Dynamical Dzyaloshinsky-Moriya interaction in KCuF₃: Raman evidence for an antiferrodistortive lattice instability

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In the orbitally ordered, quasi-one-dimensional Heisenberg antiferromagnet KCuF₃ the low-energy $E_g$ and $B_{1g}$ phonon modes show an anomalous softening (∼25% and ∼13%) between room temperature and the characteristic temperature $T_S = 50$ K. In this temperature range a freezing-in of F ion dynamic displacements is proposed to occur. In addition, the $E_g$ mode at about 260 cm⁻¹ clearly splits below $T_S$. The width of the phonon lines above $T_S$ follows an activated behavior with an activation energy of about 50 K. Our observations clearly evidence a reduction of the structural symmetry below $T_S$ and indicate a strong coupling of lattice and spin fluctuations for $T > T_S$.

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I. INTRODUCTION

The system KCuF₃ has long been known as a paradigm for an orbitally ordered system where a cooperative Jahn-Teller (JT) distortion is strongly competing with the electronic degrees of freedom as the driving force behind the orbital order. This system was investigated recently by realistic band structure calculations as a benchmark for modeling structural relaxation effects due to electronic correlations and for revealing the influence of electronic superexchange on the orbital ordering. The compound seems to be orbitally ordered throughout its solid phase, but shows long-range A-type antiferromagnetic (AFM) ordering only below $T_N = 39$ K. In literature an orbital ordering temperature of about 800 K is often evoked in this system, but astonishingly experimental evidence for a transition at this temperature seems to be evasive. Early on, however, it was reported that between 670 K and 720 K an irreversible transition takes place. Recently, the melting of the cooperative JT-transition has been studied in KCuF₃ and from the extrapolation to undoped KCuF₃ a JT transition temperature of 1350 K has been estimated. The paramagnetic (PM) susceptibility has been described by a Bonner-Fisher law with an exchange constant $J = 190$ K, indicating that the compound is a good realization of a one-dimensional (1D) spin chain in the PM regime. Inelastic neutron scattering studies did reveal a spinon-excitation continuum, a clearly 1D quantum phenomenon, existing also below the Néel temperature. From a structural point of view, the reported relatively high tetragonal symmetry ($D_{4h}^{18}$, $I4/mcm$) makes KCuF₃ one of the simplest systems to study. However, the established symmetry assignment has been questioned by an X-ray diffraction investigation which suggested the existence of orthorhombic distortions in KCuF₃ at room temperature with $D_{2h}^1$ symmetry. A low-temperature Raman scattering study revealed a difference of spectra measured in $xz$ and $yz$ polarization and anomalously broad linewidths of the stretching modes, which was interpreted as evidence of a symmetry lower than $D_{4h}^{18}$ also below the Néel temperature. Although orthorhombic distortions were involved for explaining the electron spin resonance (ESR) properties of KCuF₃ discrepancies remain for the analysis of recent NQR, AFM resonance, and further experimental and theoretical findings. Besides, in X-ray resonant scattering of the orbital ordering (OO) in KCuF₃ indications for a coupling of lattice and magnetic degrees of freedom above $T_N$ were found. Only recently, the ESR properties for $T > T_N$ could be successfully explained within the tetragonal symmetry by assuming a dynamical Dzyaloshinsky-Moriya (DM) interaction related to strong oscillations of the bridging F⁻ ions perpendicular to the crystallographic c axis. It was argued that these dynamic distortions freeze in at a temperature $T_S = 50$ K, leading to an effectively lower symmetry and the occurrence of exciton-magnon sidebands in optical absorption experiments.

Here we report on a detailed study of the temperature dependence of the Raman-active phonons in a KCuF₃ single crystal tracking the symmetry reduction during the anticipated freezing of the dynamic distortion at $T_S = 50$ K and the Néel ordering at $T_N = 39$ K. We find a large softening of the lowest lying $E_g$ mode and the $B_{1g}$ mode by 25% and 13% between room temperature and $T_S$, respectively. The linewidth and the integrated intensity of these modes also exhibit anomalies at $T_S$ and $T_N$. Moreover, the $E_g$ mode at about 260 cm⁻¹ clearly splits below $T_S$ evidencing the existence of an antiferrodistortive lattice instability in KCuF₃ which leads to a symmetry reduction at $T_S = 50$ K prior to magnetic ordering.
configurations are shown for \( T = 290 \) K. The number of lines and the selection rules are fully consistent with the theoretically expected Raman-active normal modes\(^{19}\) of KCuF\(_3\) with tetragonal \( D^{18}_{4h} \) symmetry.

\[
\Gamma_{\text{Ram}} = A_{1g}(yy, zz) + B_{1g}(yy) + 2B_{2g}(xy) + 3E_g(xz, yz)
\]

Hence, the three lines in both the \( xx \) and \( zz \) spectra correspond to the three \( E_g \) modes. The line observed with different intensities in \( yy \) and \( zz \) spectra is identified as the \( A_{1g} \) mode. The intense line observed only in the \( yy \) spectrum can be assigned to the \( B_{1g} \) mode. Finally, the two lines in the \( xy \) spectra are the two \( B_{2g} \) modes. At room temperature all lines have a Lorentzian lineshape. Figure \( \text{Fig. 1} \) shows schematically the vibrational patterns for the seven Raman-active modes of each symmetry (\( A_{1g}, B_{1g}, B_{2g}, \) and \( E_g \)) of KCuF\(_3\) derived from the \( D^{18}_{4h} \) space group. The observed spectra and mode assignments are in agreement with previously reported data at \( 10 \) K.\(^{20}\)

A direct comparison of our data at \( 4 \) K and \( 290 \) K with Ref.\(^{19}\) and theoretical estimates\(^{29}\) is presented in Tab. I. In general, there is a good agreement between the corresponding values except for the \( B_{2g}(1) \) mode with a frequency of 240.4 cm\(^{-1}\) observed in our experiments in contrast to a somewhat higher frequency of 265.8 cm\(^{-1}\) in Ref.\(^{19}\). The second discrepancy is that the lines assigned to \( E_g(1,2) \) and \( B_{1g} \) are almost two times broader in the low-temperature Raman spectra of Ref.\(^{19}\). The phonon lines of \( A_{1g} \) and \( B_{2g} \) symmetry have large linewidths in comparison with the other modes. In Fig. \( \text{Fig. 2} \) we show the temperature dependent parameters for the \( A_{1g} \) mode as an example. The \( A_{1g} \) and \( B_{2g} \) modes, aside from their broadened lineshape, show no anomalous behavior. In the full temperature range they exhibit a hardening of 1-2\%.

Moreover, we observe quasielastic scattering in \( zz \) configuration, which is a general feature in low-dimensional spin systems\(^{30}\) and should only be observed in intra-chain scattering configuration, i.e. with the light polarization parallel to the effective chain direction. This quasielastic scattering in KCuF\(_3\) has been investigated in detail by Yamada and Onda previously\(^{31}\) and will not be further considered in our work.

In the following we will focus on the temperature dependence of the modes \( E_g(1), E_g(2) \) and \( B_{1g} \). The \( E_g(1) \) mode reportedly exhibits a weak splitting at \( 10 \) K only when measured in \( yz \)-configuration. In contrast, the \( E_g(2) \) mode shows a splitting only when measuring in \( xx \)-configuration. The \( E_g(3) \) mode, which corresponds to a vibration of \( K^+ \) ions, shows no splitting in either of the two configurations.\(^{29}\) The \( E_g(1) \) and \( E_g(2) \) modes correspond to shearing vibrations of the \( F^- \) ions which involves a displacement of the fluorine ions away from the Cu-F-Cu bonding lines, while the \( B_{1g} \) mode corresponds to a tilting motion of the \( F^- \) ions around the central Cu atom (see Fig. \( \text{Fig. 2} \)). As such displacements are thought to be the origin of the dynamical DM interaction which allows to understand the ESR and antiferromagnetic resonance properties, we expect that these modes are strongly related to the proposed freezing of the dy-
TABLE I. Frequencies and linewidths of the observed Raman modes in cm$^{-1}$ in KCuF$_3$ at 4 K and 290 K compared to the experimental values reported in Ref.19 at 10 K and calculations from Ref.29.

| Mode          | Frequency (cm$^{-1}$) | Linewidth (cm$^{-1}$) |
|---------------|-----------------------|------------------------|
|               | 290K  | 4 K    | 10 K (Ref.19) | Calculated (Ref.29) | 290K  | 4K    | 10 K (Ref.19) |
| $A_{1g}$      | 367.3 | 373.5  | 374.8         | 398                 | 23.1  | 4.9    | 9.2          |
| $B_{1g}$      | 81.6  | 70.9   | 72.8          | 100                 | 7.1   | 0.9    | 1.6          |
| $B_{2g}(1)$   | 240.4 | 245.2  | 265.8         | 259                 | 30.8  | 8.7    | 7.0          |
| $B_{2g}(2)$   | 554.8 | 561.3  | 563.0         | 586                 | 22.6  | 9.1    | 9.1          |
| $E_g(1)$      | 63.0  | 47.4   | 53.2          | 50                  | 5.8   | 0.7    | 3.0          |
| $E_g(2)$      | 262.9 | 260.8  | 261.6         | 136                 | 7.5   | 1.7    | 3.0          |
| $E_g(3)$      | 132.3 | 129.3  | 131.2         | 268                 | 7.5   | 1.6    | 1.6          |

FIG. 2. Raman allowed phonon modes for the KCuF$_3$ with $D_{18}^h$ structure. The degeneracy of the $E_g$ modes is indicated using solid and dotted arrows.

Dynamic fluorine displacements below $T_S = 50$ K.27,28

Indeed, when looking at the Raman data of the $E_g(1)$ and $E_g(2)$ vibrational modes in $yz$ configuration shown in Fig. 4 an anomalous softening of both modes is observed for $T > 50$ K. While the frequency shift of the $E_g(2)$ is only about 2 cm$^{-1}$, the low-energy $E_g(1)$ mode exhibits a frequency shift of about 16 cm$^{-1}$. This corresponds to a softening of 1% and 25% with respect to the room temperature eigenfrequency.

Plotting the square of the eigenfrequency $\omega^2_{E_g(1)}$ of the $E_g(1)$ phonon mode as a function of temperature in Fig. 5(a) reveals a linear behavior for $T > 50$ K, which can be understood in terms of a soft-mode behavior indicative of a structural phase transition expected at $T_c$ where one expects \[ \omega^2_{E_g} = \alpha(T - T_c). \] (2)

The fit shown in Fig. 5(a) yields $\alpha = 6.8$ cm$^{-2}$/K and a virtual transition temperature of $T_c = -291$ K. Although the negative sign indicates that the occurrence of the structural phase transition is very unlikely, the energy scale of this virtual transition temperature is close to the orbital-ordering transition temperature $T_{OO} \sim 350$ K calculated by assuming a purely electronic superexchange mechanism.2

We believe that the softening of the $E_g(1)$ phonon mode is due to the dynamic nature in the displacement of the apical fluorine ions away from the $c$ axis, which manifests itself in an anomalously large thermal displacements parameter and the occurrence of a dynamical Dzyaloshinsky-Moriya (DM) interaction.27 As a prerequisite for the latter, the characteristic time of the dynamic distortions must be large compared to the time scale of

FIG. 3. Parameters of the $A_{1g}$ mode: Temperature dependence of (a) the squared eigenfrequency $\omega$, (b) the FWHM linewidth, and (c) the Bose corrected integrated intensity. Lines are to guide the eye.
the exchange interaction and the amplitude of these distortions must be high. This is the case for low-lying optical modes contributing to the oscillation of the F− ions with the tendency to soften to low temperatures, exactly like the $E_g(1)$ mode. In this scenario the displacement of the fluorine ions freezes with decreasing temperature and becomes static at $T_S = 50$ K. Below 50 K we observe a deviation from this softening behavior and the frequency levels off in the magnetically ordered state.

The temperature dependence of the phonon line widths full width at half maximum (FWHM) for $E_g(1)$ is shown in Fig. 5(b). Above 50 K the linewidth data can be described (solid line) using:

$$\Gamma_{tot}(T) = \Gamma_{anh}(T) + \Gamma_r(T) = AT + B \exp \left( \frac{U_r}{k_B T} \right)$$

where $\Gamma_{anh}$ is the contribution arising from phonon anharmonic interactions in crystalline solids, with zone center modes decaying into pairs of phonons with equal and opposite wave vectors. $\Gamma_r$ is the contribution to the total linewidth arising from the dynamic deviation of the F− ions away from the c axis, $U_r$ is a potential barrier, and $A$ and $B$ are constants. The data can be described very well over the temperature range 50 – 290 K by Eq. 3 yielding a energy $U_r = 56$ K very close to the temperature $T_S = 50$ K where the dynamic displacements are proposed to become static. Below $T_S = 50$ K the width of the phonon line decrease nearly linearly with temperature.

The (Bose corrected) integrated intensity of the $E_g(1)$ mode shown in Fig. 5(c) increases with decreasing temperature and reaches a maximum at $T_S$ (see inset of Fig. 5(c)) and a minimum just below $T_N$ reflecting distinct changes of the polarizability of this mode at these temperatures.

The corresponding parameters for the $E_g(2)$ and the $B_{1g}$ mode are plotted in Fig. 5 and Fig. 4 respectively. Similar to the $E_g(1)$ mode these modes exhibit a soft mode behavior with $\alpha = 3.99$ cm$^{-2}$/K and $T_c = -17016$ K for the $E_g(2)$ and $\alpha = 6.57$ cm$^{-2}$/K and $T_c = -722$ K for the $B_{1g}(1)$ mode. While for the $B_{1g}(1)$ with a softening of about 13% with respect to room temperature the virtual transition temperature is still reasonable, the value for the $E_g(2)$ mode appears not to be of physically meaningful due to the moderate softening of only 1-2%. Note that in other fluorides with rutile structure like MnF$_2$, NiF$_2$, and FeF$_2$ virtual transition temperatures of -1240 K, -1700 K, and -1780 K have been derived from the softening of Raman modes, respectively. The linewidth of both modes can again be described using Eq. 3 and $U_r = 49$ K. The intensities of both modes start to decrease below 50 K, but for the $E_g(2)$ mode the intensity levels off and becomes almost constant below $T_N$.

Although clear anomalies of these modes associated with $T_S$ and $T_N$ have been observed, we could not observe the splitting of the $E_g(1)$ mode in $yz$-configuration reported in Ref. [3] at 10 K. Hence, we tried to reproduce the reported splitting of the $E_g(2)$ mode in $xz$-configuration and trace its temperature dependence. The
obtained spectrum at 3.5 K is shown in Fig. 8 and a weak additional mode at the high-frequency side of the $E_g(2)$ is clearly visible compared to the data at $T=50$ K in the same figure. The solid line corresponds to a fit with two Lorentzian lineshapes (thin and dashed, latter shifted). As shown in Fig. 8, the appearance of this additional mode coincides with $T_S$ suggesting a splitting of the $E_g(2)$ mode in agreement with the scenario of a symmetry reduction at $T_S$ suggested previously. Nevertheless, we have to point out that this splitting of about 6 cm$^{-1}$ is larger than the reported one of about 1 cm$^{-1}$ and appears on the high-energy flank in contrast to the one reported by Ueda and coworkers which appears on the low-energy side of the original $E_g(2)$ mode. These discrepancies can not be easily explained and may be due to the different samples used for our work. We would like to point out that in a recent Raman study a splitting of the $E_g(2)$ similar to our data has been reported.

A static displacement of fluorine ions away from the $c$ axis at temperatures $T < T_S$ assumes the lowering of the KCuF$_3$ crystal symmetry. If the symmetry is lower than $D_{3d}^{14}$, a removal of the $E_g$ modes’ degeneracy and the appearance of extra lines in the Raman spectra is expected. The observed splitting of the $E_g(2)$ mode in $xz$ configuration confirms this scenario, alone, this information is not sufficient to determine the low-temperature symmetry. Additional evidence has been obtained by X-ray scattering where a splitting of a Bragg reflection associated with GdFeO$_3$ type distortions has been found below 50 K. Lee and coworkers also suggested that the observed softening of $E_g$ and the $B_{1g}$ modes is related to the finite spin correlation lengths which are inherent to low-dimensional magnets. Such effects of spin-phonon coupling are well established and occur, e.g., in frustrated magnetic systems without orbital degrees of freedom.

In this respect it is worth highlighting that in KCuF$_3$ the spin-spin relaxation time as measured by the ESR linewidth can only be explained by assuming dynamic lattice distortion of the type associated with the anomalous Raman modes. It was also reported in Ref. [27] that
the temperature dependence of the ESR linewidth $\Delta H$ can be described by $\Delta H \propto \exp(-\Delta/T)$ with an activation energy $\Delta = 114$ K which corresponds approximately to $2U_r \approx 2T_S$, two times the potential barrier derived from the temperature dependence of the linewidths of the anomalous Raman modes. This intricate feedback between spin, lattice, and possibly the orbital degrees of freedom has to be disentangled and the following questions arise and still need to be clarified: (i) Is the softening of the Raman modes directly related to the spin-spin correlations of the quasi-one dimensional spin chain KCuF$_3$? (ii) Is there a relation between the ESR spin-spin relaxation time dominated by the dynamical Dzyaloshinsky-Moriya interaction and the linewidth of the anomalous Raman modes? (iii) How and on which time scale do the orbital degrees of freedom couple to the lattice and spin fluctuations in the system? We hope that our study will stimulate further theoretical efforts in this direction.

FIG. 9. Temperature dependence of the eigenfrequency of the $E_g(2)$ and the split modes below $T_S$ in $xz$ scattering geometry. Lines are drawn to guide the eye.

IV. SUMMARY

To sum up, temperature-dependent Raman spectra of single crystalline KCuF$_3$ show a strong softening of the lowest-lying $E_g(1)$ and the $B_{1g}$ mode for $T > T_S$. Both of these modes and the $E_g(2)$ mode (at about 260 cm$^{-1}$) exhibit anomalies at the characteristic temperature $T_S$=50 K. In $xz$ scattering configuration the $E_g(2)$ doublet clearly splits with a splitting of about 6 cm$^{-1}$. The temperature dependence of the linewidth of these modes yields an activated behavior with an energy $U_r \approx 50$ K corresponding to $T_S$. We ascribe this anomalous behavior and the observed splitting to an antiferrodistortive lattice instability due to strong dynamic displacements of the F$^-$ ions away from the Cu-F-Cu bonding line along the $c$ axis. These displacements are strongly influencing the spin-spin relaxation by allowing for a dynamical Dzyaloshinsky-Moriya interaction. They become static for $T < T_S$.

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