Charge Order in NaV_2O_5 Studied by EPR

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We present angular dependent EPR measurements in NaV_2O_5 at X-band frequencies in the temperature range $4.2 \leq T \leq 670$ K. A detailed analysis in terms of the antisymmetric Dzyaloshinski-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 $T \geq 100$ K, is followed by zigzag charge-order fluctuations which become long range and static below $T_{SP} = 34$ K.

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The observation of an exponential decrease in magnetic susceptibility in α'-NaV_2O_5 below 34 K [1] triggered many experimental and theoretical investigations. Following the determination of the crystal structure by Carpy and Galy [2] as space group $P2_1mmn$ with linear chains of V^{4+} ions (spin $S = 1/2$) separated by nonmagnetic V^{5+} chains, NaV_2O_5, analogous to $CuGeO_3$, was classified as inorganic spin-Peierls system. Later on a reinvestigation of the crystal structure showed that NaV_2O_5 has to be considered a quarter-filled ladder system [3–5] 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 [3,6,7]. A recent investigation suggested a low-temperature phase consisting of modulated ladders with zigzag charge order alternating with nonmodulated ladders with vanadium ions of intermediate valence $V^{4.5+}$ [8].

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 $4.2 < T < 670$ K. The experimental details concerning the crystal growth of NaV_2O_5 and EPR measurements have been described in previous papers [9]. 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 $T > 100$ K [10], whereas it decreases exponentially below the transition temperature T_{SP}. Strong deviations from the model predictions were observed between 100 K and T_{SP} [9]. The g values are found as $g_a \approx g_b \approx 1.98$ and $g_c \approx 1.94$, which are typical for localized V^{4+} spins in octahedral crystal symmetry [11], 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 ΔH with the external magnetic field applied along the three main axis of the crystal. Starting with an isotropic value $\Delta H = 8$ Oe at the transition temperature $T_{SP} = 34$ 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 [12].

It has been reported by Yamada *et al.* [13] that the line broadening in the high-temperature regime $T > 100$ 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 Fig. 1 at four different temperatures, where the b axis was taken as rotation axis perpendicular to the static magnetic field. Following Yamada the data are well described by

$$\Delta H = A_{DM}(1 + \cos^2\vartheta) + \Delta H_0 , \qquad (1)$$

where ϑ is the polar angle with respect to the c axis. A_{DM} is proportional to the strength of the DM interaction, and ΔH_0 is the residual linewidth due to further relaxation

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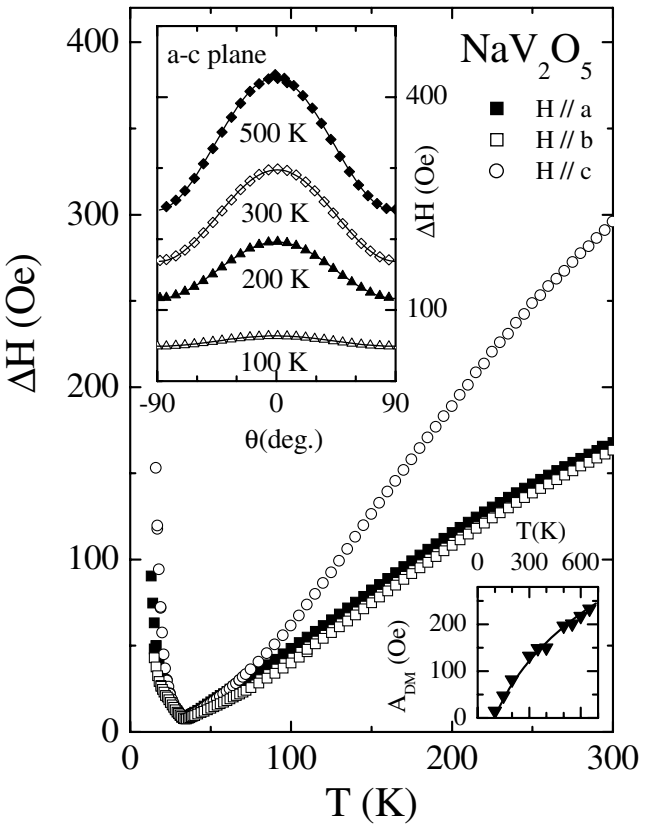

FIG. 1. EPR linewidth ΔH as a function of temperature T for the magnetic field applied along the three crystallographic axes. Upper inset: Angular dependence of the EPR linewidth ΔH for the magnetic field applied perpendicular to the b axis at temperatures $T \geq 100$ K. Lower inset: Temperature dependence of the strength parameter A_{DM} of the DM interaction [see Eq. (1) and text].

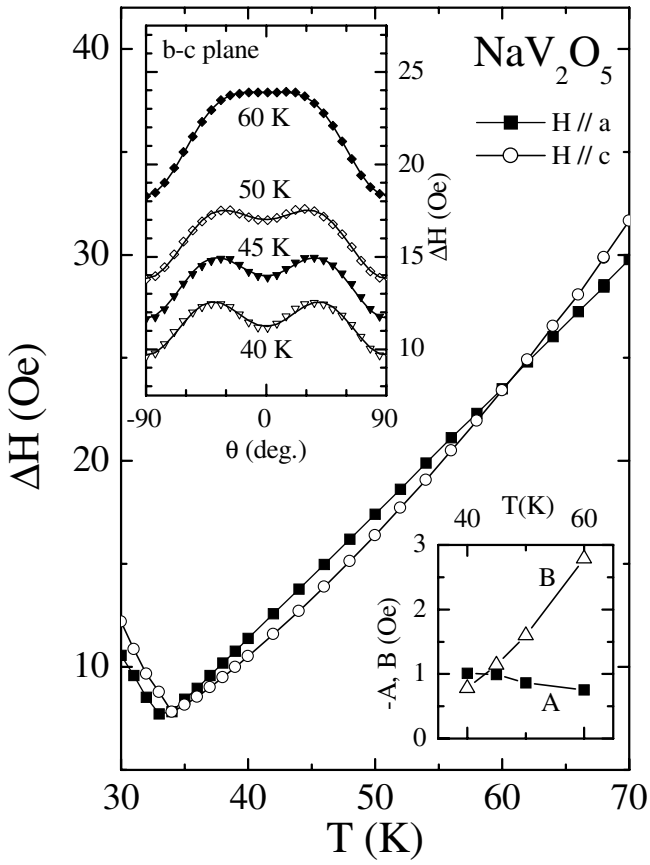

FIG. 2. Crossover regime in the temperature dependence of the EPR linewidth ΔH. Upper inset: Angular dependence of the EPR linewidth ΔH for the magnetic field applied perpendicular to the a axis at temperatures $T \leq 100$ K. Lower inset: Fit parameters A and B derived from Eq. (2) as a function of temperature T.

mechanisms. Above 100 K the parameter A_{DM} strongly increases, as it is shown in the lower inset of Fig. 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 $34 < T < 60$ 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 crossover regime. The angular dependence within the b-c plane shown in the upper inset of Fig. 2 is of special interest, because here an additional modulation appears, which is well described by

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

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 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

$$\mathcal{H}_{\mathrm{ij}} = \mathbf{d_{ij}} \cdot [\mathbf{S_i} \times \mathbf{S_j}] . \qquad (3)$$

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

$$\mathbf{d_{ij}} = d_0 \cdot [\mathbf{n_{iO}} \times \mathbf{n_{Oj}}], \qquad (4)$$

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. Therefore the relevant oxygen-bridge vectors $\mathbf{n_{iO}}$ and $\mathbf{n_{Oj}}$ must build an angle smaller than 180° within the a-b plane. Moreover, the existence of a nonvanishing DM interaction requires a local symmetry without inversion center, because otherwise the DM vectors cancel each other [14], 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. 3a). The structure determined by Carpy and Galy [2] fulfills 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. 3b). However, using the structural data [4] 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 [2] as well as the symmetric quarter-filled ladder [3–5].

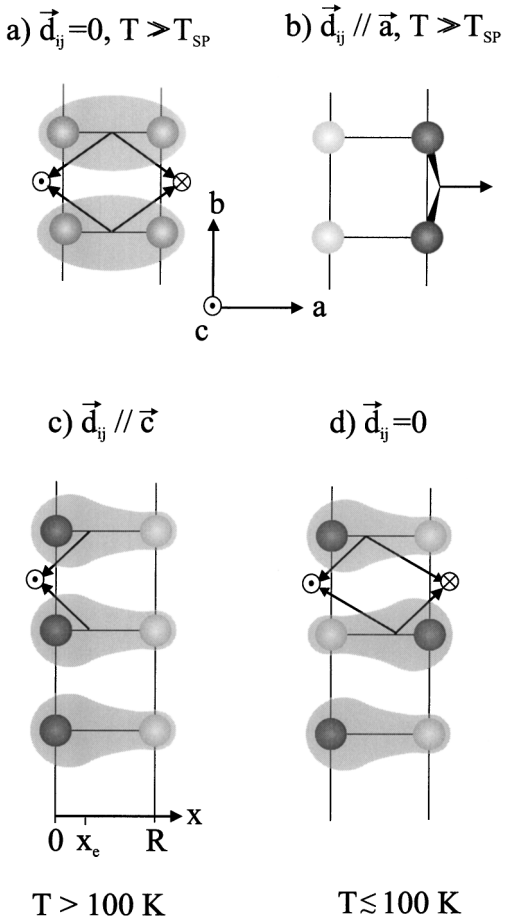

FIG. 3. Projection of the ladder structure of VO_5 pyramids into the a-b plane for different possible charge distributions. The spheres denote the vanadium ions; the oxygen ions have been omitted for simplicity. The oxygen ions of the relevant V-O-V bridges are marked by the DM vectors $\mathbf{d_{ij}}$. (a) Symmetric charge distribution (grey clouds) of a quarter-filled spin ladder $V^{4.5+}$; (b) chains of V^{4+} (dark) and V^{5+} (light); (c) local charge disproportion at high temperatures; (d) charge order fluctuations (dynamic, short-range) above T_{SP} and charge order (static, long-range) below T_{SP}. Cases (c) and (d) are in full agreement with the EPR results.

Recently, detailed optical investigations by Damascelli *et al.* [15] 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 $\psi_1 = u\psi_l + v\psi_r$, where the electron stays near the left-hand side and $\psi_2 = u\psi_r - v\psi_l$, where the electron favors the right-hand side. The atomic orbitals ψ_r and ψ_l of the right-hand and left-hand side are occupied according to the following weights:

$$u = \frac{1}{\sqrt{2}}\sqrt{1 + \frac{\Delta}{E_{\mathrm{CT}}}}, \qquad v = \frac{1}{\sqrt{2}}\sqrt{1 - \frac{\Delta}{E_{\mathrm{CT}}}}. \quad (5)$$

The parameter Δ describes the asymmetry of the onsite energy of the electron located in ψ_r with respect to ψ_l. The charge-transfer energy $E_{\mathrm{CT}} = \sqrt{\Delta^2 + 4t^2}$ 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 ψ_1 as

$$x_e = \frac{v^2 R + (R/2)2uvS_{\mathrm{RL}}}{u^2 + v^2 + 2uvS_{\mathrm{RL}}} \approx \frac{R}{2}\left(1 - \frac{\Delta}{E_{\mathrm{CT}}}\right), \quad (6)$$

where S_{RL} is the overlap integral between ψ_r and ψ_l. The last expression was obtained assuming $S_{\mathrm{RL}} \ll 1$, which is justified with respect to the distance $R \approx 3.6$ Å of both ions, and using Eq. (5). Taking the experimental values $\Delta \approx 0.8$ eV and $t \approx 0.3$ eV from [15], we calculate $x_e = 0.1R \approx 0.36$ Å, yielding a shift of the electronic charge distribution by 0.36 Å with respect to the center of the left-side V^{5+} ion. If now neighboring rungs of the ladder locally obey the same charge distribution, we obtain an overall shift of $\Delta a \approx 0.64$ Å of the vanadium spins with respect to the connecting oxygen ion. This yields a V-O-V bridge angle of about 140° within the a-b plane and therefore a dominant DM contribution in c direction. The EPR data provide strong experimental evidence for the appearance of charge disproportions in the quarter-filled spin ladder at high temperatures.

The peculiarities observed in the crossover regime ($34 < T < 60$ 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.* [16] for the one-dimensional antiferromagnet $KCuF_3$ and more extensively for ferromagnetic Cu

layers by Soos *et al.* [17]. 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 antisymmmetric 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_2O_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_2O_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 Fig. 1. This indicates that already for temperatures $T \leq 100$ K the charge disproportions change to a symmetric zigzag order of V^{4+} and V^{5+} ions in the ladder, where the DM vectors cancel each other (cf. Fig. 3d). This result is in good agreement with reports of charge-order fluctuations for $80 \geq T \geq T_{SP}$ from Raman spectroscopy [18] and the onset of a static long-range zigzag order below T_{SP} for ultrasonic [19] and dielectric results [20].

Finally the $\pi/2$-periodic modulation of the angular dependence in the b-c plane according to Eq. (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 $\pi/2$-periodic modulations only if its secular contributions are enhanced with respect to the nonsecular contributions by spin diffusion, which is characteristic for low-dimensional systems [17]. As we will report in a more detailed subsequent publication, the fact that the $\pi/2$-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 $J_{bc} \neq 0$. Under these conditions, the prefactors of Eq. (2) resemble anisotropic $A \sim J_{bc}^2$ and antisymmetric $B \sim A_{DM}$ exchange. From the lower inset of Fig. 2 we obtain that for $60 > T > 34$ 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 nonvanishing DM interaction (Fig. 3c). The direction of the DM vector is determined by the V-O-V bridge angle $\approx 140°$ 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 zigzag charge-order fluctuations, which become long-range and static below T_{SP} (Fig. 3d). The zigzag structure probably results from interlayer couplings.

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