Local thermal expansion in copper: Extended x-ray-absorption fine-structure measurements and path-integral Monte Carlo calculations

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A combined approach has been used to study thermal effects on the extended x-ray absorption fine-structure (EXAFS) of copper between 4 and 500 K. A phenomenological data analysis shows that the thermal expansions measured from the first and third cumulants significantly differ between each other and from the crystallographic thermal expansion. Path-integral Monte Carlo calculations of EXAFS cumulants have been performed, using a many-body potential. The good reproduction of experimental values validates the phenomenological analysis and opens more perspectives for applications to more complex systems. It is shown that the reproduction of EXAFS parameters allows for a test of the interaction potentials with regard to anharmonicity.

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ity and low-temperature quantum effects. PIMC is based on
the sampling of the thermal density matrix after its factori-
zation into the product of $P$ matrices with effective tempera-
ture $P$ times higher, corresponding to $P$ copies of the system
(slices). The resulting probability distribution is sampled by
means of appropriate generalized Metropolis algorithms. The
PIMC algorithm is exact in the limit $P \to \infty$. The reliability
of PIMC results only depends on the validity of the Born-
Oppenheimer approximation and on the accuracy of the
modeling crystal potential. PIMC can be exploited to con-
struct sets of atomic configurations. Relevant physical ob-
servables, such as cumulants of distance distributions, can be
directly obtained from configurational averages. Besides, the
set of atomic configurations can be used as input for EXAFS
simulations taking into account multiple-scattering paths.

In this Rapid Communication, we present a joint experi-
mental and theoretical study of the EXAFS of copper in the
temperature range from 4 to 500 K. The contribution of the
first coordination shell has been analyzed by a phenomeno-
logical procedure, in order to clarify the relation between
first and third EXAFS cumulants and the CTE. In parallel, a
PIMC simulation has been performed.

Since the available EXAFS data on copper were limited
to a few temperatures, measurements have been made at
the BM08 (Gilda) beamline of ESRF (European Synchrotron
Radiation Facility), Grenoble, using a (311) silicon crystal
monochromator. The sample was a copper foil of 99.97% purity,
5 μm thickness, light tested, and annealed at 973 K
(purchased from Goodfellow Ltd). EXAFS signals were ex-
ttracted from experimental spectra according to well estab-
lished procedures. This choice allows to avoid the pos-
sibility of the first four cumulants $\delta C_i = C_i(T) - C_i(4 K)$ of an
effective distribution $P(r, \lambda) = \rho(r) \exp(-2r/\lambda)/r^2$. The error
bars were evaluated by reasonably varying the parameters of
the analysis procedure and cross comparing the results from
different files measured at the same temperature. The differ-
ce between cumulants $C_i$ of the effective distribution and
the real distribution $\rho(r)$ was significant only for the first one:

$$C_i^* = C_1 + (2 C_2/C_1) (1 + C_1/\lambda). \quad (1)$$

Three different values of $\lambda$ (6, 9, and 12 Å) were used in Eq.
(1), to compensate for neglecting the dependence of $\lambda$ on the
photoelectron wave number.

PIMC simulations were performed on a system of 108
atoms with periodic boundary conditions. The cell parameter
was held fixed at each temperature according to available
crystallographic data. This choice allows to avoid the pos-
sible bias on the crystallographic thermal expansion due to
the choice of the potential, thus permitting to study local
phenomena with higher accuracy. Besides, it considerably
reduces the computational load. The number of slices was
varied with temperature: 8, 64, and 128 slices were found to
guarantee a satisfactory convergence for $T > 200$ K, $40 < T
< 200$ K, and $T < 40$ K, respectively. The sampling method
employed a combination of a single-slice and a multiple-
slice move. In the single-slice move, one or more atoms be-
longing to the same slice are displaced. In the multiple-slice
move, atoms belonging to more than one slice are displaced
at the same time. The single-slice move was performed ac-

FIG. 1. Parallel and perpendicular MSRD for the first shell of
copper: experimental EXAFS results (full circles and diamonds),
correlated Einstein models (dashed lines), and PIMC results (open
circles and diamonds).
measurements (315–343 K). The Einstein frequency was 4.99 THz, corresponding to a second-order force constant $k_0 = 3.24 \text{ eV/Å}^2$ for the potential $V_e(r)$. The parallel MSRD $\langle \Delta u^2 \rangle$, calculated by PIMC as $\langle (r - \langle r \rangle)^2 \rangle$, is shown by open circles in Fig. 1. The low-temperature quantum effect of zero-point energy is well reproduced, contrary to classical MD simulations.\(^{31}\) PIMC values are lower than the Debye model (7% and 1% at 4 and 500 K, respectively), the discrepancy being possibly due to the inadequacy of the Debye model at low temperatures.

In Fig. 2, the temperature dependence of the first EXAFS cumulants (full circles) is compared with the CTE from Ref. 28 (continuous line). The first cumulant $C_1^\gamma$ of the real distribution of distances is to first order connected to the crystallographic expansion $\delta R$ through\(^{5,9}\)

$$C_1^\gamma = R + \langle \Delta u^2 \rangle / 2R. \quad (5)$$

Since the perpendicular MSRD $\langle \Delta u^2 \rangle$ grows with temperature, the EXAFS thermal expansion $\delta C_1^\gamma$ is larger than the CTE $\delta R$. The experimental behavior (full circles) is well reproduced by the $\langle r \rangle$ values calculated by PIMC (open circles). Absolute values of $\langle \Delta u^2 \rangle$ were calculated, as in Ref. 5, by fitting an Einstein model to the relative values $2R(\delta C_1^\gamma - \delta R)$. The perpendicular MSRD values so obtained are shown in Fig. 1 (full diamonds) and compared with the values calculated by PIMC as $\langle \Delta u^2 \rangle - \langle \Delta u^2 \rangle$ (open diamonds). The ratio $\gamma = \langle \Delta u^2 \rangle / \langle \Delta u^2 \rangle$ calculated from PIMC is about 2.7 at high temperature. At high temperature, $\gamma$ should be 2 for a perfect parallel-perpendicular isotropy; a value of 6 was experimentally found for the first shell of germanium.\(^5\)

Let us consider the third cumulant (Fig. 3). Absolute values of $C_3^\gamma$ were obtained by fitting the temperature dependence of the experimental values $\delta C_3^\gamma$ to the quantum analytical expression of Refs. 12 and 13. The third-order force constant of $V_e(r)$ was estimated $k_3 = -1.53 \text{ eV/Å}^3$, and was then used to find the thermal expansion $a = -3k_3C_2^\gamma / k_0$ solely due to the asymmetry of the $V_e(r)$ potential.\(^{12}\) A zero-point value $a_0 = 4.5 \times 10^{-3} \text{ Å}$ was found (it was $3 \times 10^{-3} \text{ Å}$ for germanium).\(^5\). The temperature dependence $\delta a$ is compared with the CTE $\delta R$ in Fig. 4. The slope of $\delta a$ is smaller than the slope of $\delta R$, indicating that the crystallographic thermal expansion is not reproduced by the anharmonicity of the potential $V_e(r)$. The difference between $\delta C_1^\gamma$ and $\delta R$, due to thermal vibrations perpendicular to the bond direction, is connected to a rigid positive shift of the effective potential.\(^5\) The difference between $\delta R$ and $\delta a$ suggests the presence of a further positive shift. The relationship between anharmonicity of the crystal potential and asymmetry of $V_e(r)$ is thus far from trivial even for simple crystals such as copper; the behavior found for germanium, $\delta a = \delta R$, was a peculiar coincidence, and cannot be generalized. The third cumulant calculated by PIMC as $\langle (r - \langle r \rangle) \rangle^3$ is in satisfactory agreement with experimental data, including the finite value extrapolated at $T = 0 \text{ K}$ (open circles in Fig. 3). The sensitivity of PIMC results to the choice of the interaction potential was checked by using a simpler two-body potential\(^{32}\) instead of the many-body potential. While the first and second cumulants were again satisfactorily reproduced, the third cumulant was dramatically smaller than the experimental values (Fig. 3, crossed squares).

In conclusion, accurate temperature-dependent measure-
ments on copper have shown that EXAFS gives different and complementary information on thermal expansion with respect to Bragg diffraction. The first-cumulant difference can be exploited to gain original information on atomic motion perpendicular to the bond direction. The third-cumulant difference indicates that the anharmonicity of the mean-force potential has no trivial interpretation, and the one-dimensional model should be cautiously used when interpreting EXAFS results for systems with many degrees of freedom.

The EXAFS cumulants, calculated by PIMC, were in good agreement with the experimental values. This result, besides representing a validation of the phenomenological first-shell data analysis, opens more perspectives for studying vibrational dynamics not only in crystalline solids (including outer coordination shells) but also in noncrystalline systems. Moreover, the possibility has been demonstrated of offering an additive test of interatomic potentials by means of the reproduction of EXAFS thermal parameters.

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