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Phonon anomalies versus magnetic ordering in CuO

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Abstract

We report the first measurements of FIR and MIR reflectivity of single-crystal monoclinic antiferromagnetic copper monoxide (CuO) in a wide temperature range (7–300 K) when ***b***-axis and ***ac***-plane polarized modes are completely separated and excited in transverse geometry. Previously reported softening of the A_u^3 mode at the Néel transition is confirmed and found to be up to two times more significant (about 10%). For the first time an emergence of several new IR-active lines at low temperatures is observed. The highest frequency new mode at 690 cm^{-1} strongly hardens and strengthens with cooling. The data are discussed in terms of strong spin–phonon coupling and possible charge disproportionation at low T. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Charge disproportionation; Infrared spectroscopy; Magnetic ordering; Spin–phonon interaction

1. Introduction

The antiferromagnetic monoclinic cupric oxide (CuO) has been extensively studied in the last decade including FIR reflectivity measurements (see Ref. [1] and references therein), mainly due to its close resemblance to HTSC-cuprates. The problem of large single-crystal growth, however, made so far impossible full separation of optical contributions along the symmetry ***b***-axis (A_u-modes) and within the ***ac***-plane (B_u-modes) as well as probing of pure TO modes. In this work we succeeded to overcome this problem and measure characteristics of TO A_u-and B_u-modes from 7 to 300 K.

2. Experimental

Single crystals CuO were grown from the CuO–PbO–Bi_2O_3 melt. The (0 1 0) and (0 0 1) faces were cut and polished. For the study of A_u modes the incident light with $\boldsymbol{E}\|\boldsymbol{b}$ was reflected from the (0 0 1) face (Fig. 1a). Conductivity was obtained by the Kramers–Kronig (KK) transformation (Fig. 1b). For the case of the (0 1 0) face, where dipole moments of non-collinear B_u-modes lie, an original "three-polarization" measurement scheme [2] and the KK method reformulated for the low-symmetry crystals [3], were applied. Parameters of all modes were obtained from the spectral fitting using a general model of anisotropic Drude–Lorentz oscillators.

3. Discussion

In spectra six strong modes ($3A_u + 3B_u$) are clearly seen, in accordance with the factor-group analysis for the C_{2h}^6 space-group. Out of these, the A_u^3-mode (410 cm^{-1} at RT) differs drastically by strong softening at the Néel transition (~ 10%, which is two-times larger than was found in [1]) and anomalously large line width, which peaks in the vicinity of the AFM transition (Fig. 2). The A_u^3-mode most strongly varies the Cu–O–Cu angles in the [1 0 1] and [1 0–1] chains. In this way, it could strongly modulate the value and even the *sign* of the angle-dependent Cu–O–Cu superexchange thus resulting

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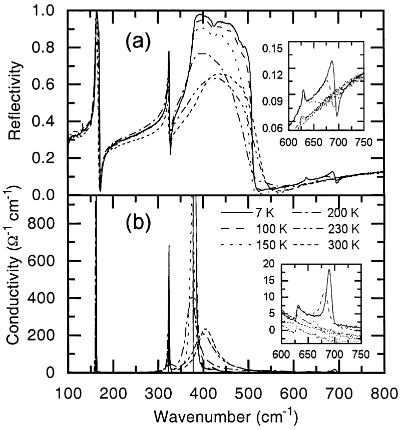

Fig. 1. (a) FIR reflectivity spectra for ***E***||***b***; (b) conductivity obtained by the KK transform of spectra.

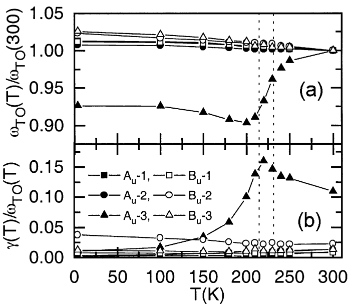

Fig. 2. Parameters of IR-active modes obtained by the Drude–Lorentz fitting of spectra: (a) RT-normalized TO frequency; (b) relative line width. Vertical lines indicate $T_{N1} = 230$ K and $T_{N2} = 213$ K.

in spin flips coupled to lattice vibrations and hence large mode anharmonicity. The long-range 3D magnetic order at low T reduces the possibility of such phonon-assisted spin excitations and the mode becomes narrow and slightly hardens at cooling in the usual way.

In addition, minor modes at 480 and 629 cm^{-1} are observed throughout the whole T range while being more strong at low T. Below transition, at least three new lines emerge: 420 cm^{-1} (both ||***b*** and ||***ac***), 507 cm^{-1} (||***ac***), 690 cm^{-1} (||***b***). The latter strongly hardens and strengthens at further cooling (see insets of Fig. 1), in a similar way as the Raman-active 240 cm^{-1} mode [4]. An occurrence of new IR lines as well as Raman lines [4] most probably is a signature of structural distortion accompanying magnetic ordering in CuO. In particular, the copper charge disproportionation might take place and result in IR-activation of zone-boundary phonons.

The data will be published in full elsewhere [5].

Acknowledgements

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