Charge Order in NaV$_2$O$_5$ studied by EPR

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We present angular dependent EPR measurements in NaV$_2$O$_5$ at X-band frequencies in the temperature range $4.2 \, \text{K} \leq T \leq 670 \, \text{K}$. A detailed analysis in terms of the antisymmetric Dzyaloshinskii-Moriya and the anisotropic exchange interactions yields the following scheme of charge order:

On decreasing temperature a quarter-filled ladder with strong charge disproportions, existing for $T \geq 100 \, \text{K}$, is followed by zig-zag charge-order fluctuations which become long-range and static below $T_{SP} = 34 \, \text{K}$.

The observation of an exponential decrease in magnetic susceptibility in $\alpha'$-NaV$_2$O$_5$ below $34 \, \text{K}$ triggered many experimental and theoretical investigations. Following the determination of the crystal structure by Carpy and Galy as space group $P2_1mmn$ with linear chains of V$^{4+}$ ions (spin $S = 1/2$) separated by non magnetic V$^{5+}$ chains, NaV$_2$O$_5$, analogous to CuGeO$_3$, was classified as inorganic spin-Peierls system. Later on a re-investigation of the crystal structure showed that NaV$_2$O$_5$ has to be considered a quarter-filled ladder system with only one vanadium site in the high-temperature phase described by space group $Pmmn$. The direction of the ladders is given by the crystallographic $b$ axis. Each rung consists of two VO$_5$ pyramids along the $a$ axis, which share one corner at their base. Based on this structure a charge-order transition followed by different kinds of spin order were proposed. A recent investigation suggested a low-temperature phase consisting of modulated ladders with zig-zag charge order alternating with non modulated ladders with vanadium ions of intermediate valence V$^{4.5+}$.

Electron-paramagnetic resonance (EPR) is ideally suited for the investigation of the magnetic properties of vanadium systems, since the vanadium ions themselves (as V$^{4+}$ with electron configuration $3d^1$ in the present case) can be used as a microscopic probe of the spin system. In this paper we present angular dependent EPR measurements at X-band frequencies (9.48 GHz) within the temperature range $4.2 \, \text{K} < T < 670 \, \text{K}$. The experimental details concerning the crystal growth of NaV$_2$O$_5$ and EPR measurements have been described in previous papers. For all temperatures the EPR spectrum consists of a single strongly exchange-narrowed Lorentzian line. The EPR intensity does not show any angular dependence within experimental error. Its temperature behavior follows that of a one dimensional antiferromagnetic Heisenberg chain at high temperatures $T > 100 \, \text{K}$, whereas it decreases exponentially below the transition temperature $T_{SP}$. Strong deviations from the model predictions were observed between 100 K and $T_{SP}$.

The $g$-values are found as $g_a \approx g_b \approx 1.98$ and $g_c \approx 1.94$, which are typical for V$^{4+}$ in octahedral crystal symmetry, and increase only slightly below $T_{SP}$. Here we confine ourselves to the discussion of the angular and temperature dependence of the resonance linewidth, which carries the information about the interactions of the vanadium spins with their local environment.

Figure 1 shows the temperature dependence of the linewidth $\Delta H$ with the external magnetic field applied along the three main axis of the crystal. Starting with an isotropic value $\Delta H = 8 \, \text{Oe}$ at the transition temperature $T_{SP} = 34 \, \text{K}$, the linewidth increases monotonously with increasing temperature and develops a remarkable anisotropy with respect to the $c$ axis of the crystal. In the respective temperature regime the curvature of $\Delta H(T)$ starts with a positive sign and changes to negative values above 100 K. Towards low temperatures $T < T_{SP}$ the line broadens anisotropically again probably due to the unresolved hyperfine structure or due to a spin-glass transition.

It has been reported by Yamada et al. that the line broadening in the high-temperature regime $T > 100 \, \text{K}$ must be due to the antisymmetric Dzyaloshinski-Moriya (DM) interaction, which is the only possible mechanism to explain the observed order of magnitude of some 100 Oe for the linewidth and its anisotropy. Estimations for anisotropic exchange and dipole-dipole interactions yield values which are 100 and 1000 times smaller, respectively. The angular dependence of the linewidth is shown in the upper inset of figure 1 at four different temperatures, where the $b$ axis was taken as rotation axis.
and the experimental ratios $\Delta$ increases, as it is shown in the lower inset of figure 1.

The angular dependence of the EPR linewidth contains important information about the local electronic distribution on the vanadium ladders. We start our discussion with respect to the high-temperature regime $T > 100$ K, where the linewidth is determined by the DM interaction

$$\mathcal{H}_{ij} = \mathbf{d}_{ij} \cdot [\mathbf{S}_i \times \mathbf{S}_j].$$

The vanadium spins $\mathbf{S}_i$ and $\mathbf{S}_j$ are coupled by superexchange via an oxygen ion. The direction of the DM vector $\mathbf{d}_{ij}$ is determined by

$$\mathbf{d}_{ij} = d_0 \cdot [\mathbf{n}_{iO} \times \mathbf{n}_{Oj}],$$

where the space vectors $\mathbf{n}_{iO}$ and $\mathbf{n}_{Oj}$ connect the spins $i$ and $j$ with the oxygen-bridge ion respectively. The maximum linewidth, which assigns the direction of the DM vector, is found for the magnetic field applied parallel to the crystallographic $c$ axis.

The amplitude $A$ of the modulation is about 1 Oe, which is of the order of magnitude estimated for the anisotropic exchange interaction, and increases slightly with decreasing temperature, whereas the prefactor $B$, which can be considered to be due to the DM interaction, using $\cos(2\vartheta) = 2\cos^2\vartheta - 1$, as discussed below, strongly decreases.

The angular dependence of the EPR linewidth is of special interest, strongly deviates from the high-temperature regime $T > 100$ K, where the linewidth is determined by the DM interaction

$$\Delta H = A \cos(4\vartheta) + B \cos(2\vartheta) + \Delta H_0$$

where $\vartheta$ is the polar angle with respect to the $c$ axis. $A_{DM}$ is proportional to the strength of the DM interaction and $\Delta H_0$ the residual linewidth due to further relaxation mechanisms. Above 100 K the parameter $A_{DM}$ strongly increases, as it is shown in the lower inset of figure 1 and the experimental ratios $\Delta H_c/\Delta H_a$ and $\Delta H_c/\Delta H_b$ nearly approximate the value of 2, underlining the dominant influence of the DM interaction.

Below $T = 100$ K the results strongly deviate from the high-temperature behavior. The positive curvature of the linewidth indicates a change of the dominant interaction. In the temperature range $34$ K $< T < 60$ K, the maximum linewidth is not found for the magnetic field applied in $c$ direction any more, but it appears with respect to the $a$ axis. Figure 2 nicely shows this cross-over regime. The angular dependence within the $b$-$c$ plane shown in the upper inset of figure 2 is of special interest, because here an additional modulation appears, which is well described by

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Therefore, the relevant oxygen-bridge vectors $\mathbf{n}_1$ and $\mathbf{n}_2$ must build an angle smaller than 180° within the $a$-$b$ plane. Moreover, the existence of a non vanishing DM interaction requires a unit cell without inversion center, because otherwise the DM vectors cancel each other, as it is the case for a quarter-filled spin ladder, where each vanadium spin is equally distributed between two V$^{5+}$ ions on the rungs of the ladder (cf. Fig. 3). The condition of asymmetry, because of the separation of the vanadium ladders in V$^{4+}$ and V$^{5+}$ chains. Here the DM interaction takes place only via one oxygen bridge between two neighboring V$^{4+}$ sites along the $b$ axis (cf. Fig. 3). However, using the structural data for the vanadium and oxygen ions under consideration, we find that, with respect to the vanadium positions, the oxygen ions within the chains are farther displaced along the $c$ axis $\Delta c \approx 0.58$ Å than along the $a$ axis $\Delta a \approx 0.28$ Å. This yields a dominant contribution of the DM vector pointing into the $a$ direction, which is not observed experimentally. We conclude that the EPR data strictly contradict both proposed high-temperature structures: the linear spin chain as well as the symmetric quarter-filled ladder.

Recently, detailed optical investigations by Damascelli et al. revealed a local charge disproportion on each rung of the ladders, which also destroys the inversion symmetry yielding a finite DM interaction. Hence the charge distribution has to be taken into account more carefully (cf. Fig. 3c). Following the analysis of Damascelli, the center of the electronic distribution $x_e$ on the rungs of the ladder can be determined. Considering each rung as an independent linear molecule of two V$^{5+}$ ions, the eigenstates of the additional electron in between are given by $\psi_1 = \psi_l + \psi_r$, where the electron stays near the left-hand side and $\psi_2 = \psi_l - \psi_r$, where the electron favors the right-hand side. The atomic orbitals $\psi_r$ and $\psi_l$ of the right-hand and left-hand side are occupied according to the following weights:

$$u = \frac{1}{\sqrt{2}} \sqrt{1 + \frac{\Delta}{E_{CT}}}, \quad v = \frac{1}{\sqrt{2}} \sqrt{1 - \frac{\Delta}{E_{CT}}}$$

The parameter $\Delta$ describes the asymmetry of the onsite energy of the electron located in $\psi_r$ with respect to $\psi_l$. The charge-transfer energy $E_{CT} = \sqrt{\Delta^2 + 4t^2}$ is determined by the hopping integral $t$ and resembles the energy splitting between the two eigenstates. We choose the origin of the coordinate system $x = 0$ in the left-hand ion, giving the position of the right-hand ion at $x = R$. If the electron favors for example the left-hand side, the center of the charge distribution $x_e$ can be obtained from the eigenstate $\psi_l$ as

$$x_e = \frac{v^2 R + (R/2)2uvS_{RL}}{u^2 + v^2 + 2uvS_{RL}} \approx \frac{R}{2} \left(1 - \frac{\Delta}{E_{CT}}\right)$$
evidence for the appearance of charge disproportions in the quarter-filled spin ladder at high temperatures.

The peculiarities observed in the cross-over regime (34 K < T < 60 K) can be described in the framework of the competition of antisymmetric DM exchange and symmetric anisotropic exchange, which has been discussed by Yamada et al. [15] for the one dimensional antiferromagnet KCuF$_3$ and more extensively for ferromagnetic Cu layers by Soos et al. [14]. In these papers the evolution of the linewidth with temperature is calculated for both interactions. In both cases the linewidth saturates at high temperatures: The antisymmetric DM exchange yields a strong temperature dependence of the linewidth with a negative curvature within the whole temperature regime. The anisotropic exchange gives rise only to a weak temperature dependence of the linewidth with a positive curvature at low temperatures changing to a negative one at high temperatures. Combining both contributions, we qualitatively obtain the temperature dependence of the linewidth observed in NaV$_2$O$_5$ experimentally. Comparing these data to those of the one dimensional Heisenberg antiferromagnet KCuF$_3$ in more detail, we recognize an important difference. Whereas in KCuF$_3$, in agreement with theoretical predictions, the DM interaction vanishes exactly at T = 0, for NaV$_2$O$_5$ the extrapolation of the high-temperature data suggests the DM interaction to disappear already at 100 K, as documented in the lower inset of figure 2. This indicates that already for temperatures T ≤ 100 K the charge disproportions change to a symmetric zig-zag order of V$^4+$ and V$^5+$ ions in the ladder, where the DM vectors cancel each other (cf. Fig. 2d). This result is in good agreement with reports of charge-order fluctuations for 80 K ≥ T ≥ T$_{SP}$ from Raman spectroscopy [13] and the onset of a static long-range zig-zag order below T$_{SP}$ for ultrasonic [16] and dielectric results [19].

Finally the π/2-periodic modulation of the angular dependence in the b-c plane according to equation 2 can be understood in terms of the anisotropic exchange, only. The DM interaction produces π-periodic modulations in any case. The anisotropic-exchange interaction yields π/2-periodic modulations only if its secular contributions are enhanced with respect to the non-secular contributions by spin diffusion, which is characteristic for low dimensional systems [16]. As we will report in a more detailed subsequent publication, the fact that the π/2-periodic modulation is only observed in the b-c plane, whereas it does not occur in both a-b and a-c plane, means that all elements of the anisotropic exchange tensor vanish except $J_{bc} = 0$. Under these conditions, the prefactors of equation 2 resemble anisotropic $A \sim J_{bc}^2$ and antisymmetric $B \sim A_{DM}$ exchange. From the lower inset of figure 2 we obtain that for 60 K > T > 34 K the Dzyaloshinsky-Moriya interaction more and more decreases with decreasing temperature whereas the anisotropic exchange slightly increases. The anisotropic exchange parameter $J_{bc}$ is due to the coupling between electron spins of adjacent layers in the c direction. This is a strong hint that the ordering below T$_{SP}$ involves vanadium ions of neighboring layers.

In conclusion the EPR data confirm the structure of a quarter-filled spin ladder with strong local charge disproportions at high temperatures T > 100 K, which result in a non-vanishing DM interaction (Fig. 2d). The direction of the DM vector is determined by the V-O-V bridge angle $\approx$ 140$^\circ$ along the chains within the a-b plane. The pronounced weakening of the DM interaction below 100 K but far above T$_{SP}$ = 34 K indicates the onset of zig-zag charge-order fluctuations, which become long-range and static below T$_{SP}$ (Fig. 2d). The zig-zag structure probably results from inter-layer couplings.

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