Raman and infrared studies of cupric oxide

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Abstract. Polarized Raman and fourier-transform infrared (FTIR) measurements have been made on a single crystal of CuO. Group theory predicts nine vibrations of which three ($A_g, 2B_g$) are Raman-active and six ($3A_u, 3B_u$) are infrared-active. We have observed three Raman modes at 296 (A_g), 346 (B_g^1) and 636 (B_g^2) cm^{-1} . We have also observed six infrared modes at 146 (B_u^3), 164 (A_u^2), 355 (A_u^3), 480 (B_u^1), 542 (?) and 603 (B_u^2) cm^{-1} . The normal frequencies and eigenvectors have been calculated using Wilson's FG method; a good fit between theory and experiment has been obtained.

Keywords. Raman; infrared; cupric oxide.

1. Introduction

Cupric oxide is a basic ingredient in the preparation of high temperature superconductors; therefore, the characterization of its magnetic and vibrational properties is important. Although the magnetic properties of CuO have been investigated recently (Forsyth *et al* 1988; Yang *et al* 1989), Raman and infrared measurements on a cupric oxide single crystal have been reported only recently (Hanuza *et al* 1989; Goldstein *et al* 1990; Irwin *et al* 1990).

We present in this paper a summary of our polarized infrared and Raman measurements on a CuO single crystal.

1.1 Crystal structure

The crystal structure of CuO is monoclinic with four CuO units in the unit cell. The monoclinic unit cell belongs to the space group $C_{2h}^6(C2/c)$ (Asbrink and Noorby 1970). The primitive cell contains two CuO units with the long direction parallel to the crystallographic c -axis. The long direction of the as-grown sample has been identified as the crystallographic c -axis, and the crystal planes are the (110) planes with angles of 72° or 108° between adjacent planes.

The crystal is biaxial—the unique $b(Y)$ axis is the bisector of the 108° dihedral angle. The other two mutually perpendicular optic axes (X, Z) were found to lie in the ac plane of the crystal.

Four samples of various sizes were studied[†]. One of the samples was cut and polished to obtain a (001) face. Experiments conducted on the (001) face allowed us to distinguish between the $A_{g,u}$ and $B_{g,u}$ modes.

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[†]CuO single crystals were obtained from two sources: (i) Superconics, St. Paul, MN, USA and (ii) Dr Terrell Vanderah, Naval Weapon Center, China Lake, CA, USA.

1.2 Normal modes and selection rules

The primitive cell contains four atoms and hence there are twelve possible normal modes. With the help of a correlation diagram, the irreducible representations associated with the lattice vibrations of the primitive cell have been determined as $\Gamma = 4A_u + 5B_u + A_g + 2B_g$. There are three acoustic modes ($A_u + 2B_u$) and six optic modes. The even modes are Raman-active, while the odd modes are infrared-active.

2. Experiments

Polarized Raman experiments were conducted in back scattering and in 90° geometry. In these experiments the scattered light was collected, digitized and analysed by a Spex 1403 monochromator, a cooled detector and Spex DM 3000 software. The laser power was kept at 50 mW, and the spectrometer resolution was 5 cm^{-1} .

Polarized reflectance data were obtained with a fourier-transform infrared (FTIR) spectrophotometer (Bomem DA 3-26 model) in a near-reflection geometry. A global source, a liquid helium-cooled-bolometer and a Mylar beam splitter were used to record the FTIR data. The data were analysed with a PDP 11-computer.

Figure 1. Raman spectra at room temperature: (a) the back-scattered YY polarization spectrum from a (001) face; (b) the back-scattered YZ polarization spectrum from a (001) face; (c) the 90° -geometry (Y + Z, Y + Z) spectrum from an as-grown sample; (d) the 90° geometry YZ spectrum from an as-grown sample.

3.1 Raman spectra

Figure 1 shows the Raman spectra taken at room temperature. The back-scattered Raman spectra from the (001) face is shown by figures 1(a) and (b). The 296 cm^{-1} peak in the YY geometry is assigned to the A_g mode, while the 636 cm^{-1} peak in the $(Y+Z, Y+Z)$ geometry is assigned to the B_g mode. Figures 1(c) and (d) are the 90° geometry Raman spectra from an as-grown sample. In this sample geometry the $(Y+Z, Y+Z)$ spectrum exhibits both the A_g and B_g modes as shown in figure 1(c), while the YZ spectrum shows only one of the B_g components. This is probably due to the weak intensity of the other (246 cm^{-1}) B_g component.

3.2 Infrared spectra

Figure 2(a) shows the reflectance data from an as-grown sample with two different polarizations of the incoming radiation. The polarizations are oriented along the two optic axes. The dashed and solid lines in figure 2 represent the X and Z polarizations of the incident radiation respectively. The real and imaginary parts of the dielectric function were obtained using a Kramers Kronig analysis. The longitudinal (LO) and

Figure 2. (a) Polarized infrared reflectance spectra from an as-grown sample. The two orientations of the incident polarizations are along the X and Z optic axes and are represented by the dashed and solid lines; (b) the TO peaks obtained from the modulus of the dielectric function; (c) the LO peaks obtained from the energy loss function.

Table 1. Calculated and observed vibrational frequencies of CuO. The LO and TO frequencies are obtained from figures 2(b) and (c); the observed Raman frequencies are indicated by the letter R.

Mode type	Calculated (cm ⁻¹)	Observed (cm ⁻¹)	Calculated (cm ⁻¹)
A_g	294	296 R	
B_g^1	348	346 R	
B_g^2	624	636 R	
A_u^1	421	?	
A_u^2	156	164 TO	165 LO
A_u^3	365	355 TO	?
B_u^1	474	480 TO	624 LO
B_u^2	598	603 TO	593 LO
B_u^3	146	145 TO	147 LO

transverse optic (TO) modes were obtained from the modulus of the dielectric function and the energy loss function $-\text{Im}(1/\epsilon)$ which are shown in figures 2 (b) and (c). The frequencies for the LO and TO modes are listed in table 1.

4. Normal mode analysis

The observed Raman and IR frequencies are listed in table 1. Normal mode frequencies were calculated using Wilson's F-G* method adapted to the crystal problem*. Five force constant parameters involving Cu–O, Cu–Cu and O–O stretches and Cu–O–Cu and O–Cu–O valence bendings were used to fit both Raman and IR data. The calculated frequencies are listed in table 1.

5. Discussion and conclusion

We have observed three Raman and six infrared modes which were identified as the A_g , B_g and A_u , B_u modes. Our assignments of the Raman frequencies to the A_g (296 cm⁻¹) and B_g (346 and 636 cm⁻¹) modes are complete and agree well with the normal mode calculation. However, the assignments of the infrared frequencies to A_u and B_u modes are only tentative at this point, since a more accurate determination of the frequencies as a function of the polarization of the incident radiation is required. This work is currently in progress.

*We recommend an excellent review of Wilson's F-G method extended to the crystal problem by George Turrell, *Infrared and Raman spectra of crystals*, p. 186, Academic Press, London and New York (1972).

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