LATTICE DYNAMICS OF CUPRITE (Cu2O)

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Abstract. - The phonon dispersion curves of Cu_2O have been calculated using a shell model which takes into account nearest neighbour O-Cu, Cu-Cu and O-O interactions, long range Coulomb interactions and the electronic polarizability of both the oxygen and the copper ions. The results are compared with the data obtained from ultrasound, infrared, Raman and inelastic neutron scattering measurements. The interrelations between fcc-Cu and Cu_2O are pointed out and the influence of deformations of the electronic charge density on the phonon dispersion curves is discussed.

Introduction.- For many years the extremely rich excitonic spectra of cuprous oxide have attracted considerable interest in the electronic properties of this compound[1]. Up to now only very few attempts[2,3] have been made to calculate the phonon dispersion curves and thus to give a unique interpretation of the different phonon frequencies deduced from recent ultra sound[4], Raman scattering[5,6], exciton luminescence[7] and inelastic neutron scattering[8] measurements. The calculation of Huang[2] is restricted to the Γ-point whereas the model of Carabatos[3] which gives a quite satisfactory description of the optical modes at the zone center does not reproduce the elastic and dielectric properties and shows serious disagreement with the neutron scattering data, in particular a softening of the acoustic branches at the R point. In this paper we show how the model has to be extended and modified in order to overcome the above mentioned deficiencies.

Cuprite crystallized in a simple but uncommon structure which belongs to the non symmorphic space group O_h^4 and can be considered as being made out of two interpenetrating Bravais lattices: a fcc-Cu lattice and a bcc-O lattice (Fig. 1). Each oxygen is the center of a regular tetrahedron the corners of which are occupied by the four nearest neighbour Cu ions. The unit cell contains two formula units of Cu_2O.

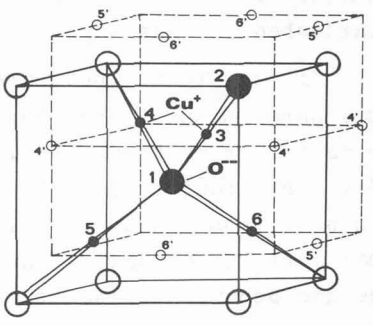

Fig. 1. Crystalline structure of Cu_2O.

At the center of the Brillouin zone the normal vibrations of Cu_2O decompose into

$$3\Gamma_{15}^{(3)}+\Gamma_{25}^{(3)}+\Gamma'^{(2)}_{12}+\Gamma'^{(1)}_{2}+\Gamma'^{(3)}_{25}$$

where the two optic Γ_{15} modes are infrared active and only the Γ'_{25} mode is Raman active. In contrast to the poor first order ordinary Raman spectrum which exhibits only one mode all odd-parity phonons can be observed in resonant Raman (RR) scattering on exciton lines. For a long time the interpretation of the RR spectra has been highly controversial. At present the different lines are well understood in terms of quadrupolar and dipolar transitions and specific polarization selection rules have been derived[9].

Lattice Dynamics.- The phonon dispersion curves up to phonon energies of about 5THz have been measured in the high symmetry directions Δ,Σ and Λ at room temperature by Beg and Shapiro[8]. Some complementary measurements in the intermediate energy region between 4 and 10 THz have been performed by ourselves in order to determine the branches connected to the Γ'_2 mode. The results of the neutron scattering measurements are represe ted in Fig. 2 together with our model calculations.

In the following we will discuss the different parameters of the model. First of all we take into account the nearest neighbour O-Cu interactions. These interactions which have already been used in the rigid ion model of Carabatos and Prevot[3] are most important and have to be considered in any model for Cu_2O. This can be concluded from band structure calculations[10] which reveal a strong hybridization of the Cu 3d orbitals with the O 2p states. This hybridization favours the cuprite structure and stabilizes the copper tetrahedra around the oxygen ions. The importance of the Cu-O interactions is also indicated by the high frequnecy (15.45 THz) of the Raman active Γ'_{25} mode in which the oxygen is displaced with respect to the rigid copper tetrahedron. In a rigid ion model this mode determines directly the force constant for the central O-Cu interaction. The second mode which is strongly dependent on the O-Cu force constants is the Γ'_2 vibration which corresponds to an isotropic deformation of the copper tetrahedron. Naturally this mode is also influenced by the Cu-Cu interactions which we now discuss. It is interesting to note that the elastic constant c_{11}[4] scaled by the mass densities of Cu and Cu_2O is the same in both crystals whereas the shear constants $\frac{1}{2}(c_{11}-c_{12})$ and c_{44} are considerably lowered in the oxide. This means that the LA and the lowest LO branch in the 100 direction are basically due to the same interactions as in metallic copper. It is

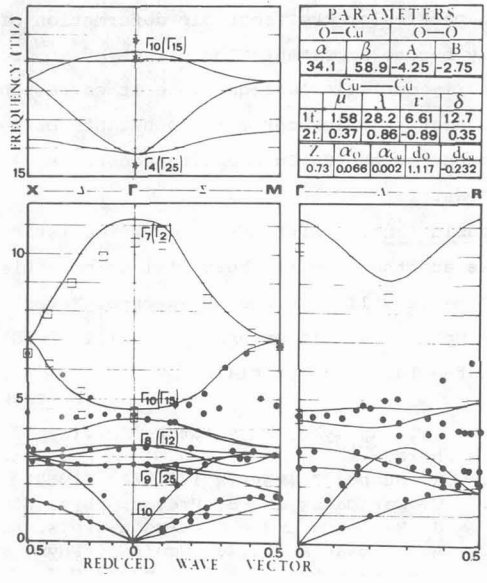

Fig. 2. Phonon dispersion curves in Cuprite (●:ref.8; □: our measurements: *optical data). The full lines are the shell model calculations.

therefore essential to take into account the nearest neighbour Cu-Cu interactions and to take care of the fact that the Cu-Cu interactions in Cu_2O are split into two distingt families. In the first family the Cu-Cu forces act together with nearest neighbour Cu-O-Cu forces which are missing in the second family. It should be mentioned that it is not the Cu-Cu interaction itself which stabilizes the frequencies in the Σ and Λ directions and in particular at the R-point, but the fact that the force constants of the two families are different. Our calculations show that the considerable lowering of the shear elastic constants in Cu_2O as compared to fcc Cu is due to strong non central O-Cu interactions weak nearest neighbour O-O interactions and a strong enhancement of the interactions between those Cu^+ ions, which are linked by Cu-O-Cu bindings. The large value of the dielectric constant ε_∞ (6.46) arises from a substantial electronic polarizability which is essentially due to the oxygen ions. Minor contributions arise from the Cu^+ ions. In our calculations it turns out that the shell change of the Cu^+ ions is positive. This indicates a strong overlap of charge density near the Cu^+ ion which is also indicated by the band structure calculations. The dipolar electronic polarizability acts mainly on the polar $\Gamma_{15}^{(3)}$ modes. Band structure calculations and RR scattering experiments indicate that electronic deformations of other than dipolar symmetry, in particular the isotropic deformation of the charge density around the O^{--} ions, may become important. The effect of an isotropic O^{--} deformation is already included in our calculations since it corresponds essentially to a special combination of nearest neighbour force constants between those Cu-O-Cu bonds. The large values found for the Cu-Cu coupling constants λ and δ for the first family support these ideas.

Conclusions. - With our model a realistic calculation of the phonon density of states and the specific heat will be possible. The inclusion of the scattering matrix elements will give the RR spectra. Investigations of the pressure dependence of the RR spectra are in progress and will yield the third order anharmonic contributions to the lattice potential.

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