Local origin of negative thermal expansion in CuCl

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Introduction

In spite of its simple zinc-blende crystal structure, since the 1970s CuCl has attracted considerable experimental and theoretical interest because of its unusual physical properties.

The most striking feature of CuCl is certainly the double-peak structure of the transverse optic (TO) phonon at zone center, which has been extensively studied with all possible experimental techniques. This anomaly has been explained in the framework of a Fermi resonance, arising from anharmonic coupling between the TO mode and a resonant acoustic two-phonon continuum. However, it was also proposed a disorder model, in which Copper ions are assumed to occupy off-center positions. This model was supported - in slightly modified versions - by recent ab-initio studies and theoretical simulations and the question is still matter of intense debate [1]. A decisive and rather conclusive contribution to the off-center problem can be given by our extended x-ray absorption fine structure (EXAFS) measurements.

CuCl is also characterized by a pronounced low-temperature negative thermal expansion (NTE) coefficient [2], the largest among all tetrahedrally bonded crystals. NTE at low temperatures in open fourfold coordinated crystals is attributed to strong relative thermal vibrations perpendicular to interatomic bond (the so-called tension mechanism [3]). However, a quantitative experimental basis of this concept is often lacking. Accurate temperature dependent EXAFS measurements can give insights on the local dynamical origin of NTE: the comparison between perpendicular and parallel mean square relative displacements shows the importance of relative vibrations perpendicular to the bond with respect to the parallel ones.

Experiment

The experiment has been done from 15 to 21 September 2004.

EXAFS temperature dependent measurements on a powdered sample of CuCl have been performed at the K-edge of copper from 6K to 300K. The sample temperature was varied at intervals from 10K at low temperatures to 50K at higher temperatures. To thermalize the sample, the liquid helium cryostat was utilized. Two or three spectra were collected at each temperature, to allow an evaluation of experimental uncertainty.

The beam time allocated was not completely exploited due to problems in the first days with the liquid helium cryostat and the temperature controller: the original research program (measurements up to 500K) was therefore not completed.

Results

Fourier transforms of our EXAFS measurements clarify the off-center question, since they do not show peaks corresponding to the argued off-center single or correlated Cu displacements. The ideal zincblende crystal structure completely explains our EXAFS experimental data.

A quantitative analysis of EXAFS temperature dependent data is performed for the first coordination shell, whose contribution can be neatly isolated and where multiple-scattering effects are absent. The distribution of distances is parameterized in terms of its cumulants and the analysis is performed through the ratio method (separate analysis of phase and amplitude of the filtered EXAFS signal, taking the lowest temperature spectra as reference). While the macroscopic thermal expansion (given, for example, by X-ray diffraction) is negative

in the temperature range of 0-100 K [2], the true bond expansion Cu-Cl (probed by EXAFS) is strongly positive (Fig. 1).

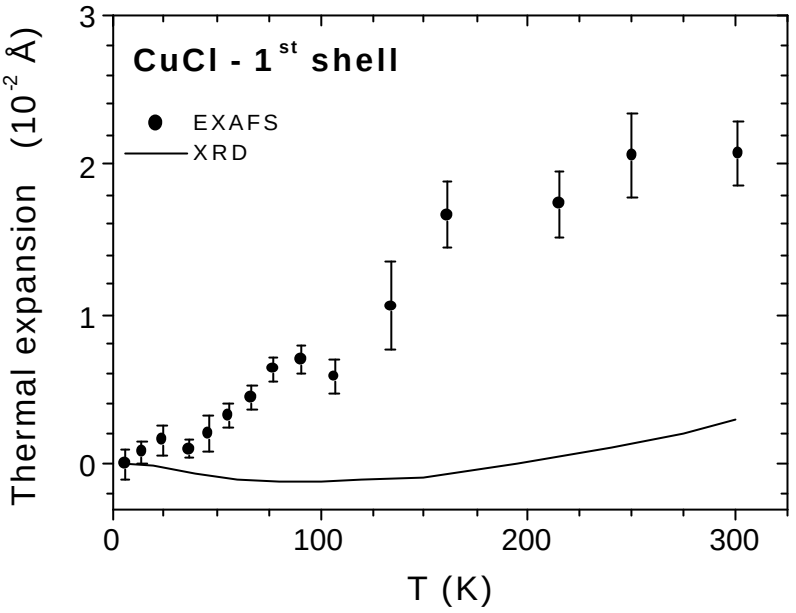

Fig. 1. EXAFS local thermal expansion (full circles) compared to the crystallographic expansion (continuous line)

The ratio between perpendicular and parallel mean square relative displacements (MSRDs) shows a rather strong increase at low temperature and reaches an asymptotic value quite higher than in the case of standard systems such as copper and germanium. This fact confirms the importance in CuCl of the tension effect, which overcomes at low temperature the stretching mechanism and produces the NTE [3]. The Einstein frequency best-fitting the perpendicular MSRD, if compared to the phonon dispersion curves [1], qualitatively indicates that the low-energy TA modes play a more determinant role with respect to the LA and optic modes for the relative atomic motion perpendicular to the bond direction. The unusually high values of the third cumulant confirm the large lattice anharmonicity in CuCl already recognized in literature.

References

[1] Y. Ma et al., Phys. Rev. B 67, 140301 (2003) and references therein
[2] T. H. K. Barron et al., J. Phys. C 10, 1617 (1977)
[3] G. D. Barrera et al., J. Phys.: Condens. Matter 17, R217 (2005)

Proposal number of the experiment

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