Optical evidence for symmetry changes above the Néel temperature in KCuF₃

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We report on optical measurements of the 1D Heisenberg antiferromagnet KCuF₃. The crystal-field excitations of the Cu²⁺ ions have been observed and their temperature dependence can be understood in terms of magnetic and exchange-induced dipole mechanisms and vibronic interactions. Above Tₖ we observe a new temperature scale Tₜ characterized by the emergence of narrow absorption features that correlate with changes of the orbital ordering as observed by Paolasini et al. [Phys. Rev. Lett. 88, 106403 (2002)]. The appearance of these optical transitions provides evidence for a symmetry change above the Neel temperature that affects the orbital ordering and paves the way for the antiferromagnetic ordering.

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The charge-transfer insulator KCuF₃ is a prototype material for a cooperative Jahn-Teller (JT) effect, orbital ordering (OO), and low-dimensional magnetism. KCuF₃ stands in line with LaMnO₃, the parent compound of the colossal magnetoresistance manganites, as role models for orbitally ordered compounds, where collective orbital modes may occur in the excitation spectrum. Moreover, KCuF₃ is one of the rare examples of an ideal one-dimensional (1D) antiferromagnetic (AFM) Heisenberg chain. This is related to the particular OO in KCuF₃, in which a single hole alternately occupies 3dₓ²−₂ᵧ² and 3dᵧ²−₂ₓ² orbital states of the Cu²⁺ ions with a 3d⁶ electronic configuration. The cooperative JT distortion is characterized by CuF₆ octahedra elongated along the a and b axis and arranged in an antiferrodistortive pattern in the ab-plane. A crossover from a 1D to a three-dimensional behavior occurs at the Néel temperature Tₙ =39 K resulting in a long-range (A-type) AFM ordering, but the fingerprint of a 1D spin chain, the spinon excitation continuum, is still observable below Tₖ and persists up to about 200 K. Together with a strong suppression of the ordered moment found below Tₙ, this establishes the impact of quantum fluctuations on the magnetism of KCuF₃.

To date even the room temperature (RT) crystal structure of KCuF₃ seems not to be determined unambiguously. The original assignment of tetragonal symmetry was challenged by the claim of an orthorhombic structure. Although such a distortion seems to allow for a better understanding of Raman and electron paramagnetic resonance (EPR) properties, discrepancies remain when trying to reconcile the observation of AFM resonances within the proposed symmetries. Paolasini and coworkers reported an X-ray resonant scattering (XRS) study of the OO-superlattice reflection in KCuF₃ and found a considerable increase of its intensity above Tₙ, indicating changes of the lattice degrees of freedom prior to magnetic ordering.

Here we report optical spectra of the crystal-field (CF) excitations in KCuF₃ in the near infrared range. The observed energy splittings are compared to theoretical estimates using crystal-field theory (CFT) and to a direct calculation in the framework of the LDA+U approximation. Furthermore, we discovered the appearance of a very sharp fine structure related to the d-d absorption bands below Tₜ=50 K, which is interpreted as a new temperature scale above Tₙ, where a dynamic distortion of the environment of the Cu²⁺ ions becomes static.

The single crystals (see Ref. for details on crystal growth) were oriented by Laue diffraction and cut along the (110)-plane. Polarization-dependent transmission measurements were performed using a BRUKER IFS 66v/S Fourier-transform spectrometer with a ⁴He cryostat (Oxford) in the frequency range between 5000-16000 cm⁻¹ and for temperatures from 4-300 K. The absorption coefficient α was obtained using the standard relation for a semitransparent layer and was obtained by estimating the refractive index n from ε₁ ≈ 2.2 given by ellipsometry data at RT. This value is in good agreement with ε₁ ≈ 2.3 obtained theoretically.

In Fig. (a) we show the absorption coefficient α for light polarized parallel (E || c) and perpendicular (E ⊥ c) to the antiferromagnetically coupled c-axis at 8 K. For both orientations one can identify four broad excitation bands which are indicated by arrows and called A₁-A₄ in the following. The onset and maximum energies of these bands are given in Table. One can recognize rather symmetric lineshapes for A₁ and A₄, while A₂ exhibits a
the intensities of $A$ which will be discussed in detail below.

Moreover, a sharp spike-like feature can be seen at the shoulder in the spectrum, its lineshape is not evident. At the low-energy side. Since $A$ very asymmetric lineshape with a steep absorption edge are guides to the eye. Inset: Full temperature dependence of

Fitting the two spectra in Fig. 1(a) one finds that anomalies of the oscillator strength $f$ above $T_N$. Lines and the maxima of bands $A$ in $D_{2h}$ symmetry. For $A_1$ the onset energy $E_{ons}$ and the maximum at $E_{max}$ are indicated. Inset: Evolution of absorption spectra with temperature for $E \perp c$. (b) Anomalies of the oscillator strength $f$ above $T_N$. Lines are guides to the eye. Inset: Full temperature dependence of $f$, solid lines are fits described in the text.

FIG. 1: (a) Absorption spectra for $E \parallel c$ and $E \perp c$ at 8 K. Arrows indicate the four absorption bands $A_1$–$A_4$ related to the CF splitting for Cu$^{2+}$ in $D_{2h}$ symmetry. For $A_1$ the onset energy $E_{ons}$ and the maximum at $E_{max}$ are indicated. Inset: Evolution of absorption spectra with temperature for $E \perp c$. (b) Anomalies of the oscillator strength $f$ above $T_N$. Lines are guides to the eye. Inset: Full temperature dependence of $f$, solid lines are fits described in the text.

very asymmetric lineshape with a steep absorption edge at the low-energy side. Since $A_3$ is visible mainly as a shoulder in the spectrum, its lineshape is not evident. Moreover, a sharp spike-like feature can be seen at the onset of the $A_2$ band (see Fig. 2(a) for an enlarged scale), which will be discussed in detail below.

Comparing the two spectra in Fig. 1(a) one finds that the intensities of $A_2$ and $A_4$ are enhanced for $E \parallel c$, while $A_3$ seems to be much more intense for $E \perp c$. The temperature behavior of the absorption bands is illustrated in the inset of Fig. 1(a) for $E \perp c$. The bands broaden and gain intensity with increasing temperature. The nature of these absorption bands can be understood in terms of local $d$-$d$ CF excitations of the Cu$^{2+}$ ions in a distorted octahedral environment [17]. Usually, electric dipole (ED) transitions between $d$-levels are parity-forbidden, but they can become allowed as a consequence of a perturbation of the CF potential by phonons. A fingerprint of such *vibronically* allowed transitions is the temperature dependence of their oscillator strength $f$ given by

$$\int_{\omega_1}^{\omega_2} \sigma_1(\omega) d\omega = \frac{\pi \epsilon^2 N}{2 m} f,$$

where $N$ is the number of absorption centers per unit volume [18]. Assuming that only a single vibrational mode with frequency $\omega_{vib}$ contributes to the intensity of the absorption one expects $f = f_{vib} \coth(\omega_{vib}/2kBT)$ [18, 19]. By adding a temperature independent term $f_{mag}$ one usually accounts for the contribution of magnetic dipole (MD) transitions. The order of magnitude of $10^{-3}$-$10^{-4}$ is in agreement with theoretical expectations [18].

We show as an inset in Fig. 1(b) the temperature dependence of $f$ obtained by integration between $\omega_1=5000$ cm$^{-1}$ and $\omega_2=16000$ cm$^{-1}$ for both orientations. Fitted over the whole temperature range from 8-295 K $f$ appears to be well described (solid lines) by this approach with $\omega_{vib}=148$ cm$^{-1}$, 144 cm$^{-1}$, $f_{vib}=2.1 \times 10^{-4}$, 1.9 $\times 10^{-4}$, and $f_{mag}=2.5 \times 10^{-4}$, 2.7 $\times 10^{-4}$ for $E \parallel c$ and $E \perp c$, respectively. When zooming in to the low-temperature regime in the vicinity of $T_N$ as shown in Fig. 1(b), one can clearly see deviations from this behavior starting below at a temperature $T_S \approx 50$ K. An additional contribution to $f$ leads to a maximum at around 43 K and a subsequent decrease upon AFM ordering at 39 K towards a constant low-temperature value. Note that the increase below 50 K is directly related with the appearance of the sharp-absorption features at the broad bands $A_2$ and $A_3$ (see Fig. 2(a)).

TABLE I: Comparison of $E_{ons}$ and $E_{max}$ for the energies of the onsets and the maxima of bands $A_1$–$A_4$ with theoretical estimates $E_{CFT}$, $E_{LDA}$ and $E_{LDA+U}$ obtained as described in the text. The energies are given in eV.

|        | $E_{ons}$ | $E_{CFT}$ | $E_{max}$ | $E_{LDA}$ | $E_{LDA+U}$ |
|--------|-----------|-----------|-----------|-----------|--------------|
| $yz$   | 1.34      | 1.34      | 1.46      | 1.62      | 1.50         |
| $xz$   | 1.21      | 1.26      | 1.37      | 1.37      | 1.41         |
| $xy$   | 1.05      | 1.06      | 1.15      | 1.28      | 1.31         |
| $3z^2-r^2$ | 0.71     | 0.69      | 1.02      | 0.94      | 1.03         |
| $x^2-y^2$ | 0         | 0         | 0         | 0         | 0            |
Having described the origin of the broad band spectra on a quantitative level, we now concentrate on the observation of two sets of sharp absorption features highlighted in Fig. 2(a), one indicating the onset of $A_2$ at 8508 cm$^{-1}$ followed by a whole sideband of excitations, and a second set starting at 9775 cm$^{-1}$ at the anticipated onset of $A_3$. Both sets are visible for $E \parallel c$ and $E \perp c$. As an inset of Fig. 2(a) we show the polarization dependence of the intensity of the peak at 8508 cm$^{-1}$ following a $\sin^2 \phi$ dependence, with $\phi$ being the angle between the polarization and the crystal axes. While the latter peak is more intense for $E \parallel c$, the peak at 9775 cm$^{-1}$ is more intense for $E \perp c$. Note that $H_z$ in the local coordinate system corresponds to $B \perp c$ or $E \parallel c$ and $H_y$ corresponds to $B \parallel c$ or $E \parallel c$, with $B = \mu(T)H$, where $\mu(T)$ is the permeability which is usually assumed to be one in optical experiments, but can increase significantly upon magnetic ordering. The observed intensity maxima comply with the selection rules for MD transitions.

Concerning the side bands of both MD transitions, we want to emphasize that the strongest features appear at a distance of 88(86), 114(112), 174(175), and 200(203) cm$^{-1}$ from the MD$_1$(MD$_2$) transitions [see Fig. 2(a)]. To understand the origin of the whole entity of MD transitions and their sidebands, we have to consider their temperature dependence, which is displayed in Fig. 2(b) for $E \parallel c$. The fine structure emerges only below a temperature $T_S=50$ K, the temperature where the overall oscillator strength starts to deviate from a purely vibrational behavior with a constant contribution from MD transitions (Fig. 2(a)). The integrated intensity of the MD transition at 8508 cm$^{-1}$ as a function of temperature is shown as an inset in Fig. 2(b) for both polarizations without any anomaly visible at $T_N=39$ K.

It was shown that magnons can become optically active via an exchange-induced dipole mechanism [28, 29], with the optical excitation energy corresponding to the magnon energy at the Brillouin zone boundary. In KCuF$_3$, neutron scattering investigations reported zone boundary energies of magnon excitations at 88.7, 117, and 221 cm$^{-1}$ [6, 30]. The first two magnon energies correspond very nicely with the first and second sideband peaks, the third sideband peak is in agreement with a two-magnon process involving the 88.7 cm$^{-1}$ magnon, the fourth would correspond to two-magnon process where both the 88.7 and the 117 cm$^{-1}$ magnon participate. For the 221 cm$^{-1}$-magnon we can not resolve any sideband in absorption. In this scenario the temperature dependence of the MD transitions and the magnon sidebands below $T_S$ is attributed to the increase of $\mu(T)$ in the vicinity of AFM ordering and can gain additional intensity due to the local spin-spin expectation value $\langle S_i(S_{i-1} + S_{i+1}) \rangle$ which contributes to the exchange-induced dipole moment $\sum_j \Pi_{ij}(S_iS_j)$ for the Cu ion at site $i$. For $E \parallel c$ the spin-spin correlations in the $ab$-plane are important, for $E \perp c$ the contributing

In the second approach, the electronic structure of KCuF$_3$ was calculated self-consistently using LDA$(+U)$. According to previous LDA calculations [23, 24] the Coulomb and exchange interaction parameters $U$ and $J$ were taken to be 8.0 and 0.9 eV, respectively. Following Streltsov et al. [14], we additionally estimate $E_{\mathrm{LDA}+U}$ as the difference between the ground state energy and an energy of an excited state in which the hole is artificially put on one of the higher levels by applying constrained LDA$+U$ calculations. This constrained method takes into account the relaxation of the electronic system, whereas the lattice remains frozen obeying the Franck-Condon principle. Hence, the resulting CF splittings have to be compared with $E_{\mathrm{max}}$ of the absorption bands in Tab. 1. Both calculations describe the experimental findings, but including electronic relaxation gives an overall better agreement between theory and experiment.

![FIG. 2: (a) Fine structures related to $A_2$ and $A_3$ for $E \parallel c$ and $E \perp c$ at 8 K. Frequency shifts with respect to MD$_1$ and MD$_2$ are indicated in cm$^{-1}$. Inset: Polarization dependence of the intensity of MD$_1$ and a fit $\propto \sin^2 \phi$. (b) Emerging of the fine structure peaks below $T_S = 50$ K for $E \parallel c$. Inset: Temperature dependence of the intensity of MD$_1$ for both orientations. Lines are guides to the eyes.

| $T$ (K) | $I$ (arb. units) |
|--------|-----------------|
| 0      | 0.0             |
| 30     | 0.3             |
| 50     | 1.0             |
| 70     | 1.5             |
| 90     | 2.0             |
| 110    | 2.5             |
| 130    | 3.0             |
| 150    | 3.5             |

| $T$ (K) | $I$ (arb. units) |
|--------|-----------------|
| 0      | 0.0             |
| 30     | 0.0             |
| 50     | 0.0             |
| 70     | 0.0             |
| 90     | 0.0             |
| 110    | 0.0             |
| 130    | 0.0             |
| 150    | 0.0             |

| $E$ (cm$^{-1}$) | $I$ (arb. units) |
|----------------|-----------------|
| 8508           | 0.0             |
| 8800           | 0.3             |
| 9200           | 1.0             |
| 9600           | 1.5             |
| 10000          | 2.0             |

| $E$ (cm$^{-1}$) | $I$ (arb. units) |
|----------------|-----------------|
| 8508           | 0.0             |
| 8800           | 0.0             |
| 9200           | 0.0             |
| 9600           | 0.0             |
| 10000          | 0.0             |

| $E$ (cm$^{-1}$) | $I$ (arb. units) |
|----------------|-----------------|
| 8508           | 0.9             |
| 8800           | 1.5             |
| 9200           | 0.0             |
| 9600           | 0.0             |
| 10000          | 0.0             |

| $E$ (cm$^{-1}$) | $I$ (arb. units) |
|----------------|-----------------|
| 8508           | 0.0             |
| 8800           | 0.0             |
| 9200           | 0.0             |
| 9600           | 0.0             |
| 10000          | 0.0             |
correlations are the ones along the c-axis.[29]

Here we would like to point out that an anomalous behavior in birefringence[26] and neutron scattering studies[27] has been reported at around $T_m=43$ K, exactly the temperature where $f$ exhibits a maximum (Fig. 1b)). At the same temperature a significant change of the OO superlattice reflection at the Cu $K$-edge has been reported by a XRS study[12,13]. Since XRS at the $K$-edge probes the JT distortion induced by the OO,[25] the anomaly certainly involves a change in the lattice degrees of freedom. On account of LDA+U calculations it has previously been suggested that the anomalous XRS data might indicate a structural transition[24].

In literature we find two hints concerning a symmetry lowering in KCuF$_3$, a X-ray diffraction study at RT claiming the presence of an orthorhombic distortion due to a shift of the apical F$^-$ ions connecting the CuF$_6$ octahedra along the c-axis, and a Raman study of the phonon modes at 10 K, observing the splitting of two $E_g$ Raman modes.[8]. To get a more consistent picture of what happens at $T_S=50$ K, the temperature dependence of the split Raman modes was investigated and the modes were found to soften strongly with decreasing temperature and split only below $T_S=50$ K[31]. The occurrence of this splitting $T_S=50$ K is a clear sign for a reduced (static) lattice symmetry. Moreover, a recent approach allows to describe the EPR properties by assuming that the displacement of the apical F$^-$ ions away from the c-axis is dynamic in nature, but becomes static at $T \approx T_N$.[32]. The phonon modes contributing to the oscillation of the F$^-$ ions should soften with decreasing temperature as the displacement of the F ions freezes in and becomes static at $T_S=50$ K, in agreement with the Raman data. This static distortion manifests itself in an increase of intensity of the MD transitions in optics, a softening of Raman-active phonon modes which favors the alignment of the spins and allows for freezing-in of the distortion leads to an additional magnetic anisotropy via a Dzyaloshinsky-Moriya interaction, and by the Swiss NSF through NCCR MaNEP.

$N_e, N_S$ and softening of Raman-active phonon modes[34], too, one may speculate that the phenomena described in the present paper could be present in many AFM transition metal compounds.

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