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ESR STUDY OF THE SPIN-PEIERLS TRANSITION IN NaV$_2$O$_5$

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α'-NaV$_2$O$_5$ is an inorganic $S = 1/2$ one-dimensional antiferromagnetic Heisenberg chain (1DAFHC) compound which exhibits a spin-Peierls (SP) transition [1–3]. At $T_{SP} = 33.5$ K a non-magnetic singlet-ground state forms via dimerization of the spin chains induced by spin–phonon coupling. α'-NaV$_2$O$_5$ crystallizes in an orthorhombic structure (space group $P2_1mn$ [4]) and is characterized by charge ordered alternating chains consisting of V^{4+}O$_5$ ($S = 1/2$) and V^{5+}O$_5$ (non-magnetic) chains along the crystallographic b-axis. Susceptibility data were reported by Isobe and Ueda [1] and Mila *et al.* [5] on polycrystalline samples and by Weiden *et al.* [3] on single crystals. From the high temperature susceptibility the next-nearest neighbor exchange coupling was estimated to be 560 K [1] or 529 K [5]. A gap of 85 K between the singlet ground state and the triplet excited state was measured in the dimerized state [3]. The SP transition has also been studied with X-ray and neutron techniques [2], by Raman scattering [3] and by NMR experiments [6]. From the neutron experiments an ordering wave vector $q = (0.5, 0.5, 0.25)$ and a gap energy of 114 K [2] were estimated. The temperature dependence of the spin susceptibility below the SP transition temperature implies a singlet–triplet gap of $\Delta = 98$ K [6].

In the search for one-dimensional conductors and one-dimensional spin chains an ESR study on NaV$_2$O$_5$ has been reported by Ogawa *et al.* [7] already a decade ago. However, they observed no indication of a phase transition in the temperature dependence of the ESR spin susceptibility and interpreted their results in terms of a spin singlet state due to the formation of bipolarons [7]. However, the analysis was hampered by a large Curie-like increase at low temperature due to isolated paramagnetic centers. At high temperatures the spin susceptibility revealed a maximum close to 350 K in accord with early d.c. susceptibility measurements by Carpy *et al.* [8]. In this communication we report ESR measurements on a high-quality single crystal. The spin susceptibility, the g-values and the anisotropy of the susceptibility can be determined directly. The experiments provide clear experimental evidence on the opening of a spin gap at the spin-Peierls transition.

The single crystals were grown in a two step process: First pellets of a nearly stoichiometric mixture of high purity NaVO$_3$ and VO$_2$ were pressed and heated in an evacuated quartz tube at 620°C for four days. Then the material was heated above the melting temperature and, in a temperature gradient, was cooled down at a cooling rate of 7°C h^{-1}. Some of the crystals prepared by this method were powdered and characterized by Debye–Scherrer X-ray diffraction, which showed the material to be single phase. The crystal used in this work was characterized by Laue diffraction.

Measurements were made with a Bruker ELEXSYS E500CW-spectrometer at X-band frequencies (9.2 GHz) equipped with an Oxford Instruments continuous He flow cryostat which allowed measurements between 4.2 K $< T <$ 300 K. The needle shaped NaV$_2$O$_5$ single crystal was mounted with the crystallographic b axis perpendicular to the external magnetic field. Due to the extremely anisotropic shape of the sample,

orientation-dependent measurements were only possible in the a–c plane, perpendicular to the spin chains. The small size of the sample limited the experiments to temperatures below 300 K. Even at room temperature the resonance absorption was ill-defined and barely observable.

The observed ESR signal in α'-NaV$_2$O$_5$ consists of a symmetric line near to a magnetic field of 3430 G which corresponds to $g \approx 2$, characteristic of a spin-only system with no contribution from orbital moments. Figure 1 shows typical ESR absorption lines at 36 K and 100 K. At both temperatures the resonance line can be well described using a single Lorentzian line shape (solid lines in Fig. 1). Just above T_{SP} the line width is of the order of 10 G. Guided by calculations in [9], this value can be estimated using anisotropic exchange interactions ($\Delta H_{AE} = 2$ G). The line width at T_{SP} may already be broadened due to temperature dependent effects which might explain the difference between the calculated and observed value. Dipole–dipole interactions obviously can be neglected ($\Delta H_{DD} = 35$ mG) [9]. We are aware that this is only a rough estimate and we cannot exclude other exchange interactions. Pilawa [9] has shown that in CuGeO$_3$, at least at high frequencies, anisotropic Zeeman interactions become important. Yamada et al. [10] claimed that the ESR linewidth in CuGeO$_3$ is dominated by Dzyaloshinsky–Moriya interactions. Further

experiments, possibly at higher frequencies are necessary to draw final conclusions.

Both, the resonance field and the line width depend on the angle θ between the external static magnetic field H and the crystallographic a axis (0–50°). The angular dependence of the resonance field (H_{res}) and the line width ΔH, as observed at 100 K, are shown in Fig. 2. The angular dependence of the resonance field can be well described using anisotropic g values ($g_c = 1.95$, $g_a = 1.97$). These g values are characteristic of V^{4+} ions in strong octahedral fields, possibly due to contributions from the covalent binding effects. This indicates that the distortion of the oxygen octahedron splits the orbital triplet of the d_ϵ^{-1} electron by an amount large compared to the spin-orbit coupling. Hence, the ground state for $T > T_{SP}$ should be a Kramers doublet with almost no contribution from the orbital moment [11].

With decreasing temperature the angular dependence of the resonance field remains almost constant, reflecting temperature-independent g values. The overall angular dependence of the line width increases with increasing temperature. However, at low temperatures more complicated behavior is observed perhaps due to increasing importance of anisotropic exchange. This is reminiscent of CuGeO$_3$, in which the anisotropy of ΔH revealed
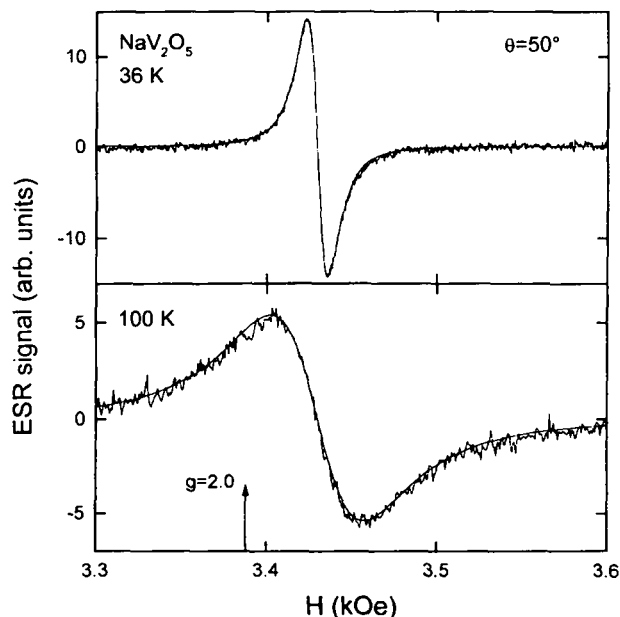

Fig. 1. Derivative of the resonance absorption in α'-NaV$_2$O$_5$ with the external field parallel to the crystallographic a-direction at two temperatures. The solid lines were calculated assuming Lorentzian line shapes.
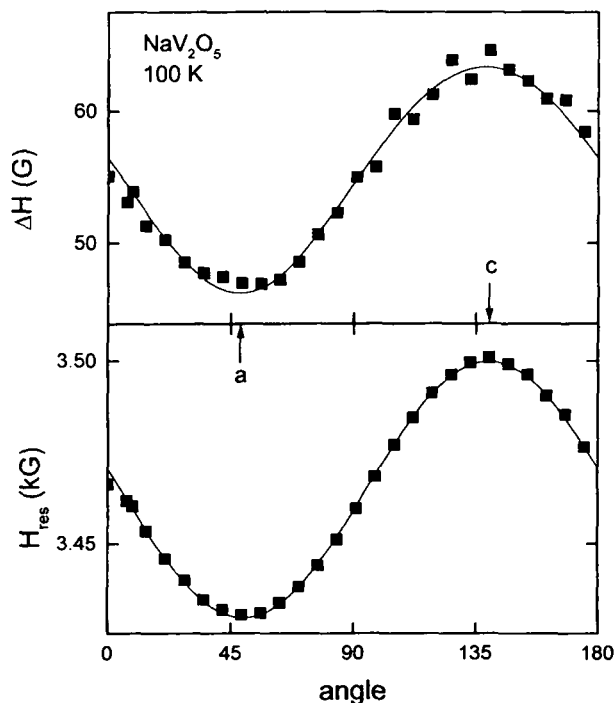

Fig. 2. Angular dependence of the line width (a) and the resonance field (b) in α'-NaV$_2$O$_5$ at 100 K. The solid lines have been calculated using anisotropic g values ($g_a = 1.976$, $g_c = 1.936$) and anisotropic line broadening ($\Delta H_a = 46$ G, $\Delta H_c = 63$ G).
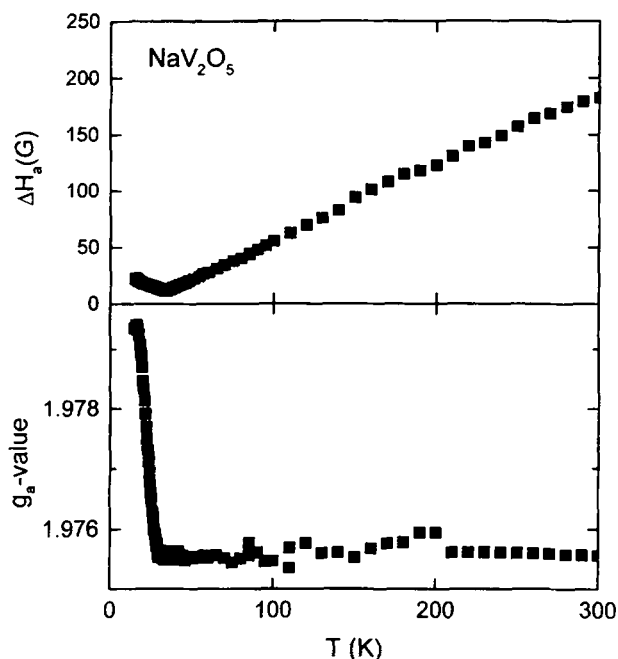
Fig. 3. Temperature dependence of the line width and the g value with the external magnetic field parallel to the crystallographic a axis. For $T > 200$ K the g value was fixed.

Fig. 4. Temperature dependence of the ESR spin intensity in α'-NaV$_2$O$_5$. Inset (a): Temperature dependence of the susceptibility compared to predictions of the Bonner–Fisher model. The susceptibilities were scaled arbitrarily to 1 at $T = 350$ K. Inset (b): Temperature dependence of the spin susceptibility below the spin-Peierls transition T_{SP}. The solid was calculated using the model of Bulaevskii with alternating exchange constants. The dashed line is the result of a mean-field BCS calculation.

temperature dependence of the orientation and the size of the orthorhombic distortion [9]. Detailed analysis is planned in the near future when larger single crystals are available which make possible measurements along the b direction as well.

Figure 3 shows the temperature dependence of the line width and of the g value, at an angle of 50°, with the a axis parallel to the external magnetic field. As noted above, the g value is almost constant for $T > T_{SP}$ (due to poor statistics, above 200 K we have fixed the g value and used the line width and the intensity as the only free fit parameters). Below T_{SP} the g value increases getting even closer to $g = 2$. This might indicate a further distortion of the oxygen octahedra, yielding a further increase of the crystalline electric field. The line width has a minimum at T_{SP} and increases continuously with increasing temperature as observed previously by Ogawa et al. [7]. The temperature dependence for $T > T_{SP}$ is characteristic for broadening effects due to spin-diffusion processes [12]. It should be noted that this increase of $\Delta H(T)$ has been explained by Ogawa et al. [7] as due to the hopping motion of electrons.

Figure 4 shows the central result of this investigation: Here the intensity of the resonance absorption is plotted as a function of temperature. In ESR experiments the intensity is a direct measure of the spin susceptibility. The exponential decrease at low temperatures unambiguously demonstrates the dimerization of the spins and hence the
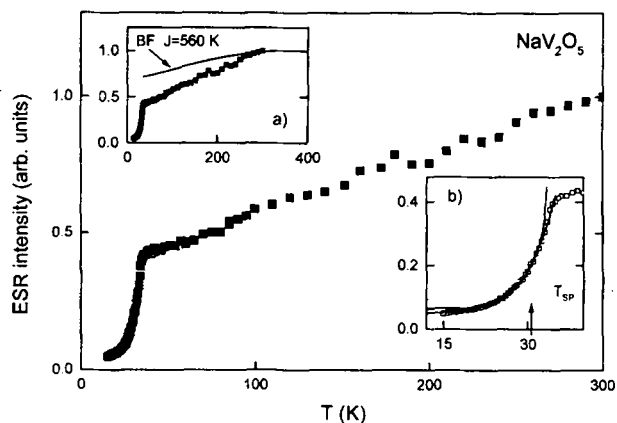
opening of a gap in the magnetic excitation spectrum. Experimentally above T_{SP} the spin susceptibility increases almost linearly in α'-NaV$_2$O$_5$. Theoretically in $S = 1/2$ 1DAFHCs with increasing temperature the susceptibility slightly increases, shows a maximum close to $0.64\,J$, where J is the exchange integral between neighboring spins and then follows a Curie–Weiss type of behavior for higher temperature. From previous susceptibility measurements we know that the maximum in the susceptibility occurs close to 350 K, yielding an exchange interaction $J \approx 560$ K and that the susceptibility can be described using the well-known Bonner–Fisher (BF) model [13]. Inset a in Fig. 4 compares the measured susceptibility with the BF predictions. The results were arbitrarily scaled to unity at 350 K. The comparison reveals that the BF model predicts a much smoother decrease than our experimental results. This is in clear disagreement with d.c.-susceptibility measurements in powdered samples at 1 T which agree well with the theoretical predictions. At present we have no explanation for the disagreement of our results with the theoretical predictions for a spin one-half 1DAFHC. However, it may signal significant deviations from the idealized one-dimensionality. It also may indicate alternating exchange constants already above T_{SP}. Further experiments to higher temperature will be necessary to clarify this.

Finally we attempt to analyze the exponential decrease of the intensity below the spin-Peierls transition. Within the frame-work of a BCS-like mean-field model we calculated the temperature dependence of the

gap and found a transition temperature of 33.5 K and a gap value of 98 K results (dashed line in inset b of Fig. 4). This result indicates significant deviations from the weak coupling limit $(2\Delta(0) = 3.52k_B T_{SP})$ and yields a ratio $2\Delta/k_B T_{SP} = 5.9$. The spin susceptibility below the spin-Peierls transition can also be described using a model of Bulaevskii [14] which estimates the susceptibility of a one-dimensional spin chain with two alternating exchange constants J_1 and J_2. The susceptibility can be fitted using $\gamma = J_1/J_2$ as a fit parameter and the result is shown as solid line in inset b of Fig. 4. From this fit we obtain $J_1 = 500$ K and $J_2 = 619$ K if we assume the average exchange $J = 560$, which is the characteristic exchange constant of the high-temperature phase [1]. In the framework of the theories of Pytte [15] and Bray *et al.* [16] the gap value can be deduced via $\Delta(0) = pJ\delta(0)$. Here J is the mean exchange constant, the constant $p = 1.637$ and δ can now be calculated from the alternating exchange constants J_1 and J_2, yielding $\delta(0) = 0.11$. We obtain $\Delta(0) = 101$ K, in almost perfect agreement with the mean-field BCS result.

In conclusion, we have presented ESR results on α'-NaV$_2$O$_5$ between 4 K and 300 K. Our results clearly indicate the opening of a spin gap below $T_{SP} = 33.5$ K. The g-values are close to $g = 2$ indicative for quenched orbital moments. The spin gap $\Delta = 100$ K ± 2 K is in good agreement with neutron scattering ($\Delta = 114$ K [2]), NMR ($\Delta = 98$ K [6]) and d.c. susceptibility results ($\Delta = 85 \pm 15$ K [3]).

After this paper was written we have learned that high-frequency ESR experiments were performed by Schmidt, Palme, Lüthi, Weiden, Hauptmann and Geibel (preprint). They determined a gap energy of $\Delta = 85 \pm 20$ K.

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