Pressure dependence of phase transitions in the quasi one-dimensional metal-insulator transition system $\beta$-Na$_{1/3}$V$_2$O$_5$

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The pressure dependence of phase transitions in the quasi one-dimensional vanadium oxide $\beta$-Na$_{1/3}$V$_2$O$_5$ has been studied by magnetic susceptibility and electrical resistivity measurements. The pressure dependence of the various transition temperatures is quite different. The transition at $T = 240$ K, previously reported and attributed to ordering on Na sites, and a second transition at $T \approx 222$ K, reported here for the first time and attributed to a further increase of order on Na sites, are almost independent of pressure. On the other hand, the metal-insulator (MI) transition at $T_{MI} = 130$ K shifts to lower temperatures, while the magnetic transition at $T_N = 24$ K shifts to higher temperatures with increasing pressure. We discuss the different pressure dependencies of $T_{MI}$ and $T_N$ in terms of increasing interchain coupling and the MI transition to be of Peierls type.

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I. INTRODUCTION

Quasi one-dimensional (1D) metals exhibit unique electronic properties, which show potential for applications and, at the same time, for an expansion of the understanding of electronic correlation effects in solids. The inorganic 1D metal $\beta$-Na$_{1/3}$V$_2$O$_5$, which exhibits a metal-insulator (MI) transition as a function of temperature at $T_{MI} = 130$ K, is a system ideally suited to study the interplay between structural instabilities and electronic correlations. This compound crystallizes in a monoclinic structure exhibiting three inequivalent vanadium sites. Two of the sites (V1, V2) have an octahedral and one (V3) a five fold square pyramidal oxygen coordination. The latter site resembles the V$^{5+}$ site in V$_2$O$_5$, which suggests a V$^{5+}$ occupation also in Na$_{1/3}$V$_2$O$_5$. The oxygen octahedra of the V1 sites form a zigzag chain in the b direction with octahedra sharing edges, while the oxygen octahedra of the V2 sites form a double chain in b direction with octahedra sharing corners along the b direction as well as in the ac-plane. It should be pointed out that the V1 octahedra also share edges with the V2 octahedra and that, in fact, the shortest V-V-distance is that between a V1 and a V2 site.

This V-O framework provides tunnels along the b direction in which Na sites form a double chain parallel b. For $x = 1/3$ in Na$_x$V$_2$O$_5$ only half of the sites are in fact occupied by Na ions, which build zigzag chains within each tunnel. At room temperature there exists no long range correlation between the zigzag chains. Below $T = 230$ K X-ray diffraction (XRD) measurements show, that the Na chains develop a long range order.

The intercalated Na atoms donate their valence electron to the host lattice, which results in a mixed valence V-state with one 3d-electron per six vanadium ions. The distribution of the 3d-electrons on the three different vanadium sites is not completely clear. Different electron configurations in a charge ordered state below $T_{MI}$ have been discussed. In contrast to related systems, like e.g. $\alpha$-NaV$_2$O$_5$ and $\eta$-Na$_{129}$V$_2$O$_5$, which are structurally low dimensional and electrically insulating, $\beta$-Na$_{1/3}$V$_2$O$_5$ is a quasi one-dimensional metal at room temperature. In resistivity measurements above $T_{MI}$ metallic behavior is observed parallel to the b axis, while perpendicular to b semiconducting behavior occurs with an anisotropy ratio of $\rho_{\perp}/\rho_{\parallel} > 100$. At $T_N = 24$ K a magnetic transition occurs which has been shown by NMR measurements to be long range in nature. From EPR and magnetization measurements it was concluded, that the ordered state is a canted antiferromagnet, with the ferromagnetic component aligned along the b axis. Large differences between zero field and field cooled magnetization measurements are observed. Such "spin glass like" behavior has been observed before in systems with magnetically strongly anisotropic behavior and was attributed to magnetic domain effects. The quasi 1D structure of $\beta$-Na$_{1/3}$V$_2$O$_5$ suggests that such a magnetic anisotropy exists in this system.

The electronic transport and magnetic properties are very sensitive to the Na-stoichiometry $x$. Metallic behavior is observed only in a very narrow range of Na-concentration and a slight deviation from $x = 1/3$ induces semiconducting behavior in the electrical resistivity, most likely due to disorder effects. Deviation from the exact stoichiometry also rapidly suppresses the magnetic transition. External pressure is expected to change the relative strength of intra- to interchain interactions and therefore can yield information about the influence of the dimensionality of the system on the different phase transitions. In this paper we report on the effect of external pressure on the phase transitions in $\beta$-Na$_{1/3}$V$_2$O$_5$ studied by magnetic susceptibility and electrical resistiv-
FIG. 1. Arrhenius plot of resistivity. The right inset shows the high temperature resistivity on a linear scale. The left inset shows the low temperature resistivity measured by a two-probe method.

II. EXPERIMENTAL

Needle like single crystals of a typical size of $4 \times 0.4 \times 0.2$ mm$^3$ were grown by a flux method similar to that described in Ref. 1. Laue diffraction showed the longest dimension was parallel to the crystallographic $b$ axis. For resistivity measurements along $b$ four gold pads were evaporated on the crystals. Then 40 µm platinum wires were attached to those pads by silver epoxy. The resistivity was measured using a standard four-probe DC-technique, i.e., for each measurement the current was reversed to eliminate voltage offsets. AC-susceptibility measurements were performed using a mutual inductance bridge (MIB) in which several crystals were aligned with the $b$ axis parallel to the magnetic field. The amplitude of the field was about 1 G at a frequency of about 1 kHz. Quasi hydrostatic pressure experiments were carried out in a self clamped CuBe piston-cylinder cell with n-pentane – isoamyl (1:1) as a pressure transmitting medium. The pressure was measured utilizing a manganin gauge in case of the resistivity measurements and the pressure dependence of the superconducting transition of lead in case of the AC-susceptibility. DC-magnetic measurements at ambient pressure were performed using a Quantum Design SQUID magnetometer.

III. RESULTS

A. Electrical resistivity

The temperature dependence of the $b$ axis resistivity of a nominally stoichiometric Na$_{1/3}$V$_2$O$_5$ sample is shown in Fig. 1. A steep increase in resistivity marks the MI transition at $T_{MI} = 130$ K. Below 80 K the resistivity is characteristic of a semiconductor with an activation energy of 0.05 eV. The left inset of the figure shows the extension of the resistivity from 50 K down to lowest temperatures measured in a special cryostat with uninterrupted triaxial wiring terminating just at the sample. A deviation from linearity in the Arrhenius plot towards lower resistivity is observed below the magnetic transition at 24 K.

The right inset of the figure shows the metallic behavior at high temperatures. At 240 K, denoted as $T_{Na-2D}$, the slope of resistivity changes rapidly, which was attributed to ordering between Na-chains. Below 230 K another noticeable anomaly in the resistivity marks a second transition, which shows a hysteresis upon thermal cycling and which we also attribute to a structural transition, associated with further ordering of the Na sublattice, as discussed below. The center of the hysteretic transition is located at $T_{Na-3D} = 222$ K.

Due to the strongly anisotropic resistivity of Na$_{1/3}$V$_2$O$_5$ an accurate alignment of current and voltage contacts is essential to avoid contributions from non $b$ axis components of the resistivity. Therefore, the negative slope of resistivity just above $T_{MI}$ might rather reflect a non ideal position of contacts than a deviation of the $b$ axis resistivity from metallic behavior in this temperature range. Some measurements on samples of the same batch as the sample shown in Fig. 1 display a maximum of resistivity at 240 K and semiconducting behavior above, which we also attribute to contributions other than the $b$ axis component of the resistivity tensor, which show semiconducting behavior as a function of temperature.

Slightly off-stoichiometric samples displayed a negative non-exponential temperature characteristic over the whole temperature range, most likely due to disorder. Owing to the quasi one-dimensional nature of the compound such a sensitivity of the transport properties to disorder can be expected. The jump in resistivity at 130 K, marking the MI transition, however, is still observed in such samples.

The transitions observed at $T_{Na-2D} = 240$ K, $T_{MI} = 130$ K and $T_N = 24$ K have been reported previously, while the transition at $T_{Na-3D} = 222$ K is reported here for the first time. Since we observed the latter transition, unresolved in earlier studies, in all of our stoichiometric samples we consider it to be an intrinsic property of Na$_{1/3}$V$_2$O$_5$.

B. Magnetic susceptibility

Fig. 2 shows the inverse magnetic DC-susceptibility as a function of temperature measured in a field of 10$^4$ G along the $b$ axis. The susceptibility follows a Curie-Weiss law in the temperature range 150 K < $T$ < 300 K with a Curie-Weiss temperature $\Theta_{CW} = -150$ K and an effec-
Inverse DC -Susceptibility

\[ T \text{ (K)} \]

\[ 0 \quad 50 \quad 100 \quad 150 \quad 200 \quad 250 \quad 300 \]

\[ 1 / \chi \text{DC} (10^3 \text{mol} / \text{emu}) \]

0 1 2 3

ZFC Curie-Weiss Fit

DC -Susceptibility

\[ T \text{ (K)} \]

\[ 5 \quad 10 \quad 15 \quad 20 \quad 25 \quad 30 \]

\[ \chi \text{DC} (10^{-3} \text{emu} / \text{mol}) \]

0 1 2 3 4 5 6

ZFC FC

B = 10^4 G

B = 100 G

FIG. 2. Inverse magnetic DC-susceptibility of single crystals as a function of temperature measured in a magnetic field of \( B = 10^4 \text{ G} \) parallel to the b axis. The inset shows the magnetic susceptibility when zero field cooled (ZFC) and field cooled (FC) measured with \( B = 100 \text{ G} \).

tive moment of 1.9 \( \mu_B \) per V\(^{4+}\) ion. This is in agreement with literature\[1-3\] where values of \( \mu_{\text{eff}} \) in the range 1.9 < \( \mu_{\text{eff}} \) < 2.2 \( \mu_B/V^{4+} \) have been reported.

The fact that the magnetic susceptibility does not show a noticeable anomaly at the phase transitions at \( T_{Na-2D} = 240 \text{ K} \) and \( T_{Na-3D} = 222 \text{ K} \), indicates that the magnetic and electronic state of the vanadium ions is not affected by these transitions. In contrast, at the MI transition a sharp upturn of the susceptibility is observed. The onset of magnetic order at 24 K is reflected by a sharp rise of \( \chi \) (as measured in a field of \( 10^4 \text{ G} \)). At lower magnetic field this rise becomes more pronounced and for zero field cooled curves a small cusp is observed at \( T_N = 24 \text{ K} \), as shown in the inset of Fig. 2.

C. Pressure dependence

The difficulties to measure the clean b axis contribution of resistivity are even more complex in a high pressure environment. Therefore, a measurement of the absolute resistivity was not possible under pressure. Nevertheless, the characteristic features marking the various phase transitions are easily resolved. The two transitions at \( T_{Na-2D} \) and \( T_{Na-3D} \), are independent of pressure within the experimental resolution. This suggests, that there is a link between these two transitions. The resistivity as a function of temperature in the vicinity of \( T_{MI} \) is shown in Fig. 3 for three different pressures, as indicated in the figure. In contrast to the transitions at higher temperatures, the MI transition reacts extremely sensitive to pressure and shifts to lower temperatures at a rate of 28 K/GPa. Qualitative information of the pressure dependence of the ratio of the resistance parallel b to the resistance perpendicular b was obtained from measurements on one sample with six contacts attached. We observe a decrease of anisotropy of resistivity with increasing pressure, indicating a crossover from 1D to two- or three-dimensional behavior, presumably due to increased interaction between vanadium chains.

To study the pressure dependence of the magnetic transition temperature \( T_N \), we performed AC-susceptibility measurements using a miniature MIB. The signal obtained from the MIB does not allow to evaluate the absolute value of \( \chi_{AC} \). The magnetic transition, however, is clearly seen as a cusp in the signal (Fig. 4) similar to the run of the ZFC DC-susceptibility curve (Fig. 2). With increasing pressure \( T_N \) shifts to higher temperatures at a rate of 5 K/GPa while the height of the cusp decreases.

Fig. 5 summarizes the pressure dependencies of the
respective phase transitions. \( T_{MI}(p) \) was investigated for two different samples (open and filled symbols in Fig. 5(b)) both showing the same pressure dependence as expected. A linear extrapolation to higher pressures would predict the magnetic and the MI transition to coincide at \( p = 3.2 \text{ GPa} \).

IV. DISCUSSION

As already mentioned above, the pressure independence of the resistivity anomaly at \( T_{Na-2D} = 240 \text{ K} \) and the hysteretic phase transition at \( T_{Na-3D} = 222 \text{ K} \) implies a common origin. XRD measurements by Yamada et al. revealed satellite reflections below 230 K, indicating a doubling of the unit cell in \( b \) direction. From a comparison to the intensity of similar satellite reflections found for \( \beta\text{-AgI}_3\text{V}_2\text{O}_5 \) Yamada et al. deduced that the reflections are due to ordering on the Na (Ag) sublattice. The steep decrease of resistivity below \( T = 240 \text{ K} \) was then attributed to this ordering. However, the reported temperature below which the satellite peaks appear (\( T < 230 \text{ K} \)), coincides rather with the hysteretic transition in resistivity observed here (see right inset of Fig. 5). We therefore attribute this hysteretic transition to ordering within the Na sublattice and suggest the following scenario: at room temperature the Na ions form regular zigzag chains along the \( b \) axis. Within each zigzag chain the Na ions have a periodicity of \( 2b \). Perpendicular to the \( b \) direction these zigzag chains are not correlated with respect to their occupation, and, therefore, the probability of occupation of each Na site is one half on the average and the lattice parameter is \( b \). Below \( T_{Na-2D} = 240 \text{ K} \) correlations regarding the occupation of Na sites between neighboring Na zigzag chains develop, resulting in the steep decrease of resistivity. Since the distance between Na chains is shorter along the \( a \) direction (\( d_a \approx 10 \text{ Å} \)) than along the \( c \) axis (\( d_c \approx 15 \text{ Å} \)), correlations probably will first develop in the \( a \) direction. This results in long range correlations of Na chains within (ab) planes, while there are no (or only short range) correlations perpendicular to these planes. Still the average occupation number of all Na sites remains one half and the periodicity of the lattice remains unchanged. Finally, below \( T_{Na-3D} \) a coherent phase relation between the 2D-ordered chains emerges, which results in a transition to a three-dimensional long range ordered state associated with a hysteresis in the resistivity measurements and the appearance of satellite reflections signaling a doubling of the lattice parameter along the \( b \) direction.

The phase transitions at \( T_{MI} = 130 \text{ K} \) and \( T_N = 24 \text{ K} \) show a pronounced pressure dependence and clear signatures in the magnetic susceptibility, indicating that the electronic and magnetic state of the V ions changes at the respective transition. According to NMR measurements\( ^4 \) the 3d-electrons occupy the V1 and V2 sites above \( T_{MI} \). Since both sites form chains in \( b \) direction (see above), the resulting electronic structure is expected to exhibit quasi one-dimensional features. This expectation is confirmed by band structure calculations based on density functional theory, which show a pronounced dispersion parallel but a very small dispersion perpendicular to the \( b \) axis\( ^6 \). This one-dimensional nature of the electronic structure and its concomitant Fermi surface nesting will leave \( \text{Na}_1/\text{Na}_2\text{V}_2\text{O}_5 \) susceptible to a Peierls like transition. The pressure dependence of the MI-transition is indeed consistent with such a scenario. In principle, a one-dimensional system is dominated by fluctuations and no phase transition is expected for \( T > 0 \text{ K} \). In reality there is always a finite coupling between the one-dimensional objects constituting the system. This finite coupling results in a phase transition at finite temperature. Assuming that the MI transition is associated with Fermi surface nesting, the shift of the transition temperature \( T_{MI} \) to lower temperature with pressure can be understood as follows: 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 3d-band dispersion perpendicular to the chains and, concomitantly, reduce the nested portion of the Fermi surface and, consequently, \( T_{MI} \) decreases. An increase of lattice stiffness increases the amount of strain.
energy necessary for the lattice distortion associated with a Peierls like transition, decreasing $T_{MI}$ further. The scenario of an increased interchain interaction with pressure is supported by the evolution of the magnetic transition temperature with pressure. Increased interchain interaction will suppress fluctuations characteristic of the quasi one-dimensional system and shift the magnetic transition to higher temperatures. At the same time, this leads to a reduction in magnitude of the magnetic signature with increasing pressure, since the three-dimensional freezing of the spin structure occurs already at higher temperatures, i.e. smaller intrachain correlation lengths.

The pressure dependence of both $T_{MI}$ and $T_N$ therefore are consistent with the Peierls like scenario described above. To put forward an explanation for the fact that such a transition results in an insulating state one has to look at the electronic structure of Na$_{1/3}$V$_2$O$_5$. The V 3d states associated with both the V1 and V2 sites (but not with the V3 site) appear to be occupied above $T_{MI}$. Accordingly, one 3d-electron is shared between two sites, i.e. there is one electron for four vanadium atoms. It also follows that the V 3d groundstate energy levels of V1 and V2 sites are (almost) degenerate, resulting in a 1/8 filling of each state above $T_{MI}$. To achieve an insulating ground state (and remove the degeneracy) the lowest lying levels have to be split. Below $T_{N\rightarrow 3d}$ the doubling of the unit cell in b direction and the concomitant band splitting will lead to 1/4 filled bands. Below $T_{MI}$ further splitting can occur due to the formation of a (commensurate) charge density wave with suitable propagation vector q below $T_{MI}$. Depending on the propagation vector q this may result in a completely filled band separated from the other bands by a band gap, or in a half filled band. In the latter case an insulating state may follow from strong on-site Coulomb interaction. The NMR results suggest a charge ordering with the 3d-electrons either completely on V1 or V2 sites. In a local picture, consistent with the Peierls like scenario described above, this can be realized by a dimerization of either V1 or V2 sites, resulting in a bonding-nonbonding splitting of the dimerized levels and the occupation of the bonding state. The resulting half filled band situation again could result in an insulating state due to on-site Coulomb interactions. Clearly these suggestions are highly speculative and more investigations on 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 Na$_{1/3}$V$_2$O$_5$.

V. CONCLUSION

The recorded pressure dependencies of the transition temperatures of the MI transition and the magnetic transition in Na$_{1/3}$V$_2$O$_5$ are consistent with the picture of a quasi one-dimensional system. The decrease of the MI transition temperature with increasing pressure is interpreted as a result of a loss of Fermi surface nesting due to increased interchain interactions and the concomitant suppression of a Peierls like transition. At the same time the increased interchain interaction causes an increase of the magnetic ordering temperature. An observed pressure independent hysteretic transition is attributed to long range three-dimensional ordering on the half filled Na sublattice.

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