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Report:

We have measured the local structure around Cu in Cu_2O (cuprite) by Cu-K EXAFS between 20 and 300 K. The measurements were carried out in transmission geometry on several powdered natural high-quality single crystals. Each run was performed in a thermal cycle from 20 K → 300 K → 20 Kin narrow temperature intervalls. In addition high-resolution scans of the near-edge structure were carried out on one sample. Usefull EXAFS-data were obtained up to $k \approx 17$ Å^{-1} for all samples. Thermal hysteresis effects turned out to be weak, if at all they existed.

The temperature dependencies of the Cu-O disorder term, $\sigma^2_{Cu\text{-}O}(T)$, from the linear *nn* Cu-O bonds can be safely attributed to vibrational disorder. $\sigma^2_{Cu\text{-}O}(T)$ is weak and exhibits no significant anomalies. Within the scatter of the data it can be approximated assuming the harmonic motion yielding a Debye-temperature, $\Theta_D > 650$ K.

$\sigma^2_{Cu\text{-}Cu}(T)$ from the *nn* Cu-Cu bonds however behaves completely different. First,

the Cu-sublattice turns out be extremely soft such that the Cu-Cu signal nearly vanishes at 300 K. Second the temperature dependence of the Cu-Cu disorder, $\sigma^2_{Cu\text{-}Cu}(T)$, deviates strongly from the harmonic approximation **exhibiting a staircase-like behaviour with steps centered at 60 K, 110 K, and changes of slope at 160 K and 220 K**. This anomalous temperature behaviour of the Cu-Cu signal was detected from all samples under investigation. Replica of the staircase-like behaviour of the single scattering Cu-Cu signal occur in the multiple scattering signal around R_{eff} = 6.5 Å, which is dominated from nearly co-linear Cu-Cu-Cu three-body configurations, *i.e.* planar hexagonal Cu-sheets perpendicular to (111). The detailed analysis of the data is in progress. Complications in the data analysis arise from interferences of the *nn* Cu-Cu signal with a neigboured Cu-O-Cu signal, and of the nearly co-linear Cu-Cu-Cu three-body configurations with several other multiple scattering configurations.

The Fourier transform spectra yield already evidence on the presence of structural phase transformations in Cu_2O between 20 K and 300 K. Taken the centers of the steps in the Cu-Cu disorder term as critical temperatures, not surprisingly we find coincidence with the anomalous intensity of the forbidden (221) reflex recorded from resonant diffraction [1] between and 60 K and 110 K, and between 150 K and 210 K, the recently reported anomalies in the thermal expansion from powder diffration, and temperature dependent Raman data [2]. Moreover, the critical temperatures coincide with the series of kinks in the electrical conductivity, $\log\sigma$ ($1/T$), and the Hall-effect [3].

It has been suggested [1] that the low temperature phase transition between 60 K and 110 K is of displacive character, tentatively described by the displacement of the more or less rigid Cu- and O-sublattices against each other. The stiffness of the Cu-O bonds and the softness of the Cu-Cu bonds emerging from our preliminary data analysis, however, points to a order-disorder transition in the Cu sublattice. The sequence of characteristic temperatures possibly indicates the formation of commensurate superstructures of the disordered Cu-sublattice.

Literature:

[1] A. Kirfel, K. Eichhorn, HASYLAB Annual Report (1987) and private communication.
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[3] G. Blankenburg, G. Schubert, Annalen der Physik 6. Folge, **12**, 281 (1953).