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Lattice vibrations in KCuF_3

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This article is dedicated to Dieter Vollhardt on the occasion of his 60th birthday.

We report on polarization dependent reflectivity measurements in KCuF_3 in the far-infrared frequency regime. The observed IR active phonons at room temperature are in agreement with the expected modes for tetragonal symmetry. We observe a splitting of one mode already at 150 K and the appearance of a new mode in the vicinity of the Néel temperature.

1 Introduction

Since the first reports about half a century ago the compound KCuF_3 has become a paradigm for studying the effects of a cooperative Jahn-Teller (JT) distortion [1], orbital ordering (OO) [2], and low-dimensional magnetism [3]. In the paramagnetic state it can be described in terms of a one-dimensional (1D) anti-ferromagnetic (AFM) Heisenberg chain [4], which results from the OO in KCuF_3 , where a single hole alternately occupies $3d_{x^2-z^2}$ and $3d_{y^2-z^2}$ orbital states of the Cu^{2+} ions with a $3d^9$ electronic configuration (see inset of Fig. 1(a)). In agreement with the Goodenough-Kanamori-Anderson rules, the OO leads to a strong AFM superexchange interaction of about 190 K along the crystallographic c -axis and a two orders of magnitude weaker ferromagnetic coupling in the ab -plane [5]. The cooperative JT distortion is characterized by CuF_6 octahedra elongated along the a and b axis and arranged in an antiferrodistortive pattern in the ab -plane. Long-range (A -type) AFM ordering occurs below the Néel temperature $T_N = 39$ K [5], but the reduced ordered moment in the AFM ground state indicates that strong quantum fluctuations are still present in KCuF_3 . Over decades KCuF_3 has received special attention from neutron studies and witnessed most of the experimental achievements in this field [5–13]. Consequently, many of the fingerprints of the magnetic excitation spectrum of quasi-one dimensional systems like spinons and longitudinal modes have been discovered in this system [6, 10, 12].

As attractive as this system appeared to experimentalists, theorists did not want to stay behind and tested their tools to understand the driving forces behind the OO, the JT distortion, and the coupling of orbital and spin degrees of freedom [14–24]. In particular, it could be shown by a combination of *ab initio* band structure calculations and dynamical mean-field theory that the JT distortion in the paramagnetic phase of KCuF_3 originates from electronic correlation effects [23, 24].

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Despite these intense research efforts, many properties of KCuF_3 are still subject to debate or have even not been measured. For example, the room temperature (RT) crystal structure of KCuF_3 is still not solved unambiguously. The established tetragonal symmetry [1,25] was reported to be actually orthorhombic [26]. Although this claim allowed for a better understanding of Raman [27] and electron spin resonance (ESR) properties [28], the observed AFM resonance could not be explained within the proposed symmetries [29]. Only recently, a consistent explanation of the ESR and AFM resonances was proposed by taking into account a dynamical Dzyaloshinsky-Moriya (DM) interaction [30]. This dynamical DM interaction is a result of strong thermal lattice fluctuations which manifest themselves in an anomalous softening of Raman-active phonons, which undergo a splitting prior to AFM ordering in KCuF_3 and, thus, indicate a symmetry lowering of the system [31].

In this work we investigate the infrared (IR) active phonons in KCuF_3 . The temperature dependence of the IR spectra indicates a possible splitting of one mode already at about 150 K far above the Néel temperature and the appearance of a new mode just above T_N .

2 Experimental details and characterization

The single crystals (see [32] for details on crystal growth) were oriented by Laue diffraction and cut along the (110)-plane. The heat capacity was measured in a Quantum Design physical properties measurement system for a temperature range $1.8 \text{ K} < T < 300 \text{ K}$. Transmission and polarization-dependent reflectivity measurements were carried out for $10 \text{ K} < T < 300 \text{ K}$ using the Bruker Fourier-transform IR spectrometers IFS 113v and IFS 66v/S with a He-flow cryostat (Cryovac). The dielectric loss ϵ_2 was obtained from the reflectivity data by the Kramers-Kronig relation. Susceptibility measurements on single crystals obtained by Bridgman method (see inset of Fig. 1(b)) were performed using a SQUID magnetometer (Quantum Design).

In Fig. 1(a) we show the temperature dependence of the magnetic susceptibility together with a fit obtained by using a rational function which approximates the Bonner-Fisher approach for an antiferromagnetic chain [33, 34]. The obtained values for the effective g -factor of 2.26 and an intrachain coupling of 393 K are in good agreement with literature [4]. The antiferromagnetic ordering at about 40 K is clearly seen as a kink-like minimum. The increase below 40 K has been attributed to intergrowth of K_2CuF_4

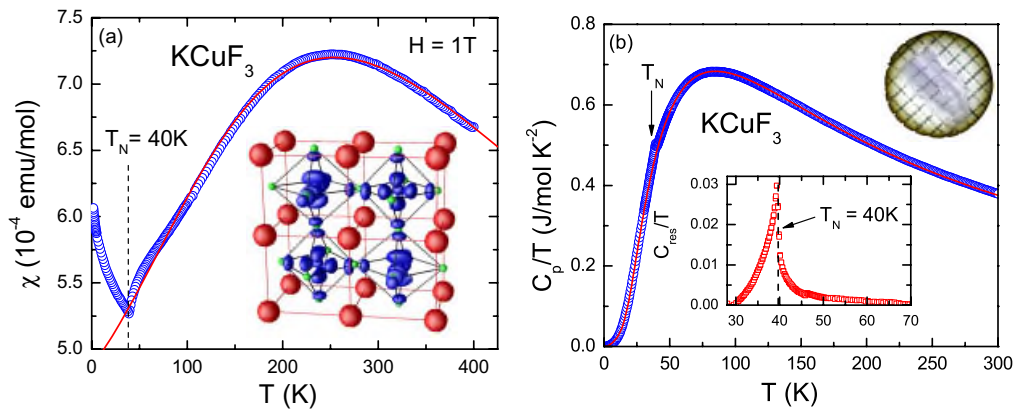


Fig. 1 (online colour at: www.ann-phys.org) (a) Temperature dependence of the dc -susceptibility measured in a magnetic field of 1 T. The solid line is a fit as described in the text. Inset: Orbital ordering pattern of KCuF_3 [24]. (b) Temperature dependence of C_p/T . The solid line indicates the lattice contribution to the specific heat as described in the text. Lower inset: Residual specific heat after subtracting the lattice contribution. Upper inset: KCuF_3 single crystal grown by Bridgman method.

traces [35]. The specific heat divided by temperature C/T (Fig. 1(b)) also clearly exhibits an anomaly at about 40 K marking the onset of antiferromagnetic ordering [36]. In order to model the lattice contribution to the specific heat we use a sum of one isotropic Debye (D) and four isotropic Einstein terms ($E_{1,2,3,4}$). The ratio between these terms was fixed to $D : E_1 : E_2 : E_3 : E_4 = 1 : 1 : 1 : 1 : 1$ to account for the 15 degrees of freedom per formula unit [27]. The resulting contribution to the specific heat shown as a solid line in Fig. 1(b) has been obtained with the Debye and Einstein temperatures $\theta_D = 205.0$ K, $\theta_{E1} = 146.1$ K, $\theta_{E2} = 292.3$ K, $\theta_{E3} = 325.8$ K, and $\theta_{E4} = 590.0$ K in agreement with the frequency ranges where optical phonons were identified (see Table 1 and [27]).

3 Optical excitations and infrared active phonons

In Fig. 2(a) we show a transmission spectrum of KCuF_3 at 294 K to give an overview of the optical excitations and the corresponding energy scales in this compound. At low energies transmission is strongly suppressed indicating the frequency range of the infrared-active phonon excitations with an upper limit of about 80 meV. This frequency range and the IR phonon spectrum will be discussed below in more detail. The next strong absorption region centered at around 1.2 eV has been identified as due to phonon-assisted d - d crystal-field excitations of the Cu^{2+} ions in a distorted octahedral environment (see inset of Fig. 2(b)). Just above T_N sharp sidebands appear at the onset of A_2 and A_3 which are attributed to exciton-magnon sidebands [37]. The comparatively weak absorption band centered at 2.4 eV (about twice the energy of the CF excitations) has not been explored in detail up to now but is attributed to exciton-exciton transitions involving two exchange-coupled neighboring ions which are excited simultaneously to higher-lying orbital states. The strongest absorption sets in at about 4.5 eV which is assigned to the onset of charge-transfer excitations.

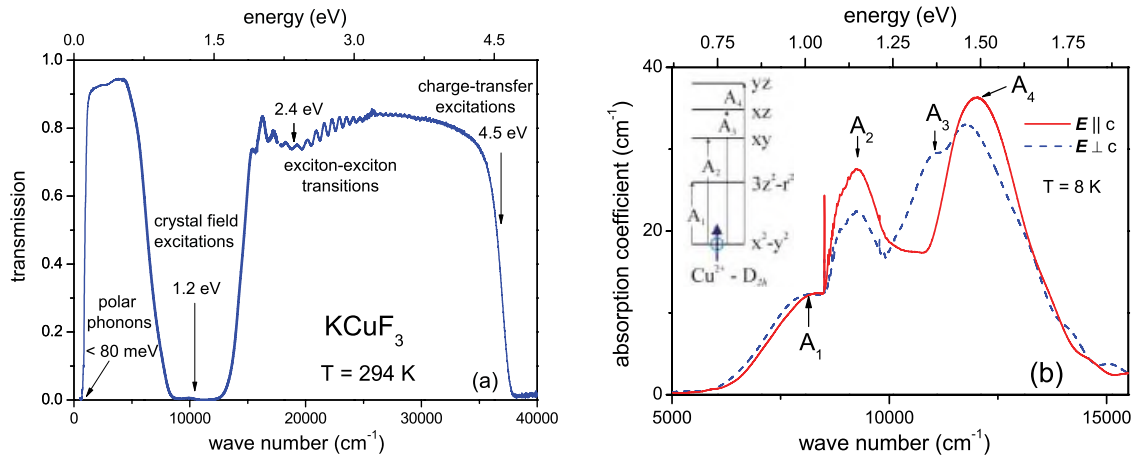


Fig. 2 (online colour at: www.ann-phys.org) (a) Transmission spectrum of KCuF_3 at 294 K. (b) Absorption spectra showing the crystal-field transition region for polarizations $E \parallel c$ and $E \perp c$ at 8 K [37]. Inset: Splitting of the Cu d -levels for a $d_{x^2-y^2}$ ground state with the longest Cu-F bond defining the local z direction.

In this study we want to discuss the optical excitations in the far-infrared regime. In Fig. 3(a) and (b) we show reflectivity spectra at 295 K and 12 K for polarizations $E \parallel c$ and $E \perp c$, respectively. At 295 K the spectra exhibit three excitations for $E \parallel c$ and five excitations for $E \perp c$ which are labeled $A_{2u}(i)$ modes with $i = 1, 2, 3$ and $E_u(j)$ modes with $j = 1, 2, 3, 4, 5$, respectively. This assignment corresponds to the expected normal modes obtained from the analysis of the irreducible representations for the Raman and IR active phonons within the tetragonal structure of KCuF_3 at room temperature with space group $D_{4h}^{18}-I4/mcm$ and two formula units in the primitive cell [1, 25, 38]:

$$\begin{aligned} \Gamma = 3A_{2u}(E \parallel z) + 5E_u(E \perp z) & \quad (\text{IR active}) \\ + A_{1g}(xx, yy, zz) + B_{1g}(xx, yy) + 2B_{2g}(xy) + 3E_g(xz, yz) & \quad (\text{Raman active}) \end{aligned}$$

Before we discuss the changes of the phonon spectra with temperature we want to point out that the feature at about 180 cm⁻¹ marked by an asterisk is present for all polarizations and temperatures and corresponds to an experimental artifact. The weak band visible for $E \parallel c$ at 295 K at the low-energy side of $A_{2u}(2)$ is attributed to a polarization leakage and corresponds to mode $E_u(3)$. As a result any change of $E_u(3)$ with temperature will also appear for $E \parallel c$ and has to be distinguished from changes of the A_{2u} modes. The corresponding transverse eigenfrequencies of the modes have been determined directly by the maxima in the corresponding dielectric-loss spectra obtained by Kramers-Kronig transformation (see Fig. 3(c) and (d)) and are listed in Table 1.

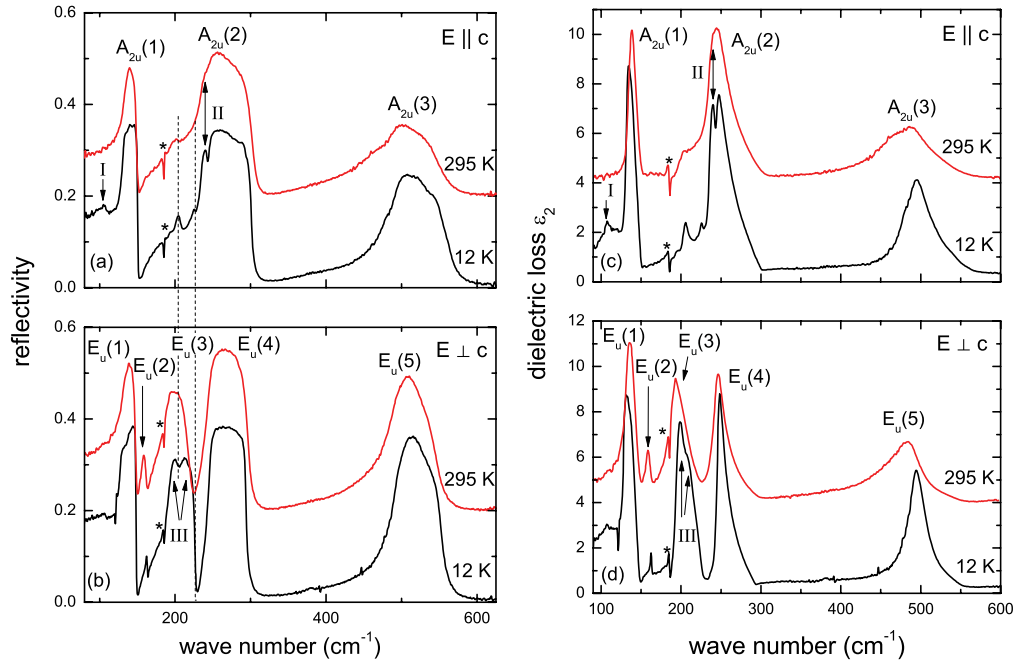


Fig. 3 (online colour at: www.ann-phys.org) Reflectivity of KCuF₃ measured at 12 K (black) and 295 K (red) for directions $E \parallel c$ (panel a) and $E \perp c$ (panel b). Dielectric loss ϵ_2 of KCuF₃ measured at 12 K and 295 K for directions $E \parallel c$ (panel c) and $E \perp c$ (panel d). The reflectivity and dielectric loss spectra at 295 K were shifted by an offset of 0.2 and 4, respectively.

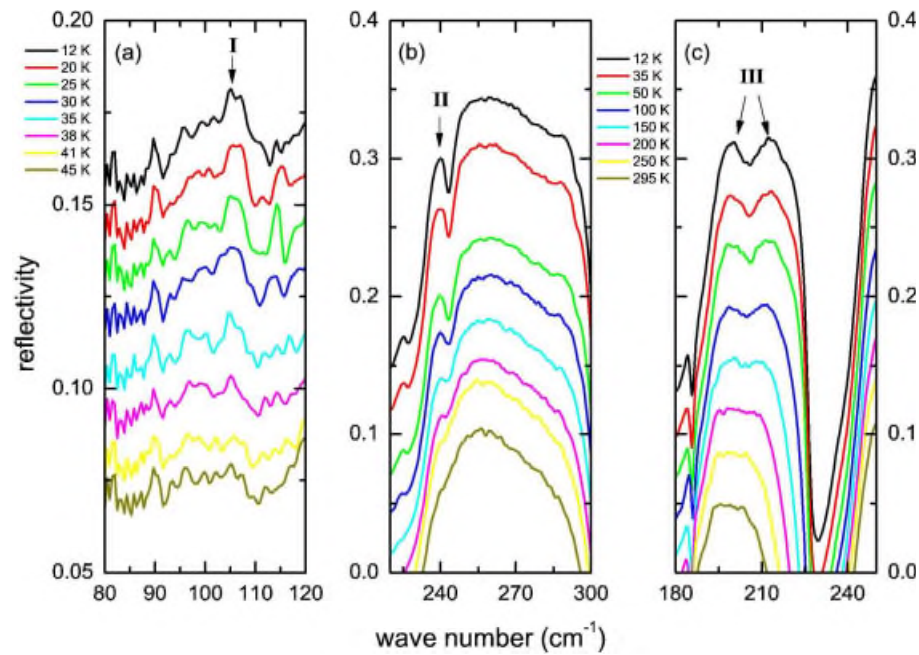
The dashed vertical lines drawn across Fig. 3(a) and (b) indicate the additional features in the range of the $E_u(3)$ leakage for $E \parallel c$. Both features can be explained as a result of the observed two-peak structure III of mode $E_u(3)$ at 12 K for $E \perp c$ (indicated by two arrows in Fig. 3(b)). This two-peak structure III can be regarded as one of the most evident changes in the IR spectra with decreasing temperature. A further clearly visible change is the dip-like feature II of the $A_{2u}(2)$ mode. Since the $A_{2u}(2)$ mode corresponds already to a one dimensional representation and can not split any further, this could either be an additional mode or the effect of multiphonon processes. However, a shoulder at this frequency is already visible at 295 K and the gradual temperature evolution of this mode shown in Fig. 4(b) favors the latter scenario of multiphonon processes which become more pronounced when the damping of the phonon modes is reduced at lower temperatures. The temperature evolution of the two-peak structure III of mode $E_u(3)$ also develops only gradually and becomes visible at about 150 K as shown in Fig. 4(c). No symmetry

Table 1 Transverse eigenfrequencies of the observed IR modes in cm^{-1} in KCuF_3 at 12 K and 295 K for polarizations $E \parallel c$ and $E \perp c$.

$E \parallel c$			$E \perp c$		
Mode	295 K	12 K	Mode	295 K	12 K
		107.5			107.0
$A_{2u}(1)$	138.9	134.5	$E_u(1)$	135.5	131.1
$A_{2u}(2)$	244.4	247.3	$E_u(2)$	158.6	162.5
$A_{2u}(3)$	486.0	495.6	$E_u(3)$	193.3	198.6
					208.0
			$E_u(4)$	246.4	248.3
			$E_u(5)$	484.5	494.2

reduction or other anomalies have been reported in this temperature range, but this feature could indicate a splitting of the doubly degenerate mode $E_u(3)$ already far above the Néel temperature.

Finally, we want to discuss the appearance of the weak mode I at about 107 cm^{-1} visible for both polarizations at 12 K (see Fig. 4(a)). This mode emerges only in the vicinity of the Néel temperature. Whether it corresponds to a phonon mode of a possible orthorhombic structure or is of magnetic nature can not be decided at the moment.

**Fig. 4** (online colour at: www.ann-phys.org) Reflectivity of KCuF_3 around the three features I (a), II (b) and III (c) (see text for details). The spectra are shifted by a constant offset of -0.01 (a) and -0.03 (b) and (c) for each temperature.

Altogether we find an experimental situation with an early claim that already at room temperature the symmetry is orthorhombic (instead of tetragonal) and does not change down to 10 K [26]. Our IR data suggests a gradual splitting of a $E_u(3)$ phonon mode which is clearly recognizable at around 150 K

and Raman-scattering studies found a splitting of doubly degenerate E_g modes to appear slightly above $T_N = 40$ K [31]. The fact that the indications of a symmetry lower than tetragonal are observed at different temperatures might be understood as a result of strong thermal lattice fluctuations which mask the effects of the orthorhombic distortion. Depending on the time-scale of the fluctuations at a given temperature different experimental probes will identify the orthorhombic distortions in different regimes. Consequently, the paramagnetic phase of KCuF_3 is not only characterized by spin fluctuations inherent to a quasi-one dimensional system, but these spin fluctuations are strongly coupled to the dynamic distortions of the lattice. On the time scale of these lattice fluctuations, spin-orbit coupling leads to a dynamical DM interaction [30]. When these dynamic distortions and the DM contribution become static at low temperatures [29], this additional anisotropic contribution to the magnetic exchange might be the decisive factor in suppressing the spin fluctuations and establish three dimensional antiferromagnetic order.

In summary, we observed all IR active phonon modes expected for the suggested tetragonal symmetry of KCuF_3 at room temperature. The splitting of one of these modes is found to occur below about 150 K and a new mode was found to appear in the vicinity of T_N . These observations are consistent with a scenario of strong lattice fluctuations of a possible orthorhombically distorted structure.

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