

Thermal Expansion Behaviour of Silver Examined by Extended X-Ray Absorption Fine Structure Spectroscopy

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Abstract. EXAFS (extended X-ray absorption fine structure) investigations are reported concerning the thermal expansion behaviour of silver in an extended range of temperature from 10 K to about 950 K measured in transmission mode. Both the ratio method and an EXAFS fitting procedure were applied to reveal the temperature dependence of EXAFS parameters. Models based on quantum and classical thermodynamic perturbation theory have been used to interpret experimental data and compared to XRD (X-ray diffraction) results of bulk silver material. The description of thermodynamic data of thermal expansion of silver in the complete range of temperature by EXAFS spectroscopy was successful by first calculations using third order quantum perturbation theory.

Keywords: X-ray absorption, cumulant expansion, thermal expansion, silver.

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INTRODUCTION

The subject of the present work is the discussion of the local thermal properties of bulk Ag as revealed by EXAFS experiments. In principle, anharmonicity in thermal fluctuations can be described by the cumulant expansion method [1,2] for moderately disordered systems. In the cumulant-expansion method the first and second cumulants describe the average value and variance of the atomic pair distribution, whereas higher-order ones, especially C_3 , are a measure of deviations from the Gaussian shape. It should be noted that the sensitivity of the EXAFS oscillations to anharmonic effects gives unique information on the local atomic arrangement, which is of particular importance for characterizing the structure and dynamics of more or less disordered systems. The value of thermal expansion can either be estimated in a direct manner from the Ag-Ag distances, i.e. the first cumulant, or by calculating higher cumulants like C_3 on the basis of a classical approach [3] or a perturbation quantum approach [4-7]. The cumulant expansion approach to EXAFS provides both the theoretical interpretation and the experimental analysis of anharmonic effects. For accurate measurements on different crystals [8] it has been shown that the first cumulant, i.e. the average distance between central and backscattering atom, is usually larger than the distance between the centres of the thermal ellipsoids. In such

cases there are some corrections necessary or the third cumulant has to be used [8] under consideration of the specific crystalline structure. Thus, the thermal expansion of a crystal determined by EXAFS is larger than the real one. However, this can be corrected for by determining and subtracting the contribution of the perpendicular vibrations from the interatomic distance R measured. More detailed information concerning the correlation of vibrations is given elsewhere (e.g., [6]).

This work shows experiments in an extended range of temperature for crystalline silver. That should allow to analyse in detail the different approaches determining the thermal expansion behaviour.

EXPERIMENTAL

Temperature-dependent EXAFS measurements at the Ag K-edge (25.514 keV) were performed at the positron storage ring DORIS III at beam line X1 of HASYLAB (Hamburg, Germany) in transmission mode, utilizing an Si(311) double-crystal monochromator. The sample was a 25 μm thick silver foil with a purity of 99.999 % supplied by Goodfellow. For temperatures from 10 to 300 K a liquid helium vapour flow cryostat was used. Experiments at elevated temperatures in the range from 300 to about 950 K were realized via a self-constructed oven based on resistance heating.

THEORY AND DATA ANALYSIS

EXAFS data were processed by means of the program package UWXAFS 3.0 [9], including background subtraction, Fourier transformation of the extracted EXAFS oscillations into real space and subsequent fitting with theoretical amplitude and phase functions obtained from the FEFF 7/8 code. For fitting of the experimental data, in addition to the interatomic distance and the Debye- Waller factor σ^2 , the third and fourth cumulants, i.e. C_3 and C_4 , were also taken into account. Moreover, in addition to EXAFS fits the ratio method (cf., e.g., [1,2] was applied to get an independent measure of the Debye-Waller factor that is identical with C_2 and C_3 cumulant. In terms of the cumulants C_i the EXAFS function $\chi(T, k_E)$ including the contributions of all atoms has been used. Hence, the EXAFS oscillations can be summarized as

$$\chi(T, k_E) = A(T, k_E) \sin[\Phi(T, k_E)] \quad (1)$$

with $A(T, k_E)$ and $\Phi(T, k_E)$ being the amplitude and phase function, respectively.

The evaluation of cumulant parameters as a result of EXAFS experiments was carried out on the basis of classical and quantum statistics. Using classical-statistical perturbation theory [3] should allow

$$\begin{aligned} \alpha(T) &= \frac{1}{r} \frac{d\langle r(T) \rangle}{dT} \\ &\approx \lambda \frac{3k_B}{r_0 k^2} \frac{z \ln(z)}{(1-z)^2} \left[1 - \gamma \frac{\hbar\omega}{k^2} \left(\frac{23(1+z)}{(1-z)} - \frac{3(1+z(4+z)) \ln(z)}{(1-z)^2} \right) + \lambda^2 \frac{15\hbar\omega}{2k^3} \left(\frac{3(1+z)}{(1-z)} - \frac{(1+z(4+z)) \ln(z)}{(1-z)^2} \right) \right] \end{aligned} \quad (6)$$

The results of second-order perturbation in comparison with the path-integral method are given already [10].

RESULTS AND DISCUSSION

Applying UWXAFS, fitting of EXAFS parameters was performed in real space between 1.8 Å and 4 Å, i.e. for the 1st and 2nd Ag-Ag coordination spheres. The energy shift of the Ag K-edge was determined only once by a fit of the 10 K spectrum and kept fixed for all higher temperatures. For this purpose, the theoretical amplitudes and phase functions used were calculated by means of FEFF. In order to improve the agreement between experiment and fit several different fitting runs were carried out. The best agreement resulted when the anharmonicity

explanation of the behavior at high temperatures up to the melting point.

In this work, the quantum statistical approach was considered in detail. With the Hamiltonian

$$H = H_0 + H_1 \quad (2)$$

the perturbation expansion of the density matrix $\rho(\beta)$ was calculated up to third order using

$$\rho(\beta) = \rho_0(\beta) - \int_0^\beta d\beta' \rho_0(\beta - \beta') H_1 \rho(\beta') \quad (3)$$

with $\rho_0(\beta) = \exp(-\beta H_0)$ and $\beta = (k_B T)^{-1}$.

A one-dimensional oscillator model was used. The Harmonic oscillator

$$H_0 = \hbar\omega(a^+ a + \frac{1}{2}) \quad (4)$$

was considered with an anharmonic perturbation

$$V_1(x) = -\lambda x^3 + \gamma x^4 \quad (5)$$

with

$$x = r(T) - r_0.$$

Then the temperature dependence of the first four moments of x and the respective cumulants were calculated. Here, it should be stated that the resulting formula of the thermal expansion $\alpha(T)$ was only developed for third order perturbation theory. That gives:

parameters C_3 obtained by the ratio method were chosen as starting values for fitting.

Considering the nearest-neighbour distances of Ag in a silver foil as determined by EXAFS from 10 to about 950 K, the data show slightly larger values than that of corresponding X-ray diffraction (XRD) data of single-crystal silver [11]. This could be attributed to the effect of thermal vibrations perpendicular to the bond direction of the atom pair treated, but this will not be discussed here.

In the next step, the experimentally fitted parameters of cumulants (C_1, C_2, C_3, C_4) for all temperatures measured were taken to find the best agreement with the anharmonic potential function. This gives the parameters k , λ and γ for this one-dimensional potential. The agreement of experimental and theoretical data is given for one example in Fig. 1.

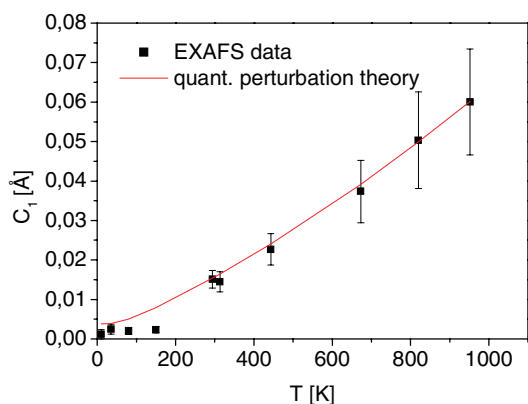


FIGURE 1. Comparison of experimental EXAFS data with the fit by means of third-order perturbation theory.

Finally, the applicability of classical and perturbation quantum approaches to the thermal expansion behaviour of crystalline silver structures has been investigated. In order to do this, the thermal expansion coefficient was calculated with the fitted potential parameters by means of corresponding equations. The results were compared with well known XRD data (see Fig. 2 and 3).

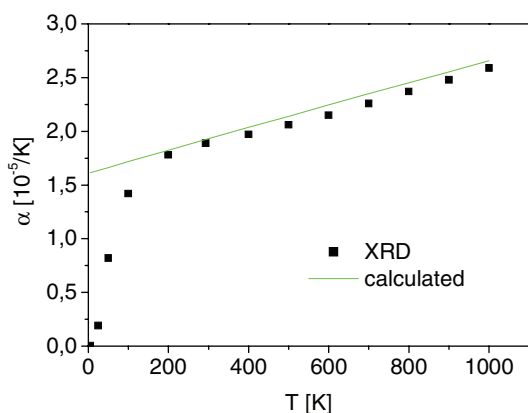


FIGURE 2. Results of classical statistics and the XRD parameters.

These results show the expected outcome that the classical approach describes the high temperature range only. However, the increase of the expansion coefficient required the consideration of third-order perturbation.

Using the quantum approach it could be shown that the low temperature range (0 – 200 K) can be fitted in any case of order of perturbation calculations. However, using first and second order perturbation there was found always strong differences with respect to the XRD data. Only in the case of third-order

perturbation by means of eqn. (6) a sufficient agreement could be established. That means, that on the one side strong anharmonic vibrations exist in the high-temperature range. On the other side, it could be demonstrated that third-order perturbation is reliable in the complete temperature range.

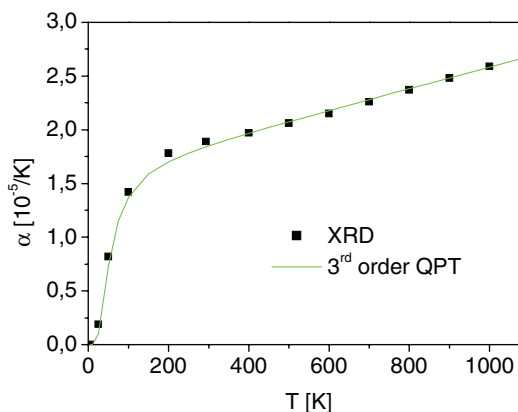


FIGURE 3. XRD data and the calculated function for third-order perturbation theory using eqn. (6).

Earlier investigations of Ag expansion by EXAFS [12,13] were restricted to a limited range of temperature by using the classical approach for calculating cumulants. An other possibility to fit the high-temperature range is given by the path-integral method [10].

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