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Raman scattering investigation of Cu¹⁸O

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Abstract. Raman scattering experiments have been carried out on powdered samples of cupric oxide (CuO) grown with the ¹⁸O isotope. The phonon frequencies have been measured and compared to those of Cu¹⁶O. The isotopic frequency shifts of the phonon modes have also been compared with the predictions of a lattice dynamics model. Previous low temperature experiments on Cu¹⁶O revealed a mode at 240 cm⁻¹ that was attributed to a magnetic excitation. The present results are consistent with this interpretation in that the same mode is observed to be unshifted in the spectra from Cu¹⁸O at low temperatures. A broad peak is also observed in the low temperature spectra at higher energies. This feature has a maximum at about 2100 cm⁻¹, is believed to arise from electronic scattering and is perhaps, at least in part, due to two-magnon scattering.

1. Introduction

Cupric oxide (CuO) represents a relatively simple system in which one can study the copper–oxygen interactions that appear to be fundamental to the occurrence of superconductivity in the high- T_c cuprates. Neutron scattering experiments [1–4], susceptibility measurements [5–9] and specific heat data [6, 9, 10] have revealed that CuO becomes ordered antiferromagnetically, but incommensurately as the temperature is reduced below $T_{N1} = 230$ K. As the temperature is lowered further the crystal transforms to a commensurate antiferromagnetically ordered state below $T_{N2} = 213$ K [1, 3]. The measured superexchange constant in CuO is approximately $J \approx 80$ meV [4], a value that is similar in magnitude to the exchange constants of La₂CuO₄ [11] and YBa₂Cu₃O₆ [12].

Recent Raman scattering experiments [13–18] in CuO have investigated the frequency and symmetry of the vibrational modes and have searched for evidence of magnetic excitations in the light-scattering spectra [13–15]. We have recently observed a very broad feature in the Raman spectra which is peaked at about 2100 cm⁻¹ [15]. This feature is qualitatively similar to the two-magnon scattering peaks observed in spectra obtained from La₂CuO₄ [11] and YBa₂Cu₃O₆ [12]. A new mode also appeared in the spectra [13] at lower energies when the sample temperature was decreased below about 200 K. As the temperature was lowered to 15 K this mode became stronger in intensity and hardened in frequency to 240 cm⁻¹. Based upon the temperature dependence of its intensity, frequency and linewidth this new mode was attributed to scattering from a magnetic excitation [15].

The present experiments on Cu¹⁸O were carried out in an attempt to corroborate the previous phonon assignments and to provide further evidence on the origin of the

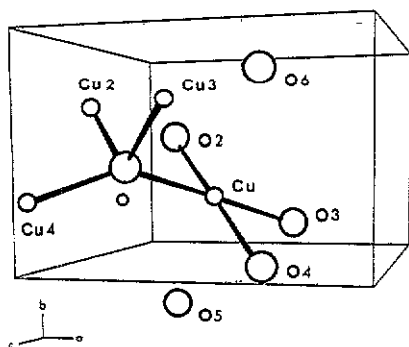


Figure 1. A portion of the CuO structure illustrating the atomic designations used in tables 1, 2, and 3. The contours of the crystallographic unit cell are also included. (From [19]).

spectral features observed at 240 cm^{-1} and 2100 cm^{-1} . If these excitations are magnetic in origin, and associated with the Cu^{2+} ion as previously proposed [15], they should of course be invariant under exchange of the oxygen isotope. The present experiments have thus enabled us to unambiguously distinguish between those features that are vibrational in origin and those that are magnetic in origin. Furthermore a simple lattice dynamics model has yielded frequencies and eigenvectors for the vibrational modes that are in good agreement with information obtained from the Raman spectra.

2. Experiment

The Cu^{18}O and Cu^{16}O powders used in this work were obtained from MSD Isotopes, a division of Merck Frosst Canada Inc. The specified isotopic purity of the ^{18}O sample was 99.3 at.%. The powders were pressed into pellets about 1.0 cm in diameter using a pressure of about 14 K bar. To avoid ^{16}O contamination the pellets were not sintered and thus the consistency of the powder was somewhat tenuous. Both the Cu^{16}O and Cu^{18}O pellets were prepared identically. The pellets were mounted on the cold finger of a displax refrigerator to obtain low temperature spectra. The relatively loose packing of the samples, however, resulted in a reduced thermal conductivity and some local sample heating resulted when the spectra were obtained with about 25–40 mW of incident laser power. It is estimated that the local sample temperature is about 40–60 K when spectra are obtained with the cold finger at 15 K. Spectra were obtained with both the 488.0 and 514.5 nm lines of an argon ion laser and the light was focused onto the sample with a cylindrical lens. The Raman spectrometer and detector have been described previously [15].

3. Results and discussion

3.1. Vibrational modes

Cupric oxide crystallizes in a monoclinic structure [19] (figure 1) described by the space group C_{2h}^6 . There are two molecular units in the primitive cell and thus there are nine optical modes at the centre of the Brillouin zone. If the site symmetries are correlated with the C_{2h} factor group of the crystal, one finds [13, 15] that there are three Raman

Table 1. Force constants for CuO .

Force constant	Bond type†	Distance (Å) or angle (deg)	Value‡
k_1	O—Cu	1.9608	62.4
k_2	O—Cu(2)	1.9509	69.8
k_3	Cu—O—Cu(2)	95.72°	78.1
k_4	Cu—O—Cu(3)	104.03°	17.3
k_5	Cu—O—Cu(4)	145.82°	2.0
k_6	Cu(2)—O—Cu(3)	108.85°	15.0
k_7	O—Cu—O(2)	84.28°	90.4
k_8	Cu—Cu(3)	3.0830	25.0
k_9	Cu(2)—Cu(3)	3.1734	36.7
k_{10}	O—O(2)	2.6246	20.1
k_{11}	Cu—Cu(4)	3.7484	2.3

† The numbers in brackets refer to the atomic designation illustrated in figure 1.

‡ Force constant units are: stretching, N m^{-1} ; and bending, $10^{-20} \text{ N m rad}^{-2}$.

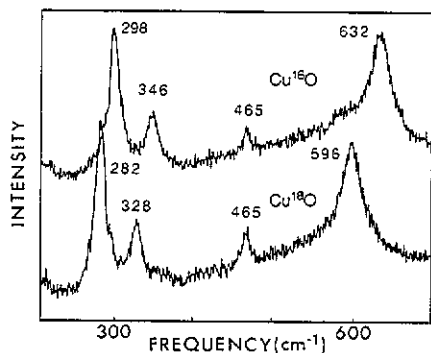


Figure 2. Room temperature Raman spectra of Cu^{16}O (upper trace) and Cu^{18}O (lower trace) showing the three Raman active phonons and the feature at 465 cm^{-1} . The spectra are vertically displaced for clarity.

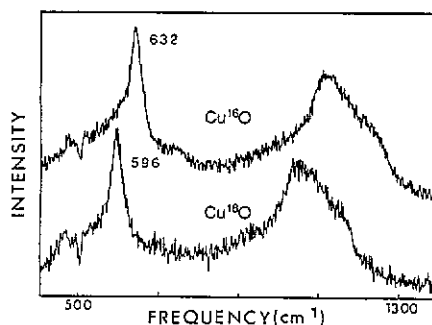


Figure 3. Room temperature Raman spectra of Cu^{16}O (upper trace) and Cu^{18}O (lower trace) in the spectral region from about 450 cm^{-1} to 1300 cm^{-1} showing the shift of the two-phonon feature at 1150 cm^{-1} . The dip in the spectra at about 500 cm^{-1} is an experimental artifact. The two spectra are vertically displaced for clarity.

active modes ($A_g + 2B_g$) and six IR active modes ($3A_u + 3B_u$). The copper atoms are situated on sites with C_2 symmetry and thus are not involved in the even Raman modes [15]; that is, the three Raman active modes arise from vibrations of the oxygen atoms only.

The frequencies and symmetry of the three most prominent Raman modes of Cu^{16}O have been measured previously [13–15] and at room temperature have values of 298 cm^{-1} (A_g), 345 cm^{-1} (B_g) and 632 cm^{-1} (B_g). These frequencies all harden by approximately 5 cm^{-1} on cooling the sample to 15 K. This data is summarized in table 2.

Figure 2 presents the lower frequency (under 700 cm^{-1}) portion of room temperature Raman spectra obtained from the pressed pellets of Cu^{16}O and Cu^{18}O . The frequencies of the three Raman modes in the isotopically exchanged sample have shifted to 282, 328

Table 2. Observed and calculated frequencies for CuO^{16}O and CuO^{18}O (in cm^{-1}). The measured Cu^{16}O Raman frequencies are from [13] and the IR frequencies are those of the transverse optic modes and were taken from [20] (see text).

Mode	Cu^{16}O			Cu^{18}O	
	obs. (15 K)	obs. (300 K)	calc.	obs. (300 K)	calc.
A_g	303	298	298	282	281
B_{1g}	350	346	346	328	327
B_{2g}	636	632	632	596	596
A_{1u}		164	164		162
A_{2u}		330	330		329
A_{3u}		423	423		410
B_{1u}		146	146		145
B_{2u}		480	480		460
B_{3u}		530	530		506

and 596 cm^{-1} for the A_g and two B_g modes respectively. This data is also summarized in table 2. The A_g mode at 298 cm^{-1} is thus shifted by 4.9%, the B_g mode at 345 cm^{-1} by 5.4% and the B_g mode at 632 cm^{-1} by 5.7% from their values in the ^{16}O compound. If one assumes that the modes should be shifted simply in proportion to the square root of the oxygen mass ratio one would predict a shift of 5.7% for each mode. The measurements are in reasonable agreement with this prediction if the experimental accuracy of $\pm 1.0 \text{ cm}^{-1}$ is considered. This result is to be expected given that only the oxygen atoms are vibrating in the Raman modes.

3.2. Lattice dynamics model

A valence-force-field (VFF) lattice dynamics model has been used to calculate the phonon energies at the centre of the Brillouin zone for the Cu^{16}O compound. The force constants used in the model were determined by fitting the three Raman frequencies [15] and the six transverse optical (TO) IR active modes. Experimental values for the zone centre TO frequencies were obtained from the neutron scattering data of Reichardt *et al* [20]. Values for the eleven parameters used in the model are summarized in table 1 and the calculated frequencies are compared with the measured values in table 2. As can be seen from table 2 the surplus of force constants over measured frequencies has enabled us to obtain exact agreement between the calculated and measured values for Cu^{16}O .

The Raman and IR frequencies for Cu^{18}O were then calculated using the same force constants (table 1) and by simply changing the mass of the oxygen atom. The resulting values are listed in table 2. The calculated frequencies for the Raman modes of Cu^{18}O are also compared to the measured values in table 2. As can be seen the calculated and measured values are, to within the experimental uncertainty of $\pm 1 \text{ cm}^{-1}$, in exact agreement. This result certainly corroborates the previous [13] phonon assignments and also implies that the ^{18}O samples were completely exchanged. Furthermore it is apparent that the model has yielded the correct eigenvectors for the Raman modes and these are summarized in table 3.

It should be noted that the present VFF model does not incorporate any Coulomb forces to represent the partially ionic nature [20] of the bonding in CuO . This is not

Table 3. Relative atomic displacements (arbitrary units) for the zone centre Raman and transverse optic modes of CuO .

Mode	A_g	B_{1g}	B_{2g}	A_{1u}	A_{2u}	A_{3u}	B_{1u}	B_{2u}	B_{3u}
ω (cm^{-1})	298	346	632	164	330	423	146	480	530
Cu x	—	—	—	-0.69	0.13	-0.20	0.08	-0.13	-0.11
y	—	—	—	-0.16	-0.10	0.17	0.60	0.12	0.02
z	—	—	—	-0.01	-0.69	-0.15	0.05	-0.11	0.13
Cu(3) x	—	—	—	0.69	-0.13	0.20	0.08	-0.13	-0.11
y	—	—	—	-0.16	-0.10	0.17	-0.60	-0.12	-0.02
z	—	—	—	0.01	0.69	0.15	0.05	-0.11	0.13
O x	—	-0.70	0.14	—	—	—	-0.32	0.51	0.43
y	0.71	—	—	0.64	0.37	-0.68	—	—	—
z	—	-0.14	-0.70	—	—	—	-0.17	0.44	-0.53
O(2) x	—	0.70	-0.14	—	—	—	-0.32	0.51	0.43
y	-0.71	—	—	0.64	0.37	-0.68	—	—	—
z	—	0.14	0.70	—	—	—	-0.17	0.44	-0.53

considered a serious omission in the context of the present paper as only the Raman modes are under consideration. As a result, however, the model yields results only for the IR TO modes and does not reflect the frequency changes that occur as these modes change in character from transverse to longitudinal with changing directions of propagation [20].

3.3. Two-phonon scattering

A strong broad feature has been observed [15] in the Raman spectrum of CuO at about 1100 cm^{-1} . Similar features also appear at about this energy in the Raman spectra of La_2CuO_4 and weakly doped $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [11, 12, 21–24]. These features have been attributed to two-magnon or spin-flip scattering by some observers [11, 23–24] and to two-phonon scattering by others [21, 22].

Given the similar strength of the antiferromagnetic interactions of CuO and the above cuprates it is interesting to determine the origin of the 1100 cm^{-1} feature in CuO by investigating its frequency dependence on the isotopic mass. The spectra presented in figure 3 provide a rather definitive answer to this question in that the mode is clearly shifted to lower frequencies in the Cu^{18}O sample and thus can be attributed unequivocally to two-phonon scattering.

The origin of the 1100 cm^{-1} feature can be determined in somewhat greater detail by comparing its shape and energy with the dispersion curves obtained from recent neutron scattering experiments [20]. The one-phonon density of states presented in [20] has a strong contribution beginning at about 520 cm^{-1} and having a high frequency cut-off at 640 cm^{-1} . There are two peaks in the density of states in this frequency region which are centred at about 565 cm^{-1} and 620 cm^{-1} . The two-phonon replicas of these features should thus have an onset at about 1040 cm^{-1} , a high frequency cut-off of 1280 cm^{-1} and have weakly defined maxima at 1130 and 1240 cm^{-1} . These numbers are in excellent agreement with the measured frequencies that characterize the shape of the broad feature at about 1150 cm^{-1} in the spectrum of Cu^{16}O (figure 3).

In the Cu^{18}O spectrum (figure 3) the second order feature is shifted to lower frequencies by about 70 cm^{-1} . The general shape is essentially unchanged from the Cu^{16}O spectrum indicating that the contributing phonons are all isotopically shifted by about the same amount. This shift would be about 35 to 40 cm^{-1} for each mode assuming that only two-phonon overtones contribute to the observed feature. This in turn is again consistent with the phonon dispersion curves of [20]. From these curves one deduces that the observed two-phonon scattering must involve the highest energy B_g and B_u modes with overtone scattering from both zone boundary points and the zone centre. The high frequency cut-off in both the Cu^{16}O (1270 cm^{-1}) and Cu^{18}O (1200 cm^{-1}) spectra corresponds almost exactly to $2B_g$ scattering from the Brillouin zone centre. Furthermore the two-phonon shift of 70 to 80 cm^{-1} is what one would predict given the measured and calculated shifts for the single phonons (table 2).

In the spectra shown in figure 2 it is evident that a relatively strong peak occurs at 465 cm^{-1} . In a previous paper [13] this peak was attributed to two-phonon scattering because it became slightly weaker as the temperature was reduced. It is clear from figure 2, however, that this peak is unaffected by exchange of the oxygen isotope. Since our lattice dynamics model predicts that any phonon with an energy greater than about 200 cm^{-1} is isotope shifted one must conclude that the 465 cm^{-1} peak is not vibrational in origin. It is possible that it arises because of the presence of an impurity. This interpretation would be consistent with the fact that this feature has not been observed in spectra obtained from single crystals [15, 17, 18]. It is difficult, however, to identify a probable impurity since Cu_2O , which is the most likely source, does not have any strong Raman peaks in this frequency region. Furthermore, any form of oxide contamination should be isotope shifted. It is perhaps possible that a particular crystal orientation might yield spectra containing this feature and in this case it could perhaps be associated with an electronic excitation of the Cu^{2+} ion [15, 18].

3.4. Magnetic excitations

When CuO crystals are cooled below the Néel temperature ($T_{N_2} = 213\text{ K}$) a new mode is observed [13–15] in the Raman spectra. This mode hardens in frequency and becomes more intense [15] as the temperature is lowered further and attains a value of 240 cm^{-1} at 15 K . On the basis of the variation of frequency, intensity and linewidth this mode has been attributed to scattering from magnetic excitons [15]. A feature with this energy and temperature dependence could also correspond to one-magnon scattering, but neutron scattering experiments [4] have not provided any evidence of an 'optic' magnon in this energy range. Ain *et al* [4] did, however, find an optic magnon at about 170 cm^{-1} , a value which cannot be reconciled with the 240 cm^{-1} mode observed in the Raman spectra. One of the principal aims of the present work was to confirm that the 240 cm^{-1} mode was not vibrational in origin and thus provide support for our previous interpretation [13, 15].

A Raman spectrum obtained with the Cu^{18}O pellet at approximately 40 K is shown in figure 4. It is clear that the 240 cm^{-1} peak is present and, within the experimental uncertainty of $\pm 1.0\text{ cm}^{-1}$, unshifted in frequency from its value in Cu^{16}O . This result is certainly consistent with the previous interpretation, namely, that this mode arises from magnetic excitations associated with the Cu^{2+} ions.

Spectra have also been obtained from Cu^{18}O in the spectral region extending from 500 cm^{-1} to 3000 cm^{-1} in order to investigate any isotopic dependence of the broad feature observed previously [15]. A spectrum obtained with the sample at about 50 K

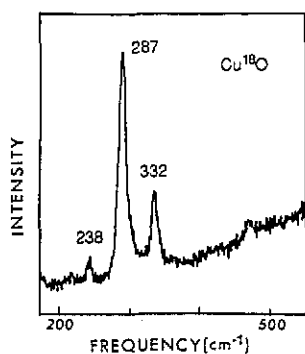


Figure 4. Raman spectra obtained from Cu^{18}O with the sample at a temperature of about 50 K in the region of excitation.

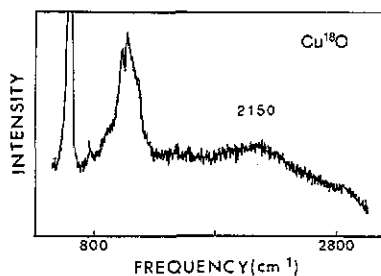


Figure 5. Raman spectrum of Cu^{18}O obtained with the 488.0 nm line and the sample at a temperature of about 50 K in the region of excitation.

and with 488.0 nm excitation is shown in figure 5. From this figure it is evident that there is a broad feature that is weakly peaked at about 2150 cm^{-1} . The peak frequency and shape of this feature are essentially identical to those of the same feature observed [15, 17] in single crystals of Cu^{16}O . Similar broad features have been observed in the Raman spectra of La_2CuO_4 [11], $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ (with small x) [12] and other derivative compounds of the high- T_c cuprates. It has been demonstrated rather convincingly that this scattering in the cuprates is predominantly multi-magnon in origin [11, 12, 25, 26]. The similar scattering observed in CuO is peaked at a somewhat lower frequency than in the cuprates but this is consistent with the somewhat smaller exchange constant in CuO ($J = 80\text{ meV}$) against those in the cuprates ($J \geq 120\text{ meV}$). On the basis of the similarity to the cuprate spectra, the broad energetic feature observed in CuO was tentatively attributed [15] to two-magnon scattering. The present results on Cu^{18}O are consistent with this interpretation but polarization studies on single crystals will be required to further characterize this high energy scattering and identify other possible mechanisms [25].

4. Conclusions

Raman scattering experiments have been carried out on pressed pellets of Cu^{18}O powder and the results compared with those for similarly prepared samples of Cu^{16}O . The three most prominent features of the Cu^{16}O spectrum, which were previously assigned to first-order phonon scattering, have all been observed to shift to lower energies in the isotope substituted sample of Cu^{18}O . The magnitudes of the measured isotope shifts of the mode frequencies are in excellent agreement with the values obtained from a simple vFF lattice dynamics model. These results thus confirm unambiguously the previous [13, 15] phonon assignments for CuO . The results of the present experiments have also demonstrated that a strong feature near 1100 cm^{-1} is due to multi-phonon scattering. Comparison with dispersion curves obtained from neutron scattering experiments [20] indicate further that this scattering arises from two-phonon overtones of the most energetic B_g and B_u modes. Since the high- T_c cuprates have modes with similar energies [27] involving vibrations of the oxygen atoms only, it is speculated that the peaks occurring in high- T_c

cuprate spectra [11, 12, 21–24] with energies in the same region ($1000\text{--}1400\text{ cm}^{-1}$) also correspond to multi-phonon processes.

The spectral features observed previously [15] at 240 cm^{-1} and 2100 cm^{-1} in spectra obtained from Cu^{16}O have been found to have the same frequency in Cu^{18}O . These features were previously assigned to scattering from magnetic excitations and thus the present results tend to corroborate the previous assignment. An additional mode at 465 cm^{-1} , that was previously [13] assigned to two-phonon scattering does not undergo an isotope shift, however, and it is believed to arise from the presence of an impurity. Further work in this area will be required to develop a quantitative model for the magnetic excitations in CuO . Such a model should have important implications for any description of the electronic properties of CuO .

Acknowledgments

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