Dynamical Dzyaloshinsky-Moriya Interaction in $KCuF_3$

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(Received 16 July 2008; published 2 October 2008)

The spin dynamics of the prototypical quasi-one-dimensional antiferromagnetic Heisenberg spin $S = 1/2$ chain $KCuF_3$ is investigated by electron spin resonance spectroscopy. Our analysis shows that the peculiarities of the spin dynamics require a new *dynamical* form of the antisymmetric anisotropic spin-spin interaction. This dynamical Dzyaloshinsky-Moriya interaction is related to strong oscillations of the bridging fluorine ions perpendicular to the crystallographic c axis. This new mechanism allows us to resolve consistently the controversies in observation of the magnetic and structural properties of this orbitally ordered perovskite compound.

DOI: 10.1103/PhysRevLett.101.147601 PACS numbers: 76.30.−v, 75.30.Et

The perovskite system $KCuF_3$ is presumably one of the best realizations of an one-dimensional (1D) antiferromagnetic (AFM) Heisenberg chain [1]. However, in spite of its paradigmatic status, the driving forces of the orbital and magnetic structure are far from being understood at the moment. Even the crystal structure originally assigned to be tetragonal D_{4h}^{18} (see Fig. 1) was claimed [2] to be orthorhombic D_2^4. Electron spin resonance (ESR) measurements [3,4] played a key role in triggering these investigations: they suggested the existence of the antisymmetric anisotropic exchange, usually termed as the Dzyaloshinsky-Moriya (DM) interaction, thereby questioning the crystal symmetry determined earlier. But the orthorhombic distortion deduced from x-ray diffraction [2] is not consistent with recent nuclear quadrupole resonance (NQR) data [5] and other experimental and theoretical findings [4,6].

In this Letter we reanalyze all *static* sources of the ESR line broadening on the microscopical level and show that the discrepancies in the understanding of this paradigm compound can be resolved by introducing a *dynamical* Dzyaloshinsky-Moriya (DDM) interaction.

Single crystals of $KCuF_3$ have been grown as described in Ref. [7]. The ESR experiments were carried out with a Bruker ELEXSYS E500 cw spectrometer at frequencies of 9 and 34 GHz. For measurements at 90 and 150 GHz a quasioptical technique was used [8]. The ESR spectrum consists of a single exchange narrowed Lorentz line at resonance fields corresponding to $g_c = 2.15$ and $g_a = 2.27$ in accordance with previous experiments at 24 GHz [9] and 34 GHz [10]. Figure 2 shows the temperature dependence of the ESR linewidth for different frequencies. Above T_N the linewidth increases monotonically from 0.3 kOe to more than 3 kOe above room temperature with a pronounced anisotropy with respect to the c axis [see Fig. 2(b)], but without any anisotropy within the ab plane. For different frequencies the linewidth data follow approximately the same temperature dependence with comparable absolute values. It can be described phenomenologically by an Arrhenius law $\Delta H \propto \exp(-\Delta/T)$ with an energy gap $\Delta = 114$ K (see Fig. 2).

Using conventional estimates [11] for all relevant sources of the ESR linewidth, it was concluded that the relaxation contribution of the antisymmetric DM interaction is several orders of magnitude larger than all other mechanisms in $KCuF_3$ [3]. However, the above mentioned inconsistencies concerning the direction of the DM vector [2–4] and a general theoretical analysis of the spin relaxa-

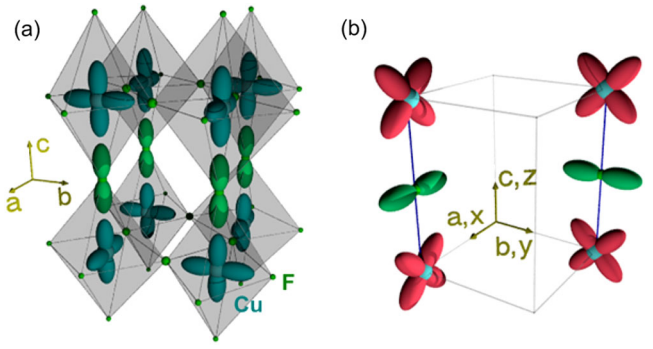

FIG. 1 (color online). (a) Schematic orbital ordering in the ground state of $KCuF_3$. The K ions, placed between the CuF_6 octahedra, are not shown. (b) Two most relevant paths of the ringlike SAE between the excited states of Cu ions.

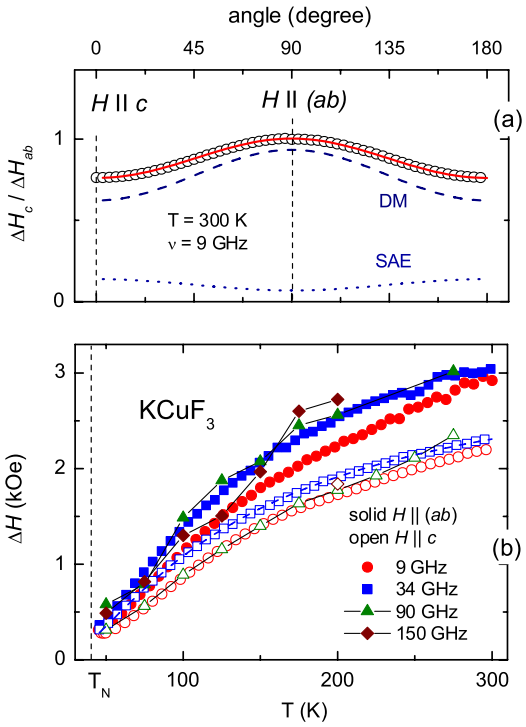

FIG. 2 (color online). (a) Temperature dependence of the linewidth at different frequencies. The blue dashed line (34 GHz, $H \parallel c$) represents a fit to an Arrhenius law. (b) Angular dependence of ΔH at $T = 300$ K. The fit is described in the text.

tion in $S = 1/2$ chains [12,13] questioned the validity of the original approach. Moreover, the microscopic analysis of the exchange paths in several one-dimensional magnets [14–17] showed that the symmetric anisotropic exchange (SAE) may strongly exceed the conventional estimate and thus dominate the spin relaxation. Therefore, it is necessary to reanalyze microscopically the magnitude of SAE and DM interactions in $KCuF_3$.

The crystal has a pseudoperovskite structure with $a = 5.855$ Å, $c = 7.852$ Å. Each Cu^{2+} ion (electronic configuration $3d^9$, spin $S = 1/2$) is surrounded by a tetragonally deformed fluorine octahedron. The principal axes of the octahedra are oriented alternating along the a and b axes, leading to the orbital ordering of the ground $|y^2 - z^2\rangle$ and $|x^2 - z^2\rangle$ states of a hole on Cu ions [see Fig. 1(a)].

The crystal structure and the orbital ordering in $KCuF_3$ allow for SAE interaction $\mathcal{H}^{(ab)}_{\mathrm{SAE}} = S^a_\alpha D^{(ab)}_{\alpha\beta} S^b_\beta$ ($\{\alpha, \beta\} = \{x, y, z\}$, a, b are the interacting ions) only along the crystallographic $c \equiv z$ axis via the ringlike processes described in Ref. [16]. The virtual exchange process consists of the excitation of a spin via spin-orbit (SO) coupling into an excited state of the starting ion a, the following hopping into an excited orbital state on the neighboring ion b and its transfer back into the initial state via the ground orbital state of the ion b (Fig. 1). Denoting the respective hopping integrals by t'_σ and t_π, we can estimate the exchange constant of SAE like in Ref. [16] as

$$D_{zz} \ll D_{xx} = D_{yy} \approx 4\lambda^2 \frac{t_\pi t'_\sigma}{\Delta^2_{cf}\Delta_{ab}} \approx 1 \text{ K}, \qquad (1)$$

where λ is the SO coupling constant, Δ_{cf} and Δ_{ab} denote the crystal-field splitting and the charge-transfer energy, respectively. Here we used $\lambda_a/\Delta_{cf} = 0.05$ [14] and $4t_\pi t'_\sigma/\Delta_{ab} \approx 4t'^2_\sigma/\Delta_{ab} \approx 380$ K [18].

The obtained value of SAE turns out to be strongly enhanced as compared to the conventional estimate [4,18], but the resulting ESR line broadening with $\Delta H \sim 10^2$ Oe cannot explain the huge ESR linewidth $\Delta H \sim 3$ kOe observed in $KCuF_3$. Note that in all compounds where SAE plays a dominant role [14–16] the characteristic linewidth at $T \approx J/k_B$ is about hundreds of Oe, i.e., an order of magnitude smaller than in the case of $KCuF_3$. This large discrepancy indicates the existence of an additional source of line broadening in $KCuF_3$. Indeed, Oshikawa and Affleck [12] supposed another type of spin relaxation to be dominant in this system, because $KCuF_3$ does not obey the universal scaling behavior of $\Delta H(T/J)$ typical for spin relaxation via SAE.

The existence of a static DM interaction is not allowed in the originally proposed tetragonal crystal structure [3]. However, AFM resonance at $T = 4.2$ K yields nonvanishing DM vectors $\mathbf{d} \parallel [100]$ and $[010]$ [4]. The reexamination of the room temperature crystal structure by x-ray diffraction [2] showed a large standard deviation of the fluorine ions placed on the magnetic chains away from the c axis. This was interpreted as a sign of a considerable *static* displacement of these ions from the c axis, leading to an orthorhombic distortion allowing for a nonvanishing DM vector directed along the [110] and equivalent directions. This kind of displacement in a perovskite structure usually means a rotation of a CuF_6 octahedron as a whole [19], but no displacement of the F^- ions from the (xy) plane has been detected in Ref. [2]. This fact was emphasized by Binggeli *et al.* [6] who found in their local density approximation plus Hubbard U (LDA + U) calculations that this structure relaxes to the conventional tetragonal structure of $KCuF_3$. This indicates that the displacements reported in Ref. [2] are rather *dynamic*, initiated by thermal fluctuations. This assumption is corroborated by the measurements of the thermal displacement coefficients of fluorine ions [20]. They were found to be very high and exceed strongly those of, e.g., oxygen atoms in an oxide with the similar crystal structure $LaMnO_3$ [21]. Such thermal motions may appear as static on the frequency scale of x-ray experiments $f \sim 10^{15}$ Hz. In the following we develop a model of *dynamical anisotropic exchange*, which accounts for the thermal vibration of an intermediate diamagnetic ion and allows us to explain both the magnitude and the anisotropy of the ESR line in $KCuF_3$.

We start from the general expression for the antisymmetric exchange interaction $\mathcal{H}_{\mathrm{DM}} = \mathbf{d}^{(ab)} \cdot [\mathbf{S}_a \times \mathbf{S}_b]$. In the fifth order of perturbation we have derived

$$d_j^{(ab)} = \frac{2i}{\Delta_{\eta\xi}}\left(\frac{1}{\Delta_{\kappa\eta}\Delta_{\rho\eta}} + \frac{1}{\Delta_{\kappa\xi}\Delta_{\rho\xi}}\right) \times \left(t_{\xi\kappa}t_{\kappa\eta}\frac{\langle\eta|\lambda_a l_j^{(a)}|\zeta\rangle}{\Delta_{\eta\zeta}}t_{\zeta\rho}t_{\rho\xi} - t_{\eta\rho}t_{\rho\xi}\frac{\langle\xi|\lambda_b l_j^{(b)}|\varphi\rangle}{\Delta_{\xi\varphi}}t_{\varphi\kappa}t_{\kappa\eta}\right), \quad (2)$$

where $j = \{x, y, z\}$, $t_{\alpha\beta}$ are the effective hopping integrals between the states $|\alpha\rangle$, $|\beta\rangle$ and a sum over all states of an intermediate ion ($|\kappa\rangle$, $|\rho\rangle$) is implied. These virtual hopping processes are displayed schematically in Fig. 3, where, e.g., frame I corresponds to the first term of Eq. (2). Note that expression (2) differs strongly from the one suggested in Ref. [22], where the position of the bridging ion, crucial in our case, was not discussed.

It is well known [3,22] that the static DM interaction is not allowed in the crystal structure of $KCuF_3$ with the space group D_{4h}^{18}, but now we go beyond the static configuration. As illustrated in Fig. 3, the intermediate ion c may be temporarily shifted from its equilibrium position due to rotation or tilting phonon modes. If the average time of this displacement $\tau_F \approx 2\pi/\omega_F$ is large compared to the characteristic time of electron exchange $\tau_{ab} \approx \hbar/t_{ab}$, several exchange processes shown in Fig. 3 can occur via the displaced ion giving rise to antisymmetric exchange. Usually $t_{ab} \sim 0.5$ eV which allows us to estimate $\tau_{ab} \approx 10^{-2}\tau_F$ using the phonon frequency $\omega_F/2\pi \sim 70$ cm^{-1} as determined from Raman scattering experiments [23].

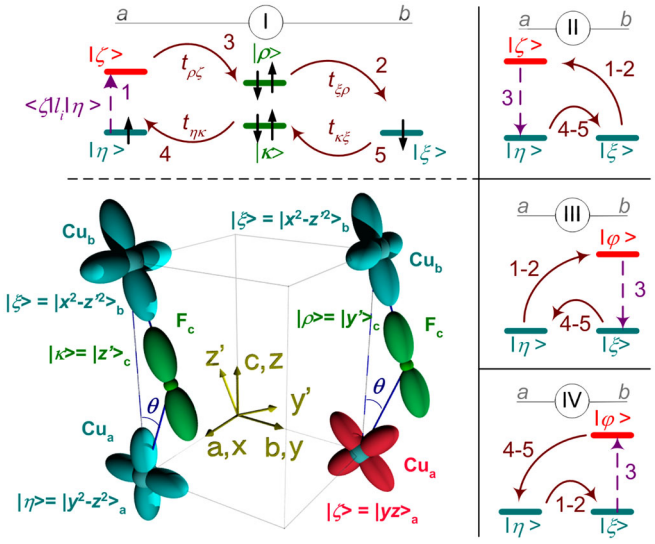

FIG. 3 (color online). Possible paths for DM interaction between two sites a (with ground state η, exited state ζ) and b (ξ and φ, respectively). Solid arrows correspond to the effective hopping integrals, dashed arrows indicate the matrix elements of the spin-orbit coupling. Numeration indicates one of the possible order of the matrix elements in Eq. (2). Additionally, frame I displays orbital configurations corresponding to this exchange process.

The relevant pattern of the F^- displacements away from the c axis is taken in accord to x-ray diffraction experiments [2]. It can be related to the orbital order in $KCuF_3$ as follows: In Fig. 3 we show the geometry of exchange along with the ground state orbitals $|\eta\rangle = |y^2 - z^2\rangle_a$ and $|\xi\rangle = |x^2 - z^2\rangle_b$. There are four short and two long Cu-F bonds in a CuF_6 octahedron. A displacement of an intermediate F^- ion along the y_c axis (as shown in the Fig. 3) corresponds to the rotation of the Cu $|x^2 - z^2\rangle_b$ orbital and fluorine ion around the x_b axis and does not destroy short bonds. Note that in this case the $|y^2 - z^2\rangle_a$ orbital is fixed by three stationary short bonds and is not rotated in accordance with the results of the structural analysis [2], which does not reveal any deviations of F^- ions from the (ab) plane. The second equivalent possibility, a displacement of the F^- ion along the x_c axis, is not displayed in Fig. 3 but will be taken into account. Substituting the excited state $|\varphi\rangle = |yz\rangle_a$ ($\langle d_{yz}|l_x|d_{y^2-z^2}\rangle_a = 2i$), Eq. (2) gives only one nonzero component of $\mathbf{d}$,

$$|d_x^{(ab)}| = 4\frac{\lambda_a}{\Delta_{cf}}\frac{(2t'_\sigma + t_\pi)(t'_\sigma + t_\pi)t'_\sigma}{\Delta_{ab}\Delta_{ac}^2}[-t'_\sigma\cos^2(2\theta) + t_\pi\sin^2(2\theta)]\cos(2\theta)\sin(2\theta). \quad (3)$$

Note that the factor $\sin(2\theta)$ can be rewritten as a modulus of the vector product $[\mathbf{n}_{ac} \times \mathbf{n}_{bc}]$, where the unit vectors $\mathbf{n}_{ac}$ and $\mathbf{n}_{bc}$ connect the spins a and b with the bridging ion c, respectively. Therefore, the rule $\mathbf{d} \parallel [\mathbf{n}_{ac} \times \mathbf{n}_{bc}]$ suggested in Refs. [24,25] for the static case is preserved in our case, too.

The value of θ is related to the displacement of a F^- ion from equilibrium position $\sin(2\theta)R_{Cu\text{-}F}$, where $R_{Cu\text{-}F}$ is the distance between the Cu and F ions and can be expressed via phonon operators. Thus we arrive at a new dynamical form of DM interaction (DDM) containing simultaneously a phonon and two spin operators. A closely related form of spin-lattice interaction was introduced by Kochelaev [26] [see Eq. (5) in Ref. [27]] in the context of explanation of the isotope effect on the ESR linewidth in lightly doped La_2CuO_4. In our case, however, we do not need to recall the conventional spin-phonon interaction (coupling parameter G in Refs. [26,27]) at all, which was a crucial ingredient in that approach. Furthermore, the importance of DDM interaction for explanation of the singlet-triplet infrared optical transition was pointed out in Ref. [28], but its microscopical derivation was not performed.

In the following, we will use this dynamical Hamiltonian to calculate the ESR linewidth by the method of moments [11,15,17]. This method is well established for the case of strong exchange interaction J and allows us to estimate the ESR linewidth via the relation $\Delta H = \frac{1}{g\mu_B}M_2/J$, where μ_B is the Bohr magneton and M_2 is the second moment of the line

$$M_2 = h^2\langle(\nu - \nu_0)^2\rangle = -\frac{\langle[\mathcal{H}_{\text{int}}, S^+][\mathcal{H}_{\text{int}}, S^-]\rangle}{\langle S^+S^-\rangle}. \quad (4)$$

In this way one can directly estimate the parameters of the interaction Hamiltonian $\mathcal{H}_{\rm int} \equiv \mathcal{H}_{\rm DM}, \mathcal{H}_{\rm SAE}$ from the angular dependence of the ESR linewidth. After that, the thermal averaging over the phonon variables has to be performed. Applying the Einstein model of vibration we get $\langle \sin^2(2\theta) R^2_{\text{Cu-F}} \rangle = \frac{2\hbar}{m\omega_{\rm F}} \coth(\hbar\omega_{\rm F}/2k_BT)$, where m denotes the mass of an oscillating fluorine ion and $\omega_{\rm F}$ is the frequency of the rotating mode. The quantity $\langle \sin(2\theta) R_{\text{Cu-F}} \rangle$ is naturally equal to zero and the static DM interaction does not exist. To compare with the results of x-ray analysis, it is useful to introduce the root-mean-square deviation of the F^- ion away from the c axis $\Delta R_\perp = \sqrt{\langle \sin^2(2\theta) R^2_{\text{Cu-F}} \rangle}$. Using the typical rotation frequency of CuF_6 octahedra $\omega_{\rm F} \sim 70\ \text{cm}^{-1}$ [23] one can estimate $\Delta R_\perp \approx 0.07$ Å at $T = 100$ K, which coincides with Ref. [2]. Therefore, we conclude that these displacements are dynamic rather than static at $T > T_N$. This conclusion is supported by the latest NQR study [5] which does not give any evidence for a static dislocation of F^- ions from the z axis at 77 K as well. To estimate $d_x^{(ab)}$ we will use the values given in Eq. (3). Recalling the second possible direction of motion of intermediate F^- ions, we derive finally

$$|d_x^{(ab)}| = |d_y^{(ab)}| \approx 5.6\ \text{K}. \tag{5}$$

Note that this estimate coincides very well with the value $d^{(ab)}_{\rm AFM} \approx 5.13$ K employed by Yamada and Kato [4] to describe the anisotropy of the AFM resonance line below T_N. Moreover, it yields the correct linewidth of about 10^3 Oe in the high-temperature limit.

The anisotropic interchain exchange can be neglected, because of the small constant of isotropic exchange $J_\perp \ll J$ and the orthogonality of orbital states. The anisotropic Zeeman effect does not contribute, because we do not observe any significant field dependence of the linewidth up to the frequency of 150 GHz (Fig. 2). Therefore, the spin relaxation mechanisms described above, the static SAE [Eq. (1)] and the DDM interaction [Eq. (5)] between the Cu ions along the c axis, are the only relevant sources of the ESR line broadening in $KCuF_3$. Figure 2(b) shows a fit of the angular dependence of ΔH at room temperature and emphasizes the contributions of SAE and DDM interaction to the linewidth, which reflects clearly the dominant role of the DDM interaction. This indicates that $KCuF_3$, despite its paradigmatic status for orbital order, is governed by strong fluctuations in the lattice and orbital sector.

In summary, we have introduced a dynamical Dzyaloshinsky-Moriya interaction which allowed us to explain the long-standing mystery about the origin of the huge ESR linewidth in $KCuF_3$ at $T > T_N$, consistent with other experimental findings about the properties of this quasi-1D system. Such a DDM interaction becomes effective if the characteristic time of the dynamic distortion resulting in a nonzero DM vector is large compared to the time scale of the exchange interaction and if the amplitude of these distortions is high. This is the case for low-lying optical modes with the tendency to soften to low temperatures. Therefore, such kinds of interaction may be in general useful for understanding the spin dynamics of other materials with soft-mode vibrations.

We thank I. Leonov for useful discussions. This work was supported by the DFG within SFB 484 (Augsburg) and by the RFBR (Grant No. 06-02-17401-a). One of us (D. V. Z.) was supported by VW-Stiftung.

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