrons on the various V sites in the metallic and insulating state of $\text{Na}_{1/3}\text{V}_2\text{O}_5$.

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