Phonon spectrum of copper oxide

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The partial spectra of vibrations of copper atoms and oxygen in CuO were obtained experimentally using isotopic contrast in inelastic neutron scattering. The phonon spectrum of the compound is constructed based on these data. The obtained spectrum is compared with calculations based on the rigid-ion model.

It is customarily assumed (see, for example, Ref. 1) that the superconducting properties of high-T_c cuprates are strongly associated with the presence of CuO conducting planes in the structure of these systems as well as structural fragments (planes or chains) which supply free carriers. In the binary copper oxide CuO, which has a monoclinic lattice (space group $C2/c$) and is a Mott insulator, the same structural motifs, namely, CuO planes, in which copper is surrounded by four oxygen atoms (see Ref. 2), can be distinguished. In addition, as in many high-T_c superconductors, antiferromagnetic ordering is observed in CuO ($T_N = 229.5$ K).[3] For this reason, CuO can be regarded as a simpler model system for high-T_c cuprate superconductors.

There are a large number of works on the physical properties of CuO, including also the dynamics of its crystal lattice. In particular, the dispersion curves for phonons in the principal directions of symmetry of the crystal lattice have been measured by the method of inelastic neutron scattering and the phonon spectrum has been calculated in an interaction-force model with 22 parameters.[2]

Application of the method of isotopic contrast in inelastic neutron scattering makes possible model-independent reconstruction of the partial vibrational spectra of separate atoms from the experimental data, and in the case of CuO the phonon spectrum of the entire compound can also be reconstructed. In the present work we solved this problem.

EXPERIMENT

The manifestation of isotopic contrast is based on the large difference between the neutron scattering cross sections of the isotopes Cu^{65} and Cu^{63} (14.5 and 5.2 b, respectively). In this connection, ~30 g specimens of CuO were prepared from copper with the following isotopic composition: a) 99% Cu^{65} and 1% Cu^{63}; b) 99.7% Cu^{63} and 0.3% Cu^{65}. At the first stage of synthesis copper nitrates $Cu(NO_3)_2$ were obtained and roasted in oxygen. At the final stage the resulting oxides were allowed to stand for 6 h in an oxygen atmosphere at $T = 500$–600 °C. The specimens were single-phase, according to x-ray diffraction data, and they had a monoclinic unit cell with $a = 4.6848(4)$ Å, $b = 3.4242(4)$ Å, $c = 5.1251(4)$ Å, and $\beta = 99.41(3)$ Å.

The inelastic neutron scattering spectra were measured at room temperature on a time-of-flight spectrometer with a source of cold neutrons[4] ($E_0 = 4.4$ meV). The experimental data obtained at five scattering angles were analyzed in the incoherent approximation. In this case the generalized vibrational density of states $G(E)$ can be reconstructed directly from the measurements (Fig. 1):

$$G(E) = \frac{\sigma_{\mathrm{Cu}}}{M_{\mathrm{Cu}}} g_{\mathrm{Cu}}(E)\exp(-2W_{\mathrm{Cu}}) + \frac{\sigma_{\mathrm{O}}}{M_{\mathrm{O}}} g_{\mathrm{O}}(E)\exp(-2W_{\mathrm{O}}), \tag{1}$$

where all notation is standard, and $g_{\mathrm{Cu}}(E)$ and $g_{\mathrm{O}}(E)$ are the partial vibrational spectra of the Cu and O atoms. From the relation (1) it is evident that in contrast to the true vibrational density of states $g(E) = g_{\mathrm{Cu}}(E) + g_{\mathrm{O}}(E)$ the partial vibrational spectra enter into the function $G(E)$ with the weighting factors $\sigma_i/M_i \exp(-2W_i)$, and it is the presence of these factors that allows the isotopic-contrast method to be applied for determining the contribution of the vibrations

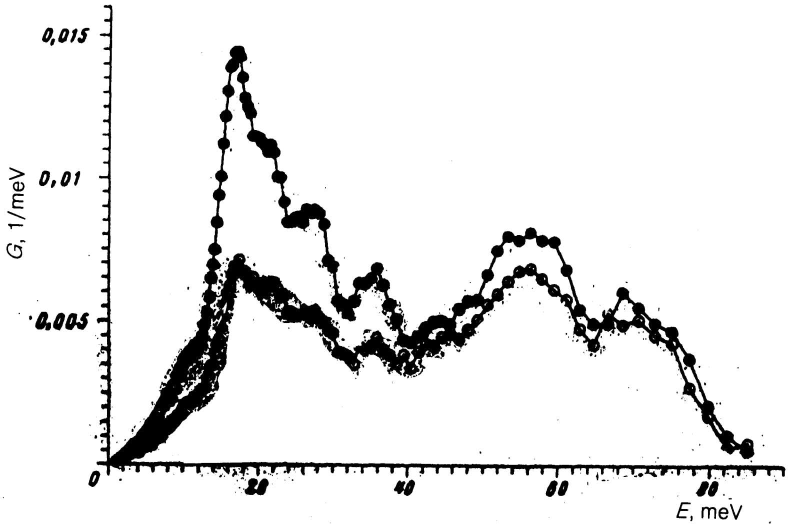

FIG. 1. $G(E)$ for $Cu^{63}O$ (○) and $Cu^{65}O$ (●).

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of separate elements to the total spectral distribution of the vibrational states of the lattice.

RESULTS

As follows from the relation (1), the difference of $G(E)$ for $Cu^{65}O$ and $Cu^{63}O$ (Fig. 1) is proportional to the function $g_{Cu}(E)$:

$$\Delta G(E) = G_{Cu^{65}O}(E) - G_{Cu^{63}O}(E)$$

$$= \left(\frac{\sigma_{65}}{M_{65}} - \frac{\sigma_{63}}{M_{63}}\right) g_{Cu}(E) \exp(-2W_{Cu})$$

(it is assumed that the partial vibrational spectrum of copper and therefore the thermal factor are identical for Cu^{65} and Cu^{63}—the difference of the masses of the isotopes is equal to $\sim 3\%$).

In order to obtain the partial vibrational spectrum of the O atoms the spectrum $g_{Cu}(E)$ was calculated from the functions $G(E)$ for $Cu^{65}O$ and $Cu^{63}O$ taking into account the weighting factors:

$$g_O(E)\exp(-2W_O) = \frac{M_O}{\sigma_O}\left(G(E) - \frac{\sigma_{Cu}}{M_{Cu}} g_{Cu}(E)\exp(-2W_{Cu})\right).$$

In order to achieve higher statistical accuracy, the data on the partial vibrational spectra of oxygen which were obtained for specimens with different isotopic composition were summed. The functions g_{Cu} and g_O obtained in this manner are the partial vibrational spectra, distorted by the contribution of multiphonon neutron scattering processes, of Cu and O atoms. The correction to the multiphonon scattering was calculated on the basis of the partial spectra with the help of an iteration procedure, and in the process only two-phonon processes were taken into account, since they make the determining contribution. The spectra $g_{Cu}(E)$ and $g_O(E)$ reconstructed directly from the experimental data were employed as the initial approximation. The contribution obtained for the two-phonon neutron scattering processes was calculated from the starting spectra $G(E)$, and the entire procedure of reconstructing the partial spectra was repeated. The iteration process was terminated if the next approximation changed the area under the partial spectral distributions by less than 0.01. The obtained partial spectra were employed to calculate the thermal factors of Cu and O atoms. The partial spectra presented in Fig. 2 were obtained after all corrections were introduced.

DISCUSSION

As one can see from Fig. 2, copper atoms undergo vibrations primarily at energies $E < 40$ meV. The spectrum contains, however, a wide vibrational band at $E \sim 55$ meV, in which the probabilities of vibrations of Cu and O atoms are comparable. According to the data in Ref. 5, where the oscillations of the crystal lattice of CuO were investigated by the method of infrared spectroscopy, the following optical vibrations are observed at energies of ~ 55 meV: B_g^1 321 cm^{-1} (43.1 meV), A_u^3 478 cm^{-1} (59.3 meV), and at the point X at the boundary of the Brillouin zone with energy 414 cm^{-1} (51.3 meV). Hence it can be concluded that copper atoms make a significant contribution to the indicated vibrational modes.

The low-temperature part ($E < 40$ meV) of the partial spectrum of Cu in CuO is similar to the spectrum of Cu in YBCO (Fig. 3).[6] In YBCO the features of the partial spectrum of Cu at 18 and 23 meV are associated with vibrations of Cu atoms lying in the planes Cu2–O2–O3 with interatomic distances Cu–O2 = 1.93 Å and Cu2–O3 = 1.96 Å. The presence in CuO of an analogous planar coordination of Cu atoms with close interatomic distances (1.95 and 1.96 Å) suggests that the features in the vibrational spectrum of Cu atoms in CuO at 17 and 20.5 meV correspond to mutual vibrations of copper and oxygen in these planes. This conclusion is confirmed by the data of Ref. 5, according to which

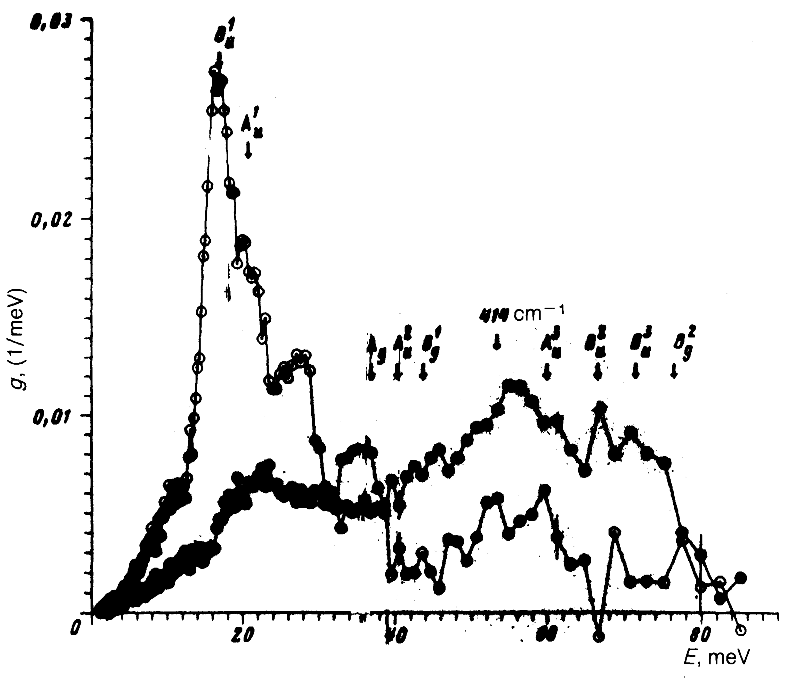

FIG. 2. Partial vibrational spectra of Cu (○) and O (●) atoms in CuO.

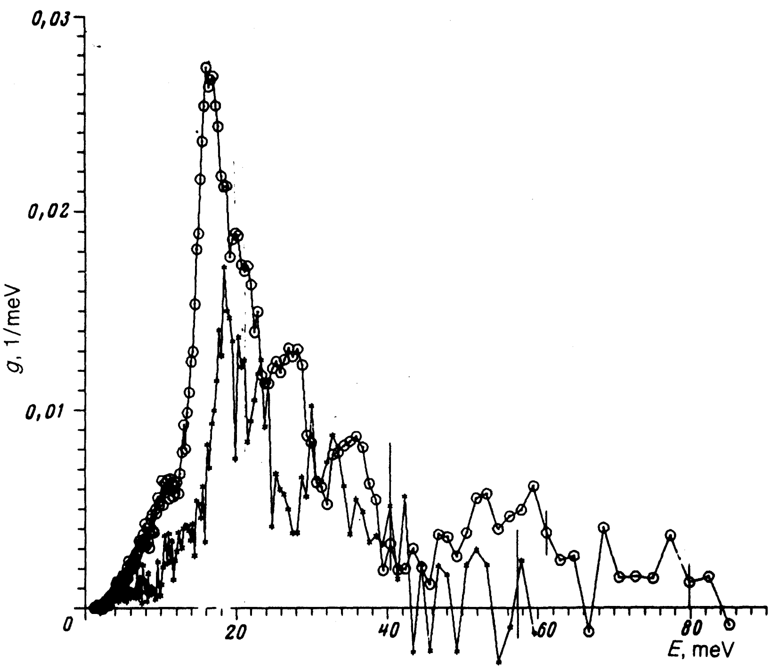

FIG. 3. Partial spectra of Cu atoms in CuO (O) and $YBa_2Cu_3O_{6.93}$ (*).

the optical modes B_u^1 147 cm^{-1} (18.2 meV) and A_u^4 161 cm^{-2} (20 MeV) correspond to vibrations of Cu and O atoms with planar coordination. As far as other features in the vibrational spectrum of copper are concerned, they are probably associated with the presence of flat sections on the dispersion curves for phonons in CuO (Ref. 2), to each of which there corresponds a maximum in the vibrational spectrum.

The partial vibrational spectrum of O atoms extends over all allowed energies and its energy dependence is weaker than that of the vibrational spectrum of copper. At energies $E < 4$ meV the vibrational density of O atoms is higher than that of Cu atoms. Since this energy range corresponds to acoustic vibrations of the lattice[2] and the mass of an oxygen atom is smaller than that of a copper atom, this behavior of the partial spectra seems unexpected. It has not been excluded that the obtained excess is associated with the contribution of neutron scattering by magnetic excitations. This proposition agrees with the data of Refs. 3 and 7 on the presence of strong magnetic correlations at temperatures $T > T_N$, right up to $T \sim 673$ K.

The phonon spectrum $g(E)$ for copper oxide was constructed from the partial vibrational spectra of Cu and O atoms from the experimental data (Fig. 4). For comparison Fig. 4 shows the phonon spectrum of CuO calculated in Ref. 2 in the rigid-ion model using measurements of the disper-

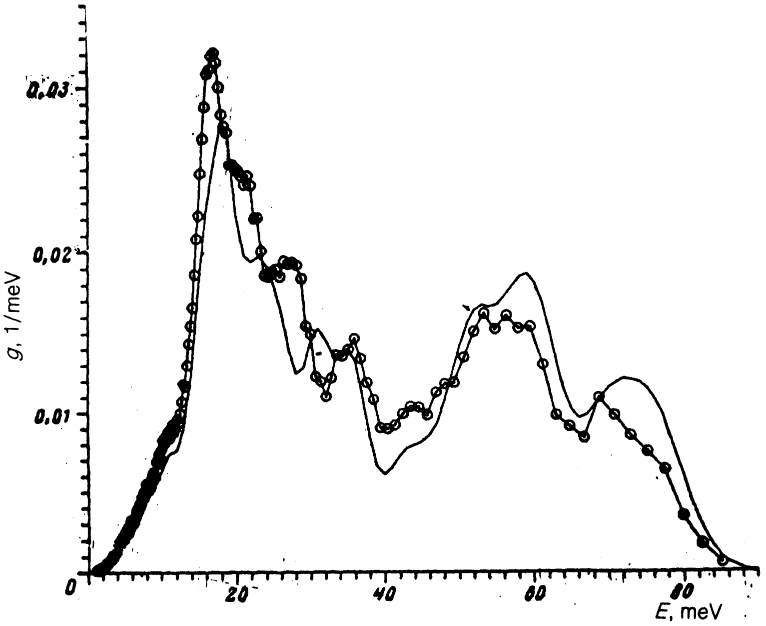

FIG. 4. Phonon spectrum of CuO. The solid line corresponds to the model and the dots are the experimental data.

sion relations for phonons. The effect of the resolution function of the time-of-flight spectrometer is included in the spectrum. One can see that the model calculation on the whole describes our reconstructed phonon spectrum well, though some features of the model spectrum are shifted in the direction of higher energies.

CONCLUSIONS

1. The partial vibrational spectra of Cu and O atoms in CuO were obtained experimentally for the first time and the phonon spectrum of the oxide was constructed on the basis of these spectra.

2. It was established that the basic features of the vibrational spectrum of copper atoms are associated with the mutual vibrations of Cu and O atoms with planar coordination.

3. It was shown that the rigid-ion model describes well the constructed phonon spectrum of the compound.

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