EXAFS measurements of local thermal expansion in copper

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Introduction

The influence of temperature on EXAFS amplitude is well known, and the EXAFS Debye-Waller factor has been exploited to gain information on correlation of vibrational motion parallel to the bond direction. Only recently, however, has the possibility been evidenced of obtaining more refined information on correlation perpendicular to the bond direction and on local thermal expansion. [1,2] As a consequence, a deeper insight can be gained on the very meaning of EXAFS parameters (in particular average value and asymmetry of the distance distribution) and their relationship to physical properties of a three-dimensional solid system. To this purpose, it is important to re-calibrate the procedures of EXAFS analysis on systems of well-known structural and dynamical properties. Copper is one of the most obvious candidate materials. The available experimental data on Copper, mainly dating back to pioneering times of EXAFS, were limited to a few temperatures. This proposal aimed at obtaining a set of high quality measurements in a large temperature range, suitable for a refined analysis.

Experiment

The experiment has been done from 13 to 18 November 2002.

Two samples have been used: both were Cu foils 5μm thick, 99.97 % purity (purchased from Goodfellow Ltd), one as rolled, the other annealed at 973 K. The monochromator had Si (311) flat reflecting faces. EXAFS measurements have been performed on both samples in the temperature interval from 4 to 500 K, at steps varying from 5 K at low temperatures to 50 K at high temperatures. The temperature was controlled by the He cryostat at and below 300 K and by the LN-controlled thermostat at and above 300 K.

The quality of each file, checked in real time through a fast but complete data analysis, was good enough to fulfil the requirements of the project. The measurements were apparently free from the random shifts of the energy axis, which bothered a previous experiment on Copper (08-01-290).

Results

The data analysis, based on the cumulant expansion method, has been carried on for the annealed sample, separately considering the first-shell signal and the signal from outer shells. Two different procedures have been used and compared: the first one based on the phenomenological 'ratio method', the second one based on theoretical simulation and non-linear fitting (through the FEFF6 and FEFFIT codes).

The results for the 1st-shell can be summarized as follow:

a) A good agreement is found between the relative values of cumulants obtained through the two different procedures (ratio method and FEFF+FEFFIT).

b) The 2nd cumulant (parallel MSRD) exhibits very regular temperature dependence, well reproduced by a Debye model with the specific heat Debye temperature.

c) The 1st cumulant has very regular temperature dependence, confirming the possibility of detecting distance variations of the order of 0.001 Å. The anomalous behavior at low temperatures, observed in

previous measurements at LURE and ESRF, cannot be confirmed. As expected, the EXAFS thermal expansion is larger than the crystallographic one: the difference has been exploited to get the perpendicular MSRD. The ratio between perpendicular and parallel MSRDs is about 2.5, say larger than the value 2 of a perfectly isotropic system. EXAFS can thus measure the anisotropy of the relative vibrational motion.
d) The 3rd cumulant clearly exhibits the low-temperature quantum deviation from the classical parabolic behaviour. The thermal expansion extracted from the 3rd cumulant differs from both the 1st cumulant and the crystallographic thermal expansion. This means that in principle the crystallographic thermal expansion cannot be obtained from EXAFS; the agreement found for germanium should then be considered a peculiar coincidence.
The experimental relative values of the 1st-shell cumulants are in good agreement with the values recently calculated by means of path-integral Monte Carlo techniques [a].
The results for 2nd, 3rd and 4th shells can be summarized as follow:
a) The temperature dependence of the 2nd cumulant obtained by the ratio method is in good agreement with the more refined analysis based on FEFF+FEFFIT (taking into account multiple scattering effects) and is consistent with a unique Debye temperature (specific heat) for all shells.
b) No significant results have been obtained from the phase analysis by the ratio method.
c) The phase analysis by FEFF+FEFFIT is in progress; meaningful preliminary values of 1st and 3rd cumulants have been obtained at low temperatures.
Only a preliminary 1st-shell analysis has been up-to-now done for the as-rolled sample. Further work is planned, to check the sensitivity of EXAFS to local strains induced by lamination.

Conclusions

EXAFS gives different and complementary information on thermal expansion with respect to Bragg diffraction. From the 1st cumulant difference one gets information on atomic motion perpendicular to the bond direction. The 3rd cumulant has no trivial interpretation. Further work is in progress, in order to: a) complete the analysis of outer shells; b) extend the PIMC calculations to the outer shells; c) better understand the limits of the one-dimensional model based on the effective potential.

References

[1] G. Dalba, P. Fornasini, R. Grisenti, and J. Purans, Phys. Rev. Lett. 82, 4240 (1999).
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Publications

[a] S. a Beccara, G. Dalba, P. Fornasini, R. Grisenti, F. Pederiva, A. Sanson, D. Diop, and F. Rocca: "Local thermal expansion in copper: EXAFS measurements and path-integral Monte Carlo calculations", Phys. Rev. B 68, 140301(R) (2003).

Experiment number: 08-01-617