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## Unconventional Anisotropic Superexchange in $\alpha'$ - $\text{NaV}_2\text{O}_5$

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The strong line broadening observed in electron spin resonance on  $\text{NaV}_2\text{O}_5$  is found to originate from an unusual type of the symmetric anisotropic exchange interaction with *simultaneous* spin-orbit coupling on both sites. The microscopically derived anisotropic exchange constant is almost 2 orders of magnitude larger than the one obtained from conventional estimations. Based on this result we systematically evaluate the anisotropy of the ESR linewidth in terms of the symmetric anisotropic exchange only, and we find microscopic evidence for precursor effects of the charge ordering already below 150 K.

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The isotropic exchange constants in one-dimensional antiferromagnets are obtained by measurements of the magnetic susceptibility or by inelastic neutron scattering. The anisotropic exchange contributions, however, are only accessible by means of electron spin resonance (ESR), because the spin-spin relaxation measured by the ESR linewidth is driven primarily by the corresponding effective local fields. Conventional theoretical estimations of anisotropic exchange parameters yield values by far too small to describe the experimental results. A prominent example for this problem is the spin ladder  $\alpha'$ - $\text{NaV}_2\text{O}_5$ . This compound was initially identified as a spin-Peierls system [1] which triggered enormous efforts to investigate the nature of this transition. It was found that the system actually undergoes a charge-order (CO) transition at  $T_{\text{CO}} \approx 34$  K [2] from a uniform oxidation state of  $V^{4.5+}$  ions at high temperature [3] into a state with “zigzag” type charge distribution [4] accompanied by spin-gap formation. Moreover, various experimental studies revealed an anomalous behavior at about 200 K, far above  $T_{\text{CO}}$ , which has been attributed to the existence of charge fluctuations in the system [5–7].

Previously, it was proposed that the spin relaxation in  $\text{NaV}_2\text{O}_5$  is strongly affected by these charge fluctuations [8]. ESR directly probes the spin of interest and, hence, is extremely sensitive to such dynamic processes of the electronic structure. The underlying mechanism of the spin relaxation, however, still remained a matter of heavy debate [9,10]. In this work, we identify the anisotropic exchange (AE) interaction as the dominant source of line broadening and we calculate the AE parameters on the basis of a microscopic charge-distribution picture. With these parameters we are able to describe the angular dependence of the ESR linewidth  $\Delta H$  at temperatures above  $T_{\text{CO}}$ . The resulting temperature dependence of the exchange parameters is a clear fingerprint of the increasing charge fluctuations on approaching  $T_{\text{CO}}$ .

All details concerning the preparation and characterization of the crystals and the experimental ESR set-up have been published previously [11]. The observed ESR signal in  $\alpha'$ - $\text{NaV}_2\text{O}_5$  consists of a Lorentzian line with a  $g$  value,  $g \approx 2$ , characteristic of a spin-only system with quenched orbital moments [11]. The linewidth increases monotonously from a value of 10 Oe at  $T_{\text{CO}}$  up to several hundred Oe above room temperature, with the linewidth  $\Delta H_c$  for the magnetic field applied along the crystallographic  $c$  axis being about twice as large as  $\Delta H_a$  and  $\Delta H_b$  (along the  $a$  and  $b$  axes).

At first, let us consider possible origins for the line broadening  $\Delta H$  in  $\text{NaV}_2\text{O}_5$ . Single-ion ( $S = 1/2$ ), hyperfine, and spin-lattice relaxation were shown to be less important in  $\text{NaV}_2\text{O}_5$  [7,12,13]. The anisotropic Zeeman effect is not relevant, because of nearly equivalent  $g$  tensors for all vanadium sites. Therefore, only three sources remain to account for the broadening of the ESR spectra in  $\text{NaV}_2\text{O}_5$ —the dipole-dipole, the symmetric AE, and the antisymmetric Dzyaloshinsky-Moriya exchange (DM) interactions. These contributions have been already estimated and discussed in Ref. [12]. The assumption that the DM interaction is the main perturbation was based on the conventional relation for the DM vector  $|d| \approx (\Delta g/g)|J|$  (where  $g$  and  $\Delta g$  are the  $g$  factor and its anisotropy, respectively) [14]. The ESR data could be modeled by this approach, but it was necessary to assume the presence of strong charge disproportions even at highest temperatures to allow for an appropriate direction of the DM vector [8]. Later, Choukroun *et al.* [9] questioned the dominance of the DM interaction, showing that the contribution of the DM interaction to the ESR linewidth in quantum-spin chains cannot be larger than that of the AE. But the AE itself as taken from conventional estimations is by far too small to account for the large linewidth observed in  $\text{NaV}_2\text{O}_5$ . Therefore, such conventional estimations have to be taken with care. A recent field-theoretical treatment

of quasi-1D  $S = 1/2$  antiferromagnetic chains came to similar conclusions [10], because the DM interaction was found to produce a divergence in the temperature dependence of the linewidth  $\Delta H_{\text{DM}} \sim T^{-2}$  for  $T \ll J/k_B$ . This is in contrast to the monotonic increase of  $\Delta H$  with increasing temperature in  $\text{NaV}_2\text{O}_5$  [8]. Such behavior, however, is in agreement with the theoretical expectation for a dominant AE [10]. Experimental investigations of related compounds corroborate this expectation, too [15–18]. In this respect  $\text{LiCuVO}_4$  played a key role [18], because the DM interaction can be completely ruled out by its crystal symmetry. The linewidth is dominated by the AE, because the ring-exchange geometry in the  $\text{Cu-O}_2$  chains strongly

enhances the AE as compared to the conventional estimation  $|J_{\text{AE}}| \approx (\Delta g/g)^2 |J|$  [14]. In the following we will provide detailed microscopical estimations of this term in  $\text{NaV}_2\text{O}_5$  and show that the angular and temperature dependencies of  $\Delta H$  can be completely described in terms of this relaxation mechanism, only.

Starting with the microscopic analysis of the AE paths, the Hamiltonian for AE between two neighboring sites  $A$  and  $A'$  can be written as  $\mathcal{H}_{\text{AE}} = S_A^\alpha D_{\alpha\beta}^{AA'} S_{A'}^\beta$ , where  $\{\alpha, \beta\} = \{x, y, z\}$ . Taking into account all possible virtual processes (displayed schematically in Fig. 1) between site  $A$  to site  $A'$ , we derive the following expression for  $D_{\alpha\beta}^{AA'}$  in the fourth order of perturbation theory:

$$D_{\alpha\beta}^{AA'}(\eta \rightarrow \xi) = \frac{\lambda_A \lambda_{A'}}{2\Delta_{AA'}} \left\{ \frac{\langle \eta | l_\alpha | \zeta \rangle}{\Delta_{\zeta\eta}} t_{\zeta\xi} t_{\xi\xi'} \frac{\langle \xi' | l_\beta | \eta \rangle}{\Delta_{\xi'\eta}} + t_{\eta\varphi} \frac{\langle \varphi | l_\alpha | \xi \rangle}{\Delta_{\varphi\xi}} \frac{\langle \xi | l_\beta | \varphi' \rangle}{\Delta_{\varphi'\xi}} t_{\varphi'\xi} + \frac{\langle \eta | l_\alpha | \zeta \rangle}{\Delta_{\zeta\eta}} t_{\zeta\xi} \frac{\langle \xi | l_\beta | \varphi \rangle}{\Delta_{\varphi\xi}} t_{\varphi\eta} \right. \\ \left. + t_{\eta\varphi} \frac{\langle \varphi | l_\alpha | \xi \rangle}{\Delta_{\varphi\xi}} t_{\xi\xi'} \frac{\langle \xi' | l_\beta | \eta \rangle}{\Delta_{\xi'\eta}} + t_{\eta\xi} \frac{\langle \xi | l_\alpha | \varphi \rangle}{\Delta_{\varphi\xi}} t_{\varphi\xi} \frac{\langle \xi | l_\beta | \eta \rangle}{\Delta_{\zeta\eta}} + \frac{\langle \eta | l_\alpha | \zeta \rangle}{\Delta_{\zeta\eta}} t_{\zeta\varphi} \frac{\langle \varphi | l_\beta | \xi \rangle}{\Delta_{\varphi\xi}} t_{\xi\eta} \right\}, \quad (1)$$

where, e.g.,  $t_{\xi\xi'}$  is the effective hopping integral between the states  $|\xi\rangle$  and  $|\xi'\rangle$  via intermediate oxygens, and  $\langle \xi | l_\alpha | \zeta \rangle$  denotes the matrix element of the spin-orbit (SO) coupling  $\mathcal{H}_{\text{SO}} = \lambda l_\alpha s_\alpha$ . Here we assume that the charge-transfer energy  $\Delta_{AA'}$  from site  $A$  to site  $A'$  is large compared to the crystal-field splittings  $\Delta_{\text{cf}} \equiv \Delta_{\zeta\eta}, \Delta_{\xi'\eta}$ . The first two correspond to conventional AE processes [19,20], while the others [Figs. 1(c)–1(f)] and the general expression (1) are presented to the best of our knowledge for the first time. For example, in case 1(f) the electron at site  $A$  is excited via SO coupling from the ground state  $|\eta\rangle$  into the state  $|\zeta\rangle$ , then it is transferred to the empty state  $|\varphi\rangle$

at site  $A'$  and interacts via SO coupling with the electron in the corresponding ground state  $|\xi\rangle$ . Finally, one of the electrons hops from state  $|\xi\rangle$  to the initial state  $|\eta\rangle$ .

Focusing now on  $\text{NaV}_2\text{O}_5$ , we recall that the electron is distributed between two V ions on the same rung. Correspondingly, its ground state wave function  $|\eta\rangle$  is given as a superposition  $c_1|d_{xy}\rangle - c_2|d_{xy}\rangle$  of the two vanadium  $d$  orbitals. Analogously, the ground state of the electron on the adjacent rung is given by  $|\xi\rangle = c'_1|d_{xy}\rangle - c'_2|d_{xy}\rangle$ . We illustrated the corresponding  $d$  orbitals together with relevant bridging oxygen  $p$  orbitals ( $\pi$  bonding with hopping integral  $t_{\xi\eta} = t_\pi$ ) in Fig. 2(a) for the high-temperature limit, where all coefficients  $c_1, c_2, c'_1, c'_2$  become equal to  $1/\sqrt{2}$ . Note, that due to the orthogonality of the wave functions processes 1(a)–1(d) (Fig. 1) do not contribute to AE within one ladder in  $\text{NaV}_2\text{O}_5$ . Therefore, we will now concentrate on processes 1(e) and 1(f) and discuss the relevant excited states  $|\zeta\rangle$  and  $|\varphi\rangle$  involved. Considering the possible excitations of the electrons via SO coupling we find that the largest contribution is obtained by the matrix element  $\langle d_{xy} | l_z | d_{x^2-y^2} \rangle = 2i$ . Hence, the relevant excited states are the combinations  $c_1|d_{x^2-y^2}\rangle - c_2|d_{x^2-y^2}\rangle$  and  $c'_1|d_{x^2-y^2}\rangle - c'_2|d_{x^2-y^2}\rangle$  for  $A$  and  $A'$  rungs, respectively. The charge-distribution picture for the excited states ( $\sigma$  bonding via oxygen  $p$  orbitals with hopping integral  $t_{\zeta\varphi} = t'_\sigma$ ) is shown in Fig. 2(b).

Thus, using expression (1) one can derive  $D_{zz}$  as

$$D_{zz} = 8\lambda^2 \frac{t_\pi t'_\sigma}{\Delta_{\text{cf}}^2 \Delta_{AA'}} [c_1^* c'_1 + c_2^* c'_2]^2. \quad (2)$$

To estimate  $D_{zz}$  we use the free ion value  $\lambda = 31$  meV [21], the splitting between the  $d_{xy}$  and the  $d_{x^2-y^2}$  states

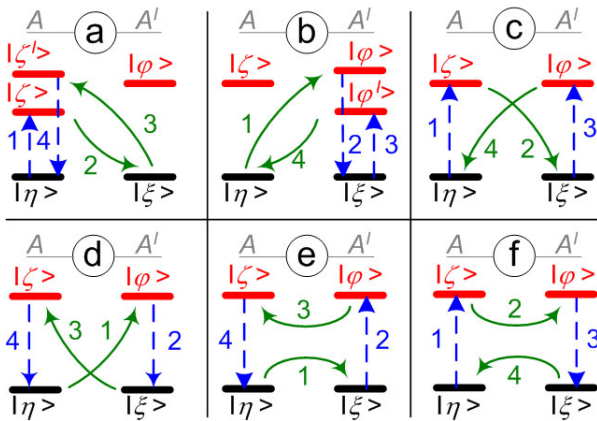


FIG. 1 (color online). Possible paths for AE between two sites  $A$  (with ground state  $|\eta\rangle$ , excited state  $|\zeta\rangle$ ) and  $A'$  ( $|\xi\rangle$  and  $|\varphi\rangle$ , respectively). Solid arrows correspond to the effective hopping integrals, dashed arrows indicate the matrix elements of the spin-orbit coupling. Numeration corresponds to the sequence of the matrix elements in fourth order perturbation expansion [see Eq. (1)].

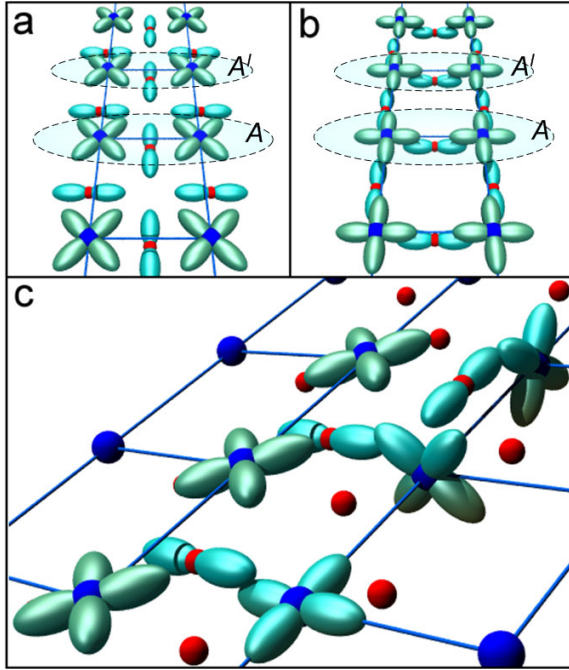


FIG. 2 (color online). Schematic pathway of AE between V ions in  $\text{NaV}_2\text{O}_5$ . Big spheres denote V ions, small spheres O ions. (a) Intraladder exchange between the ground state  $d_{xy}$  orbitals. (b) Intraladder exchange between the excited  $d_{x^2-y^2}$  states. (c) Possible interladder exchange paths.

$\Delta_{cf} \approx 0.36$  eV [22,23], and the charge-transfer energy  $\Delta_{AA'} = 3$  eV [24]. The hopping integral  $t'_\sigma$  cannot easily be calculated; however, one can assume  $t'_\sigma \approx t_\pi = 0.17$  eV [3] as a lower bound for  $t'_\sigma$ , and we obtain  $D_{zz} \approx 0.6$  meV in the high-temperature limit where the electron is equally distributed on each rung. This yields a characteristic linewidth  $\Delta H \sim 300$  Oe in very good agreement with the experimental linewidth. Note that our estimate is about 2 orders of magnitude larger than previous results [12], corroborating the importance of microscopic considerations for the estimation of AE parameters.

Taking now into account possible interladder exchange paths as shown in Fig. 2(c), we obtain contributions of comparable strength for the interladder AE. These paths involve a  $90^\circ$ -exchange geometry, which has been discussed in detail in Refs. [18,25,26]. Considering all possible interladder exchange paths in the appropriate local coordinate systems [17,27] we find a maximal component of the effective AE tensor along the crystallographic  $a$  axis.

Having identified and estimated the source of the ESR line broadening in  $\text{NaV}_2\text{O}_5$ , we will now apply this model to the experimental data. The analysis of the angular dependencies in terms of second moments has been described previously [17,18]. The experimental angular dependencies [28] of  $\Delta H$  are shown in Fig. 3 together with the fit curves. As a result we derive the ratio of the two essential fit parameters  $D_{\text{intra}}$  and  $D_{\text{inter}}$  for the AE param-

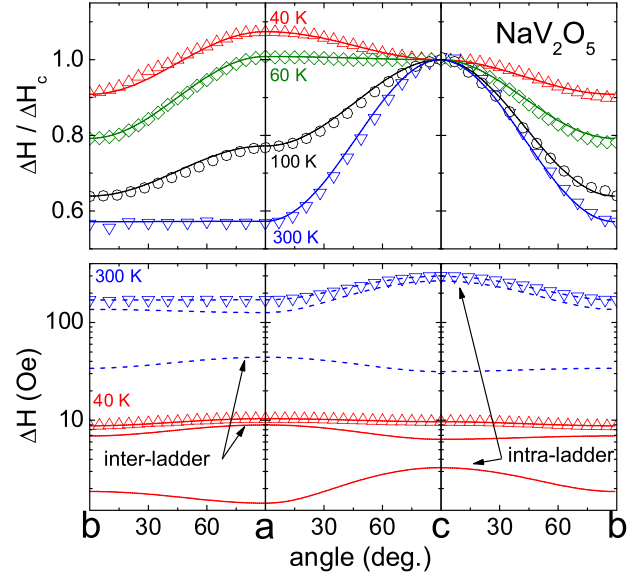


FIG. 3 (color online). Angular dependence of the ESR linewidth at different temperatures. Fit curves (lines) are described in the text. Upper frame: normalized to the linewidth for the magnetic field applied along the  $c$  axis. Lower frame: illustration of the contributions of intraladder and interladder AE to the linewidth far above (dashed line) and near  $T_{\text{CO}}$  (solid line).

eters within and between the ladders, respectively. Figure 4 shows the temperature dependence of the ratio  $D_{\text{inter}}/D_{\text{intra}}$  together with the linewidth ratios  $\Delta H_a/\Delta H_c$ ,  $\Delta H_b/\Delta H_c$  (note that only the ratio of the exchange parameters can be determined from the ESR linewidth at temperatures  $T < J/k_B$  as discussed in Ref. [17]). It can be clearly seen that at high temperatures ( $T > 150$  K) the dominant contribution to the line broadening is given by the intraladder AE. On decreasing temperature, below 150 K, the ratio strongly increases and the interladder contribution becomes domi-

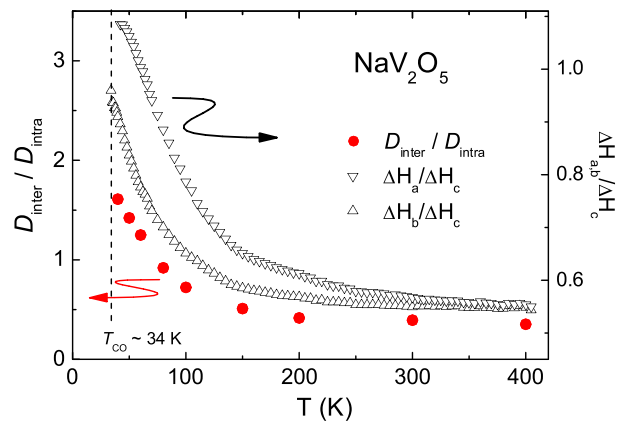


FIG. 4 (color online). Right ordinate: temperature dependence of the linewidth ratio for the magnetic field applied along the  $a$  or  $b$  axis normalized to  $\Delta H_c$ . Left ordinate: temperature dependence ratio of the interladder to intraladder AE constants obtained from the fitting of the angular dependencies of  $\Delta H$ .

nant. This can be understood taking into account the strong dependence of the AE parameters from the coefficients  $c_1, c'_1, c_2, c'_2$  which describe the electronic occupation on the vanadium sites. That means, e.g., for  $D_{\text{intra}} = D_{zz}$  [Eq. (2)] the coefficient  $[c_1^*c'_1 + c_2^*c'_2]$  is equal to 1 for the case  $V^{4.5+} - V^{4.5+}$ , and vanishes for the zigzag charge order ( $V^{5+} - V^{4+}$ ) realized below  $T_{\text{CO}}$  [4]. The observed increase of the  $D_{\text{inter}}/D_{\text{intra}}$  ratio already far above  $T_{\text{CO}}$  indicates that precursors of the developing CO set in at about 150 K, weakening considerably the intraladder AE.

Further evidence for the onset of charge disproportionations above  $T_{\text{CO}}$  has been reported by the strong frequency dependence of the ESR linewidth between 34–100 K [29], and the anomalous features observed by optical spectroscopy measurements [5,6,30]. Note that the uniform susceptibility has significant deviations from the Bonner-Fisher law already at  $T < 200$  K, too [7]. The coupling of these charge fluctuations to the lattice has been revealed by a softening of the elastic constants below 100 K detected by ultrasound experiments [31,32] and by the shift of the phonon energy found in light-scattering measurements around 80 K [33]. Moreover, we would like to point out that similar observations in  $\text{CuGeO}_3$  have been explained in terms of lattice fluctuations existing already far above the spin-Peierls transition [17]. We believe that the proposed spin-relaxation mechanism and the microscopic estimations do not only apply for the case of  $\text{NaV}_2\text{O}_5$ , but may allow us to describe the spin dynamics in many transition-metal compounds.

In summary, we have identified the symmetric anisotropic superexchange to be the source of the immense ESR line broadening in  $\text{NaV}_2\text{O}_5$ . In this microscopic picture the dominant process consists of the simultaneous virtual hopping of electrons between the ground states and excited states of vanadium ions on neighboring rungs of the ladder involving the spin-orbit coupling on both rungs. This novel unconventional exchange process has not been considered in the discussion of ESR line broadening before. The corresponding AE parameter is found to be of the order of 1% of the isotropic exchange constant resulting in a high-temperature limit of the ESR linewidth of approximately  $10^2$  Oe. On the basis of this microscopic analysis we have shown that the ESR data can be entirely described in terms of the symmetric anisotropic exchange only. The temperature dependence of the linewidth and derived exchange parameters evidences the presence of charge fluctuations in  $\text{NaV}_2\text{O}_5$  up to 150 K on a microscopic level.

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