Thermal expansion and interatomic potentials of silver revealed by extended x-ray absorption fine structure spectroscopy using high-order perturbation theory

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Extended x-ray absorption fine structure investigations are reported concerning the thermal expansion behavior of silver in a wide range of temperatures from 10 to about 950 K as measured in the transmission mode. Models based on the quantum and classical thermodynamic perturbation theory are used to interpret the experimental data and compared to x-ray diffraction results of the crystalline silver material. To this aim, the third- and fourth-order perturbation formulas of the cumulants and of the thermal expansion coefficient have been developed by means of the quantum-statistical theory and are presented here. By using these formulas, the thermal expansion of silver bonds can be described by the temperature-dependent first cumulants as well as by an anharmonic potential function in correlation with the cumulant expansion in the complete range of temperatures.

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I. INTRODUCTION

Extended x-ray absorption fine structure (EXAFS) spectroscopy represents a sensitive method to characterize the local atomic structure as well as the dynamics of crystalline and disordered systems.^{1,2} Improving the accuracy of experiments allows one to precisely determine the parameters estimated on the basis of x-ray absorption spectroscopy (XAS), such as interatomic distances, coordination numbers, as well as the parameters of the corresponding static and thermal disorder. This yields information on anharmonicity effects and, thus, on the local thermal expansion by means of temperature-dependent experiments. In order to interpret the experimental results, the cumulant expansion method^{3,4} was developed with respect to the anharmonicity in thermal fluctuations for moderately disordered systems. In the cumulant expansion method, the first and second cumulants describe the average values of the interatomic distance and of the variance of the atomic pair distribution, usually under the assumption of a Gaussian radial distribution. In addition, the higher-order cumulants as the third and fourth-order ones reflect the deviations from the Gaussian shape. Especially, the third cumulant, i.e., the mean cubic relative displacement, represents the asymmetric distribution of distances that can be related to thermal expansion. It was found that the third and fourth cumulants of the nearest-neighbor distance distribution are quite significant, even at elevated temperatures.^{3,4}

The evaluation of cumulant parameters as a result of EXAFS experiments has been performed on the basis of classical and quantum statistics. The classical-statistical perturbation theory⁵ allows us to explain the behavior at high temperatures (HTs), especially, at and above the melting transition, but not at low temperatures (LTs). In the present work, the quantum-statistical approach will be applied in detail in order to include the whole range of the solid states of the respective material. The classical results can serve to examine the quantum-mechanical calculations at the high-temperature limit. The quantum-statistical theory that uses first-order perturbation was developed by several authors to

find out correlations to EXAFS data by means of vibrational potentials.^{6–10} The extension by the second-order perturbation was represented by Yokoyama,¹¹ who discussed the EXAFS cumulants C_1 – C_4 as well as the thermal expansion for diatomic and linear triatomic systems. It was demonstrated that the first- and second-order perturbation theory is insufficient to appropriately describe the anharmonicity at higher temperatures. Nevertheless, the cumulant expansion has been widely applied successfully for bulk materials and for surfaces too (see, e.g., Refs. 12–16).

On the basis of the cumulant expansion, the interesting thermal expansion should be available from the temperature dependence of the first and third cumulants if the asymmetry of the distribution of interatomic distances is caused by thermal expansion only.^{6,7,17,18} However, it was argued¹³ that the expansion coefficient determined from the difference of interatomic distances is limited by the accuracy of the EXAFS phase. This is a disadvantage for calculations that use the temperature dependence of the first cumulant. Moreover, several authors who investigated crystalline structures found out that the first cumulant of EXAFS data is usually larger than the distances of the corresponding structure determined by x-ray diffraction (XRD).^{15,16} One reason for this behavior should be the mean-squared vibrational disorder perpendicular to the line between the average position of the observed pair of atoms in the scattering process of photoelectron waves^{15,16,19–21} as a result of x-ray absorption. Therefore, a comparison of distance parameters determined by EXAFS spectroscopy to corresponding crystallographic data should provide additional information on the vibrational behavior of materials.

Several investigations of the thermal expansion as a function of the temperature dependence of the third-order cumulant have been performed for different crystalline lattices, e.g., Ge, Cu, Kr, AgI, CuBr, and CdSe. The data evaluation showed that the values of thermal expansion are partly similar to the crystallographic data as well as deviations thereof.^{15,16,18,21–24} To interpret the differences that are observable with respect to diffraction data, one has to consider thermal atomic vibrations in relation to the crystal structure

and the bond directions. Also, the combination of EXAFS data and x-ray powder diffraction data of Cu_2O and Ag_2O yielded negative thermal expansions.²⁵ Because of these various results, thorough experiments have to be carried out in combination with the evaluation of theoretical models in order to describe the thermal disorder of crystalline materials in detail.

It should be noted here that the path-integral effective potential theory is another quantum-statistical approach for calculating EXAFS cumulants.^{11,26–28} This method is advantageous for large anharmonic systems and many-atom compounds. However, the main disadvantage is its incorrect estimation of the third cumulant in the low-temperature range, i.e., for temperatures less than 100 K. Thus, this method is not reliable for strong quantum systems.

In this work, we present EXAFS investigations of polycrystalline silver in a wide temperature range from 10 to 950 K, i.e., the data comprise nearly the complete range of the solid states of silver. That should allow a detailed test of the theoretical models that interpret the temperature-dependent EXAFS data by the cumulant expansion, in particular, with respect to the thermal expansion of local interatomic distances. Earlier EXAFS investigations of bulk Ag and supported silver nanoparticles were restricted by a limited range of temperatures and by using the classical approach for calculating the cumulants.^{29–32} Some authors have estimated the thermal expansion directly from the first cumulants. Nevertheless, most of the thermal expansion coefficients for several temperatures are in good agreement with the data in literature. However, the data cannot describe the whole range of temperatures without considering quantum effects, in particular, in the low-temperature range.

The idea of this work and some first results were already presented in a short contribution.³³ Here, the complete theoretical calculations are represented and the parameters of the anharmonic potential function are determined by a simultaneous fit of the whole EXAFS scans. After this outline of the motivation, in Sec. II, the theoretical background is given with the extension of cumulant expansion to third- and fourth-order perturbation in connection with an effective pair potential of fourth order. Section III represents the experimental procedures and details of data analysis. In Sec. IV, the data acquisition at the Ag *K*-edge and the corresponding evaluation procedure is described. Finally, the results obtained by means of the third- and fourth-order perturbation and the potential functions are discussed in Sec. V.

II. THEORY

A. Path-by-path approach

The standard theory of x-ray absorption is based upon a curved-wave multiple-scattering formalism.² In the path-by-path approach,³⁴ the oscillatory part in the x-ray absorption coefficient follows from

$$\chi(T, k) = \text{Im} \sum_{\Gamma} N_{\Gamma} S_0^2(k) \frac{f_{\text{eff}}^{\Gamma}(k)}{k} e^{2i\delta_c(k)} \left\langle \frac{e^{2ikr} e^{-2r/\lambda(k)}}{r^2} \right\rangle, \quad (1)$$

where both multiple-scattering and curved-wave effects are included. The sum in Eq. (1) is about all nonequivalent paths

Γ with length $r_{\Gamma} \equiv 2r$ and degeneration N_{Γ} . The quantity $f_{\text{eff}} = |f_{\text{eff}}| \exp(i\varphi)$ in Eq. (1) is the effective scattering amplitude for path Γ . Here, δ_c is a phase shift due to the interaction of the excited photoelectron with the absorber. The inelastic electron scattering is described by the photoelectron mean free path λ . The quantity S_0^2 in Eq. (1) takes into account the many-body effects of the excitation process.

The angular brackets $\langle \dots \rangle$ in Eq. (1) denote the thermal average for a finite temperature T . The evaluation of the temperature dependence of EXAFS requires the evaluation of the ensemble average over a canonical ensemble defined by the Hamiltonian H of the system. In many cases of interest, the vibrations of atoms are described by a harmonic oscillator where the oscillatory part in Eq. (1) of EXAFS is multiplied by a Debye–Waller factor that gives

$$\chi(T, k) \approx \sum_{\Gamma} \chi^{\Gamma}(k; \langle r \rangle) \exp[-2k^2 \sigma_{\Gamma}^2(T)]. \quad (2)$$

Instead of the effective path length r introduced in Eq. (1), the effective thermal average value $\langle r \rangle$ of path Γ appears. Note that in EXAFS the vibrations of atoms and their displacements are correlated. The thermal average value of the effective n -leg path with scatters at $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n$ is given by

$$\langle r \rangle = \frac{1}{2} \left\langle \sum_{i=0}^n |\mathbf{R}_{i+1} - \mathbf{R}_i| \right\rangle, \quad (3)$$

where $\mathbf{R}_{n+1} = \mathbf{R}_0$ (absorber position). A finite temperature T leads to displacements $\mathbf{u}(T)$ from the equilibrium positions $\mathbf{R}^0$ of atoms with $|\mathbf{u}| \ll R^0$. Therefore, the distance between two atoms i and j at a finite temperature T is approximately given by

$$|\mathbf{R}_i - \mathbf{R}_j| \approx R_{ij}^0 + \mathbf{u}_{ij} \cdot \mathbf{e}_{ij} + \frac{|\mathbf{u}_{ij} \times \mathbf{e}_{ij}|^2}{2R_{ij}^0}, \quad (4)$$

where the vector $\mathbf{e}_{ij}$ is a unit vector parallel to the vector connecting atoms i, j . The vector $\mathbf{u}_{ij}$ is the relative displacement of two atoms. Concerning only linear terms in $\mathbf{u}_{ij}$ in Eq. (4) and single-scattering contribution in Eq. (1), we get the well-known relation for the first coordination shell within the harmonic approximation $\sigma^2 = \langle (\mathbf{u}_{10} \cdot \mathbf{e}_{10})^2 \rangle$. In case of multiple scattering, we have to take into account multiple-correlation effects.³⁴

B. Cumulant expansion

Going back to the EXAFS fundamental formula [Eq. (1)], the thermal average extending beyond the harmonic approximation can be carried out with cumulant expansion.³⁵ By using the definition

$$\langle e^{2ikr} \rangle = \exp \left[\sum_{n=1}^{\infty} \frac{(2ik)^n}{n!} C_n \right], \quad (5)$$

the cumulants C_n can be expressed in dependence on the moments $\langle r^n \rangle$ of a statistical distribution,

$$\begin{aligned}
C_1 &= \langle r \rangle \equiv R(T), \\
C_2 &= \langle (r - C_1)^2 \rangle \equiv \sigma^2(T), \\
C_3 &= \langle (r - C_1)^3 \rangle, \\
C_4 &= \langle (r - C_1)^4 \rangle - 3C_2^2.
\end{aligned} \tag{6}$$

It should be noted that the moments C_2 , C_3 , and C_4 are defined about $\langle r \rangle$, the average effective radial distance of path Γ at temperature T .

Following the proposal given in Ref. 35, we may now calculate the mean value in Eq. (1). Assuming that the difference $a \equiv r - R$ is small in comparison to λ and R , we get from Taylor series expansion the following approximation:

$$\left\langle \frac{e^{2ikr} e^{-2r/\lambda}}{r^2} \right\rangle \approx e^{2ikR} \left[\langle e^{2ika} \rangle - \left(\frac{2}{\lambda} + \frac{2}{R} \right) \frac{1}{2i} \frac{d}{dk} \langle e^{2ika} \rangle \right] \frac{e^{-2R/\lambda}}{R^2}. \tag{7}$$

Using $\langle e^{2ika} \rangle = \langle e^{2ikr} \rangle e^{-2ikR}$ and the cumulant expansion [Eq. (5)], we get $\frac{d}{dk} \langle e^{2ika} \rangle \approx -4kC_2 \langle e^{2ika} \rangle$; therefore,

$$\left\langle \frac{e^{2ikr} e^{-2r/\lambda}}{r^2} \right\rangle \approx \langle e^{2ikr} \rangle e^{-2ikC_2(2/R+2/\lambda)} \frac{e^{-2R/\lambda}}{R^2}. \tag{8}$$

In the last step, we have used the approximation $1 + \Delta \approx \exp(\Delta)$ if $|\Delta| \ll 1$. Sometimes the first and second factors in Eq. (8) are related to the cumulant expansion [see Eq. (5)] and give a different first cumulant in the form of an effective distribution,¹⁸

$$C'_1 = C_1 - \frac{2C_2}{R} \left(1 + \frac{R}{\lambda} \right). \tag{9}$$

Now, the contribution of each path to the oscillatory part in the EXAFS equation [cf. Eq. (1)] at temperature T can be written in the form³⁵

$$\chi(T, k) = \sum_{\Gamma} A_{\Gamma}(T, k) \sin \Phi_{\Gamma}(T, k), \tag{10}$$

where the phase of the path contribution is given by

$$\Phi(T, k) = 2k \left[R - \frac{2C_2}{R} \left(1 + \frac{R}{\lambda} \right) \right] - \frac{4}{3} k^3 C_3 + \varphi(k) + 2\delta_c, \tag{11}$$

and its amplitude by

$$A(T, k) = \frac{NS_0^2 |f_{\text{eff}}(k)|}{kR^2} \exp \left(-\frac{2R}{\lambda} - 2k^2 C_2 + \frac{2}{3} k^4 C_4 \right). \tag{12}$$

In principle, the cumulants C_n may be determined with the help of a reference system (ratio method) from EXAFS experiments.

In this paper, the analysis of EXAFS data is restricted to the first coordination shell, wherein multiple-scattering effects are negligible. In this case, the cumulants C_1 – C_4 defined in Eq. (6) may be expressed by the equilibrium distance R^0 and the relative displacement vector $\mathbf{u}(T)$ between the

absorbing atom and the scattering atoms in the first coordination shell [see Eq. (4)]. Neglecting cross correlations between $u_{\parallel}$ and $u_{\perp}$ and taking into account that $|\mathbf{u}| \ll R^0$, we may calculate the cumulants of the first coordination shell in the following way:

$$C_1 = R(T) \approx R^0 + \langle u_{\parallel} \rangle + \frac{\langle u_{\perp}^2 \rangle}{2R^0} \equiv L(T) + \frac{\langle u_{\perp}^2 \rangle}{2R^0},$$

$$C_2 = \sigma^2(T) \approx \langle u_{\parallel}^2 \rangle - \langle u_{\parallel} \rangle^2,$$

$$C_3 \approx \langle u_{\parallel}^3 \rangle - \langle u_{\parallel} \rangle^3 - 3\langle u_{\parallel} \rangle C_2,$$

$$C_4 \approx \langle u_{\parallel}^4 \rangle + 3\langle u_{\parallel} \rangle^4 - 3(C_2)^2 + 6C_2 \langle u_{\parallel} \rangle^2 - 4\langle u_{\parallel}^3 \rangle \langle u_{\parallel} \rangle. \tag{13}$$

Within the harmonic approximation, all cumulants with $n > 2$ are zero. It should be noted that the quantity $R(T)$ in EXAFS theory and experiment is different from the distance measured in XRD experiments because of the correlated motion of atoms and the effect of vibrations perpendicular to the atomic bond direction treated. Within the one-dimensional model of vibrations (Einstein model), we set $\langle u_{\perp}^2 \rangle = \gamma \langle u_{\parallel}^2 \rangle$ and consider γ as an additional parameter.

C. Quantum-mechanical effects

In order to discuss quantum-mechanical and anharmonic effects, we have calculated the ensemble average in Eq. (1) and the related cumulants of the first shell in Eq. (13) within the quantum-statistical perturbation theory. Therefore, we consider an effective one-dimensional potential $V(x)$, where x now means the parallel displacement $u_{\parallel}$ between two atoms ($u_{\parallel} = \mathbf{e}_{ij} \cdot \mathbf{u}_{ij}$) in the sample.

First, we take into account the influence of anharmonic contributions on a one-dimensional harmonic oscillator given in the form

$$V(x) = V_0 + \frac{K}{2} x^2 - bx^3 + cx^4, \tag{14}$$

where K , b , and c are constants. Within the perturbation theory, the anharmonic contributions in Eq. (14) are considered as a small perturbation of the harmonic oscillator with the Hamiltonian $H_0 = \hbar \omega_E (a^{\dagger} a + 1/2)$, where a and $a^{\dagger}$ are the annihilation and creation operators. As well known, the operator of the anharmonic perturbation $H_1 = -bx^3 + cx^4$ is written in terms of the operators a and $a^{\dagger}$ by using $x = \sigma_0 (a + a^{\dagger})$ with $\sigma_0 = \sqrt{\hbar / 2m\omega_E} = \sqrt{\Theta_E / 2K}$, where we have defined the quantity $\Theta_E \equiv k_B T_E = \hbar \omega_E$. Within this picture, the vibration of two atoms at the temperature T is assumed as a single one-dimensional oscillator of frequency ω_E (Einstein model), where m is the reduced mass of both atoms and T_E is the Einstein temperature.

In quantum-statistical mechanics, all information about a system in equilibrium at a finite temperature T is given by the statistical operator $\rho = \exp(-\beta H)$, where $\beta = (k_B T)^{-1}$. The average value of an observable F follows from

$$\langle F \rangle = \frac{\text{Tr } \rho F}{\text{Tr } \rho}, \quad (15)$$

where Tr is the trace of the operator. If the Hamiltonian H of the system is close to H_0 , i.e., $H = H_0 + H_1$, we may obtain an approximation to ρ that is close to $\rho_0 = \exp(-\beta H_0)$, as shown by Feynman,³⁶

$$\rho(\beta) = \rho_0(\beta) - \int_0^\beta d\beta' \rho_0(\beta - \beta') H_1 \rho(\beta'). \quad (16)$$

The last term in Eq. (16) is small if the contribution of the perturbation H_1 is small. In this case, we can use an approximate $\rho(\beta')$ to obtain a much more accurate approximation to $\rho(\beta)$ and so on.

Within the perturbation theory, the moments $\langle x^n \rangle$ follow from the eigenstates of the harmonic oscillator H_0 and the well-known properties of the operators a and $a^\dagger$ in these states.³⁷ We have expanded these calculations up to the fourth order of the perturbation theory in order to explain the experimental data with very high accuracy. The perturbation order $\nu = m + n$ of the following terms is related to the exponents m and n of the constants b and c of the considered potential in Eq. (14), respectively. Here, the calculated terms are represented up to the third-order perturbation theory for $L(T)$, $C_2(T)$, and $C_4(T)$ and to the fourth-order perturbation theory for $C_3(T)$, which were sufficient to describe the experimental data with high accuracy. Furthermore, the high-temperature approximations are given, as denoted by the superscript HT, where we have introduced the quantity $\Theta \equiv k_B T$. Within our calculations, we get

$$\begin{aligned} L(T) = & R^0 + b \frac{3\Theta_E}{2K^2} \frac{1+z}{1-z} - bc \frac{\Theta_E^2}{2K^4} \left[\frac{31+z(94+31z)}{(1-z)^2} - \frac{18z(1+z)\ln z}{(1-z)^3} \right] + b^3 \frac{3\Theta_E^2}{2K^5} \left[\frac{11+z(38+11z)}{(1-z)^2} - \frac{15z(1+z)\ln z}{(1-z)^3} \right] \\ & + bc^2 \frac{9\Theta_E^3}{8K^6} \left[\frac{(1+z)[187+z(996+187z)]}{(1-z)^3} - \frac{4z[64+z(183+64z)]\ln z}{(1-z)^4} + \frac{12z(1+z)[1+z(8+z)]\ln^2 z}{(1-z)^5} \right] \pm \dots, \\ L^{(HT)} = & R^0 + b \frac{3}{K^2} \Theta - bc \frac{96}{K^4} \Theta^2 + b^3 \frac{135}{K^5} \Theta^2 + bc^2 \frac{4752}{K^6} \Theta^3 \pm \dots, \end{aligned} \quad (17)$$

$$\begin{aligned} C_2(T) = & \frac{\Theta_E}{2K} \frac{1+z}{1-z} - c \frac{3\Theta_E^2}{2K^3} \left[\frac{(1+z)^2}{(1-z)^2} - \frac{2z(1+z)\ln z}{(1-z)^3} \right] + b^2 \frac{\Theta_E^2}{4K^4} \left[\frac{13+z(58+13z)}{(1-z)^2} - \frac{30z(1+z)\ln z}{(1-z)^3} \right] \\ & + c^2 \frac{3\Theta_E^3}{8K^5} \left[\frac{5(1+z)[7+z(20+7z)]}{(1-z)^3} - \frac{12z[8+z(21+8z)]\ln z}{(1-z)^4} + \frac{12z(1+z)[1+z(8+z)]\ln^2 z}{(1-z)^5} \right] \\ & - b^2 c \frac{3\Theta_E^3}{8K^6} \left[\frac{(1+z)[275+z(1976+275z)]}{(1-z)^3} - \frac{12z[71+z(209+71z)]\ln z}{(1-z)^4} + \frac{60z(1+z)[1+z(8+z)]\ln^2 z}{(1-z)^5} \right] \\ & - c^3 \frac{9\Theta_E^4}{8K^7} \left[\frac{4(1+z)^2[37+z(176+37z)]}{(1-z)^4} - \frac{z(1+z)[535+z(2072+535z)]\ln z}{(1-z)^5} + \frac{12z\{6+z[93+z(205+93z+6z^2)]\}\ln^2 z}{(1-z)^6} \right. \\ & \left. - \frac{4z(1+z)(1+z\{38+z[144+z(38+z)]\})\ln^3 z}{(1-z)^7} \right] \pm \dots, \end{aligned}$$

$$C_2^{(HT)} = \frac{1}{K} \Theta - c \frac{12}{K^3} \Theta^2 + b^2 \frac{36}{K^4} \Theta^2 + c^2 \frac{384}{K^5} \Theta^3 - b^2 c \frac{3924}{K^6} \Theta^3 - c^3 \frac{19008}{K^7} \Theta^4 \pm \dots, \quad (18)$$

$$\begin{aligned} C_3(T) = & b \frac{\Theta_E^2}{2K^3} \frac{1+z(10+z)}{(1-z)^2} - bc \frac{3\Theta_E^3}{4K^5} \left[\frac{(1+z)[17+z(224+17z)]}{(1-z)^3} - \frac{12z[2+z(9+2z)]\ln z}{(1-z)^4} \right] \\ & + b^3 \frac{3\Theta_E^3}{8K^6} \left[\frac{(1+z)[41+z(680+41z)]}{(1-z)^3} - \frac{60z[2+z(9+2z)]\ln z}{(1-z)^4} \right] \\ & + bc^2 \frac{\Theta_E^4}{16K^7} \left[\frac{4717+z\{92\,234+z[215\,994+z(92\,234+4717z)]\}}{(1-z)^4} - \frac{180z(1+z)[68+z(497+68z)]\ln z}{(1-z)^5} \right] \end{aligned}$$

$$\begin{aligned}
& + \frac{216z(2+z\{49+z[124+z(49+2z)]\})\ln^2 z}{(1-z)^6} \Big] - b^3 c \frac{3\Theta_E^4}{16K^8} \left[\frac{5483+z\{134\,182+z[333\,174+z(134\,182+5483z)]\}}{(1-z)^4} \right. \\
& - \frac{36z(1+z)[572+z(4483+572z)]\ln z}{(1-z)^5} + \frac{360z(2+z\{49+z[124+z(49+2z)]\})\ln^2 z}{(1-z)^6} \Big] \\
& - bc^3 \frac{3\Theta_E^5}{32K^9} \left[\frac{5(1+z)(15\,035+z\{378\,526+z[1\,265\,526+z(378\,526+15\,035z)]\})}{(1-z)^5} \right. \\
& - \frac{12z(23\,215+z\{310\,531+z[668\,432+z(310\,531+23\,215z)]\})\ln z}{(1-z)^6} \\
& + \frac{144z(1+z)(97+z\{3564+z[13\,435+z(3564+97z)]\})\ln^2 z}{(1-z)^7} \\
& \left. - \frac{144z\{2+z[187+z(1712+z\{3404+z[1712+z(187+2z)]\})\}\ln^3 z}{(1-z)^8} \right] \pm \dots, \\
C_3^{(HT)} &= b \frac{6}{K^3} \Theta^2 - bc \frac{504}{K^5} \Theta^3 + b^3 \frac{864}{K^6} \Theta^3 + bc^2 \frac{42\,912}{K^7} \Theta^4 - b^3 c \frac{206\,064}{K^8} \Theta^4 - bc^3 \frac{4\,084\,992}{K^9} \Theta^5 \pm \dots, \tag{19}
\end{aligned}$$

$$\begin{aligned}
C_4(T) &= -c \frac{3\Theta_E^3}{4K^4} \left[\frac{(1+z)[1+z(8+z)]}{(1-z)^3} - \frac{12z^2 \ln z}{(1-z)^4} \right] + b^2 \frac{3\Theta_E^3}{8K^5} \left[\frac{(1+z)[5+z(104+5z)]}{(1-z)^3} - \frac{60z^2 \ln z}{(1-z)^4} \right] \\
& + c^2 \frac{9\Theta_E^4}{16K^6} \left[\frac{(1+z)^2[29+z(304+29z)]}{(1-z)^4} - \frac{12z(1+z)[4+z(55+4z)]\ln z}{(1-z)^5} + \frac{24z^2[5+z(16+5z)]\ln^2 z}{(1-z)^6} \right] \\
& - b^2 c \frac{9\Theta_E^4}{16K^7} \left[\frac{237+z\{5930+z[15\,482+z(5930+237z)]\}}{(1-z)^4} - \frac{4z(1+z)[92+z(1613+92z)]\ln z}{(1-z)^5} \right. \\
& + \frac{120z^2[5+z(16+5z)]\ln^2 z}{(1-z)^6} \Big] - c^3 \frac{3\Theta_E^5}{32K^8} \left[\frac{(1+z)(3707+z\{59\,310+z[133\,046+z(59\,310+3707z)]\})}{(1-z)^5} \right. \\
& - \frac{12z(861+z\{13\,803+z[29\,524+3z(4601+287z)]\})\ln z}{(1-z)^6} + \frac{432z(1+z)(1+z\{82+z[371+z(82+z)]\})\ln^2 z}{(1-z)^7} \\
& \left. - \frac{144z^2(19+z\{230+z[492+z(230+19z)]\})\ln^3 z}{(1-z)^8} \right] \pm \dots,
\end{aligned}$$

$$C_4^{(HT)} = -c \frac{24}{K^4} \Theta^3 + b^2 \frac{108}{K^5} \Theta^3 + c^2 \frac{2016}{K^6} \Theta^4 - b^2 c \frac{25\,488}{K^7} \Theta^4 - c^3 \frac{171\,648}{K^8} \Theta^5 \pm \dots. \tag{20}$$

The first and second-order terms agree with the results published by Frenkel *et al.*⁷ and by Yokoyama,¹¹ respectively. In the HT and LT cases, the quantity $z = \exp(-\Theta_E/\Theta)$ has to be replaced by $z \approx 1 - \Theta_E/\Theta$ and $z \approx 0$ in Eqs. (17)–(20), respectively. The last line in Eqs. (17)–(20) represents the HT case corresponding to the results of Stern *et al.*⁵

The linear thermal expansion coefficient $\alpha(T)$ follows from the definition

$$\alpha(T) = \frac{1}{L(T)} \frac{dL(T)}{dT}. \tag{21}$$

In the classical (HT) limit within the lowest-order perturbation theory, the thermal expansion coefficient may be written in the form^{5,38}

$$\alpha^{(HT)}(T) \cong \frac{1}{TR^0} \frac{C_3}{2C_2} = b \frac{3k_B}{R^0 K^2}. \tag{22}$$

This formula was generalized by Frenkel *et al.*⁷ to the LT case but only within the first order. We have calculated $\alpha(T)$ by using Eq. (21) and a higher-order perturbation theory,

$$\alpha(T) = b \frac{3k_B}{R^0 K^2} \frac{z \ln^2 z}{(1-z)^2} \left[1 - c \frac{\Theta_E}{K^2} \left(\frac{23(1+z)}{(1-z)} - \frac{3[1+z(4+z)] \ln z}{(1-z)^2} \right) \right. \\ \left. - b \frac{3\Theta_E}{2R^0 K^2} \frac{(1+z)}{(1-z)} \left[1 - c \frac{\Theta_E}{3K^2} \left(\frac{4[25+z(58+25z)]}{(1-z)(1+z)} - \frac{9[1+z(6+z)] \ln z}{(1-z)^2} \right) \right] \right] \pm \dots \quad (23)$$

III. EXTENDED X-RAY ABSORPTION FINE STRUCTURE MEASUREMENTS AND DATA ANALYSIS

A. Extended x-ray absorption fine structure measurements

Temperature-dependent EXAFS measurements at the Ag *K*-edge (25.514 keV) were performed at the positron storage ring DORIS III at beamline X1 of HASYLAB (Hamburg, Germany) in the transmission mode, by utilizing a Si(311) double-crystal monochromator with an energy resolution of $\Delta E/E \cong 2 \times 10^{-4}$. Harmonic rejection was achieved by detuning the monochromator crystals by 50%. The x-ray intensities were measured by means of ionization chambers. The sample was a 25 μm thick silver foil with a purity of 99.999% and was supplied by Goodfellow. For temperatures from 10 to 300 K, a liquid helium vapor flow cryostat equipped with an electric heater was used, wherein the temperature was monitored by a thermocouple mounted on the sample holder. Experiments at elevated temperatures in the range from 300 to about 950 K were realized via a self-constructed oven based on resistance heating. Here, during the XAS measurements, the temperature was measured near the wire windings and controlled by the electric power. The specimen temperature was adjusted with a certainty of approximately ± 3 K by using a calibration curve that had been previously recorded.

B. Extended x-ray absorption fine structure data analysis

1. Phase difference and amplitude ratio method

As a first analysis procedure, the ratio method (cf., e.g., Refs. 3, 4, and 39) was applied to determine the relative variation in C_1 – C_4 by separate analyses of phase and amplitude of the EXAFS data. Here, the first coordination will be considered. Therefore, the contributions of multiple scattering effects can be neglected and the ratio method allows us to determine the cumulants in a more straightforward way than the fitting procedures.¹³ The following equations were derived under the assumption that for two data sets Φ_T and $\Phi_{\text{ref}}(T_1)$, the quantities $f(k, \pi)$, S_0^2 , and $\varphi(k)$ are the same at all temperatures.

By considering Eqs. (11) and (12) and truncating the cumulant expansion at the fourth cumulant, the following expression can be found for the difference of the corresponding phase functions divided by $2k$:

$$\frac{\Phi_T(T) - \Phi_{\text{ref}}(T_1)}{2k} = \Delta C_1' - \frac{2}{3} k^2 \Delta C_3 \\ \cong \Delta R - \frac{\Delta C_2}{R(T)} \left(1 + \frac{R(T)}{\lambda(T)} \right) - \frac{2}{3} k^2 \Delta C_3, \quad (24)$$

where the indices T and ref are labels for the temperature T and the reference temperature T_1 , respectively, at which the Ag sample is investigated. As reference, we have taken spectra at the lowest temperature ($T_1 \cong 10$ K). Hereby, the difference $\Delta\lambda = \lambda(T) - \lambda_{\text{ref}}$ gives the contribution of the second order in comparison to ΔR or ΔC_2 and may be neglected. Similarly, the logarithm of the EXAFS amplitude ratio is

$$\ln \left[\frac{A_T(T)}{A_{\text{ref}}(T_1)} \right] = \ln \left[\frac{N_T R_{\text{ref}}^2}{N_{\text{ref}} R_T^2} \right] - 2k^2 \Delta C_2 + \frac{2}{3} k^4 \Delta C_4. \quad (25)$$

Usually, the cumulant coefficients C_3 and C_4 of the reference spectrum taken at the lowest temperature are set to zero or can be calculated by fitting procedures. Plotting both the logarithmic amplitude ratio and the phase difference divided by $2k$ versus k^2 and subsequently fitting the resulting graphs yield the variation ΔC_2 and ΔC_3 , respectively. The change in a possible cumulant C_4 is available by a plot versus k^4 or by a fit of Eq. (25) and $\Delta C_1'$ from the vertical intercept of Eq. (24) at $k^2=0$. By means of these procedures, the relevance of higher cumulants can be easily checked. Thus, the ratio method is a relatively simple method for calculating the EXAFS parameters at a certain temperature, which then can also be used in combination with fitting procedures as demonstrated in the following.

2. Temperature-independent data analysis using the cumulant method

In addition, EXAFS data were processed by means of the program package UWXA3.0,³⁴ including background subtraction, normalization, Fourier transformation of the extracted EXAFS oscillations into real space, and subsequent fitting with theoretical amplitude and phase functions obtained from the FEFF7.01 code (cf., e.g., Ref. 40). As usual, the EXAFS signal was extracted by assuming the photoelectron binding energy E_0 at the maximum of the first derivative of the spectrum. For fitting of the experimental data, in addition to the interatomic distance R and the Debye–Waller factor σ^2 , the third and fourth cumulants, i.e., C_3 and C_4 , were also taken into account. The cumulant values C_1 – C_4 were obtained by separately fitting the experimental spectra for each temperature by using the FEFFIT code.⁴¹ Thus, the influence of any fixed correlations on the resulting EXAFS

parameters, e.g., the assumption of a constant thermal expansion coefficient in the whole temperature range, can be excluded.

The experimental EXAFS is a sum of single-scattering and multiple-scattering contributions of form (1), including three-body and many-body correlation functions. The contribution of the first shell of atoms can be extracted from the measured total EXAFS by conventional Fourier-transform techniques, i.e., by transforming into r space, isolating of the first shell of atoms through a window function, and inverse Fourier transformation into k space again. Absolute values of the parameters of interest like N , R , C_2 , C_3 , and C_4 can be obtained by fitting the experimentally recorded first-shell contribution in k or r space with the theoretical amplitude and phase functions from the FEFF7 code as input. For that purpose, the low-temperature data of crystallographic distances⁴³ were used as the reference for the FEFF program. Corresponding results of a silver foil are given below, where the normalized spectra $\chi(T, k)$ weighted by k^2 were Fourier transformed by using a Hanning window function (k from 2.6 to 18 $\text{\AA}^{-1}$) and subsequently fitted in real space between 1.4 and 3.6 $\text{\AA}$. The energy shift of the Ag K -edge was determined by a fit of the 10 K spectrum and kept fixed for all higher temperatures.

It should be pointed out that the distance $R(T)$ fitted from EXAFS data is not equivalent to the distance R_{XRD} due to correlation effects and to the effect of vibrations perpendicular to the treated atomic bond direction. According to^{21,42}

$$R_{\text{XRD}} \approx R(T) - \frac{\langle u_{\perp}^2 \rangle}{2R^0} \approx L(T), \quad (26)$$

we may get information about the correlated motion of atoms if we compare the XRD and EXAFS measurements. Within our model calculations, we consider the approximation $\langle u_{\perp}^2 \rangle = \gamma \langle u_{\parallel}^2 \rangle$, where γ is considered as a parameter. Often $\gamma=2$ is used, which is applicable to isotropic crystal systems.^{19,20,23}

3. Simultaneous, temperature-dependent data analysis using the force constants

As a third procedure, a fitting model that includes the temperature dependence of the anharmonic force constants was used according to Eq. (14). Therefore, ten EXAFS spectra from 10 to 952 K were simultaneously fitted with the cumulants from the third- and fourth-order perturbation theory written in terms of the force constants K , b , and c [Eqs. (17)–(20)]. By following this procedure, all of the experimental data for all temperatures were simultaneously included after Fourier transformation in the r range between 1.4 and 3.6 $\text{\AA}$. By constraining the four cumulants for each temperature to a generalized parameter set of three force constants, the number of parameters is significantly reduced compared to the separate fitting of four cumulants for ten different temperatures. This simultaneous fitting increases the number of independent points and also provides a consistent set of parameters over a broad range of temperatures that can be used to interpret the macroscopic properties. In this case, the parameter γ calculated from the temperature-

FIG. 1. Fourier transforms of the EXAFS oscillations of silver measured between 10 and 952 K.

independent analysis was included in the fit procedure. Therefore, we can compare the temperature-dependent fit results directly to the values for R_{XRD} and α obtained from XRD measurements.⁴³

IV. RESULTS

By using a liquid helium vapor flow cryostat and an oven, respectively, Ag K -edge extended fine structures were taken from a thin silver foil in two different runs, one for temperatures from 10 K to room temperature (RT) and subsequently another from RT up to about 950 K. After energy alignment of all raw-data spectra, where the maximum of the first derivative of the 10 K spectrum was chosen as the Ag K -edge onset, the data evaluation was performed as described before. Figure 1 shows the corresponding Fourier transforms of the experimentally obtained EXAFS oscillations of silver in an r range from 0 to 6 $\text{\AA}$, including the first Ag-Ag coordination sphere. Obviously, the amplitudes of these curves decrease with increasing temperature owing to a rise of the Debye-Waller factor of enhanced lattice vibrations.

To determine the higher-order cumulants, all EXAFS spectra were analyzed via the ratio method. In detail, for each temperature, the EXAFS oscillations of solely the first Ag-Ag shell was extracted from the radial distribution function through inverse Fourier filtering in the r range from 1.4 to 3.6 $\text{\AA}$. The corresponding amplitude and phase functions were subsequently related to those of the 10 K spectrum in accordance to Eqs. (24) and (25). In Fig. 2 the graphs of the logarithmic ratio of the amplitude functions and of the difference of the phase functions multiplied by $1/2k$ can be seen, which were used to determine the ΔR , ΔC_2 and of the ΔC_3 cumulants for temperatures from 10 to 952 K by applying the corresponding ratios.

The evaluation of ΔC_4 according to Eq. (25) showed that this cumulant is extremely small. Neither the plot versus k^4 nor the fit of the equation yield parameters that significantly differ from zero. That means the cumulant C_4 can be neglected according to the ratio method. The Ag-Ag distances

FIG. 2. Determination of the C_2 and C_3 cumulants for temperatures from 10 to 952 K by applying the ratio method: (A) the logarithm of the ratio of the amplitude functions and (B) difference of the phase functions multiplied by $1/2k$. The dashed lines represent the exemplary fit functions for three temperatures.

ΔR (ratio) has been estimated by the intercept of the straight lines calculated from Eq. (24). However, the determined parameters show differences from the parameters resulting from the fit procedure up to 0.4% by a fluctuation around these values. Hence, the ΔR values of the ratio procedure do

not show a sufficient accuracy that is necessary for further data evaluation with respect to thermal expansion. The reasons for this uncertainty should be the limited accuracy in the EXAFS phase calculation in general and, especially, the entailed difficulties to find the best k range for the fit by straight lines by using the ratio method. In order to get the absolute values of the Debye–Waller factors by means of the ΔC_2 data as a result of the first-order polynomial fit, the parameter $C_2 = 0.00266 \text{ Å}^2$ resulting from the separate fit of the 10 K spectrum was taken as low-temperature equilibrium value. The value of C_3 was assumed to be zero at 10 K in a good approximation. The Debye–Waller factors from the ΔC_2 and third-order cumulants ΔC_3 found by linear fits of the logarithmic amplitude ratios and differences of phase functions, respectively, for k^2 from 25 to 100–300 are listed in Table I together with the EXAFS parameters C_1 , C_2 , C_3 , and C_4 obtained from the below-mentioned fit.

UWEXAFS fitting was performed in real space between 1.4 and 3.6 Å, i.e., for the 1st Ag–Ag coordination spheres, to determine the first four cumulants. 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, theoretical amplitude and phase functions were calculated by means of FEFF7.1 for the first scattering path. In order to improve the agreement between experiment and fit, several different fit runs were carried out, including separate fits of single spectra recorded at a certain temperature as well as simultaneous fits of a spectral series from low to high temperatures with constant energy shift E_0 and amplitude S_0^2 . The best agreement resulted when the anharmonicity parameters C_3 obtained by the ratio method were chosen as the starting values for fitting. The cumulants from this fit are listed in Table I. In Fig. 3, the experimental Fourier transforms of the Ag K -edge EXAFS oscillations were compared to the corresponding fits to the 10, 294, and 952 K data. These exemplary fits are part of a simultaneous fit series with constant E_0 (−0.5 eV) and S_0^2 (0.98), resulting in a goodness-of-fit parameter (P-factor, see Ref. 41) of 0.0105 for the whole series. The parameter γ was derived from EXAFS data of C_1 , C_2 and compared to XRD results⁴³ by using

TABLE I. Cumulant parameters as a result of EXAFS data evaluation by means of fit procedure and by the ratio method.

T (K)	R (fit) (Å)	C_2 (fit) (10^{-2} Å^2)	C_2 (ratio) (10^{-2} Å^2)	C_3 (fit) (10^{-3} Å^3)	C_3 (ratio) (10^{-3} Å^3)	C_4 (fit) (10^{-4} Å^4)
10	2.8809 ± 0.0050	0.266 ± 0.043	0.266 ± 0.000	0.00 ± 0.04	0.00 ± 0.01	0.00 ± 0.06
35	2.8811 ± 0.0040	0.273 ± 0.035	0.291 ± 0.017	0.00 ± 0.03	0.02 ± 0.01	0.00 ± 0.05
80	2.8819 ± 0.0029	0.358 ± 0.027	0.408 ± 0.059	0.00 ± 0.03	0.02 ± 0.03	0.00 ± 0.04
150	2.8827 ± 0.0028	0.503 ± 0.028	0.524 ± 0.012	0.00 ± 0.03	0.03 ± 0.03	0.00 ± 0.05
294	2.8929 ± 0.0029	0.999 ± 0.040	0.989 ± 0.015	0.20 ± 0.05	0.26 ± 0.03	0.02 ± 0.12
313	2.8956 ± 0.0031	1.236 ± 0.046	1.151 ± 0.016	0.31 ± 0.06	0.31 ± 0.12	0.28 ± 0.14
443	2.9065 ± 0.0045	1.677 ± 0.079	1.499 ± 0.033	0.67 ± 0.11	0.79 ± 0.12	0.51 ± 0.31
673	2.9257 ± 0.0060	2.352 ± 0.115	2.141 ± 0.020	1.59 ± 0.22	1.08 ± 0.45	0.73 ± 0.61
820	2.9364 ± 0.0083	2.909 ± 0.163	2.776 ± 0.549	2.33 ± 0.41	1.98 ± 0.63	1.06 ± 1.24
952	2.9477 ± 0.0077	3.410 ± 0.149	3.186 ± 0.958	3.25 ± 0.43	2.91 ± 0.38	1.68 ± 1.28

FIG. 3. Comparison of the Fourier transforms of the Ag K -edge EXAFS at 10, 294, and 952 K to corresponding fits (dashed lines) of the cumulants C_1 – C_4 by using the FEFF code.

Eq. (26) and the relation $\langle u_{\perp}^2 \rangle = \gamma \langle u_{\parallel}^2 \rangle$. That yields an average value of $\gamma = 2.2 \pm 0.7$ for the whole temperature range.

Additionally, the EXAFS spectra measured between 10 and 952 K were simultaneously fitted by using three free parameters to determine the anharmonic force constants. There are two for the force constants b and c and one for the Einstein temperature T_E . The force constant K was replaced with T_E with the relation $K = mT_E^2 k_B^2 / \hbar^2$ because of the necessity to use $z = \exp(-T_E/T)$ for the temperature-dependent fitting. The parameters E_0 and S_0^2 were set to be constant as a result of UWXAFS fitting at 10 K as described before. As for the temperature-independent fit, the EXAFS scans were analyzed in real space between 1.4 and 3.6 Å. The best fit values for the force constants were $b = 1.38 \pm 0.10$ eV/Å³ and $c = 0.25 \pm 0.02$ eV/Å⁴; and for the Einstein temperature, $T_E = 168.35 \pm 1.46$ K, resulting in a force constant $K = 2.72$ eV/Å². This Einstein temperature is in good agreement with the thermodynamic data of $T_E = 165$ – 170 K.^{44,45} The cumulants C_1 – C_4 calculated from these parameters are listed in Table II. Representative fits to the 10, 294, and 952 K data are shown in Fig. 4. The simultaneous temperature-dependent fits resulted in a goodness-of-fit parameter $P \leq 0.0602$.

TABLE II. Cumulant parameters calculated from the temperature-dependent fit of the force constants with the results: $K = 2.72$ eV/Å² ($T_E = 168.35$ K), $b = 1.38$ eV/Å³, and $c = 0.25$ eV/Å⁴.

T (K)	L (Å)	C_2 (10 ⁻² Å ²)	C_3 (10 ⁻³ Å ³)	C_4 (10 ⁻⁴ Å ⁴)
10	2.8784	0.269	0.007	0.00
35	2.8785	0.274	0.008	0.00
80	2.8796	0.347	0.023	0.00
150	2.8826	0.543	0.078	0.02
294	2.8901	1.022	0.322	0.16
313	2.8912	1.089	0.367	0.19
443	2.8987	1.560	0.763	0.48
673	2.9133	2.432	1.787	1.27
820	2.9235	3.007	2.589	1.82
952	2.9332	3.527	3.336	2.16

V. DISCUSSION

A. Results of ratio method and fit procedure

As a first step, the EXAFS parameters resulting from the ratio method and the fit process should be discussed. Com-

FIG. 4. Comparison of the Fourier transforms of the Ag K -edge EXAFS at 10, 294, and 952 K to the results of simultaneous temperature-dependent fits (dashed lines) of the potential parameters K , b , and c .

FIG. 5. Ag-Ag first-shell atomic distances as a function of temperature: (■) XRD measurements (Ref. 43), (●) EXAFS parameters C_1 fitted by means of FEFF, (○) EXAFS parameters L according to Eq. (13) with $\gamma=2.2$, (—) EXAFS parameters fitted with pair potential by using the third order quantum perturbation theory (QPT) (Eq. (17)), (·····) temperature dependence of L calculated with the first order QPT, and (---) temperature dependence of L calculated with the second-order QPT.

paring both approaches, the results of cumulants C_2 and C_3 are in a reasonably good agreement taking into consideration the uncertainty of both methods. The EXAFS data of the first and the fourth cumulants used for further discussion were only available from the fit procedure. This is attributed to a large variation in the first cumulant and to small values of C_4 by applying the ratio method, which do not allow a further detailed evaluation. Thus, the use of the ratio method sensitively depends on the range of parameters as well as on the existence of clear straight lines in the corresponding plots. It should be noted here that the presented accuracy of the ratio parameters have been estimated by variations in the data evaluation to find out the possible range of parameters. On the other hand, the uncertainty of fitted data corresponds to the statistical error of the fit procedure.

In Fig. 5, the first cumulant of EXAFS data of Ag K -edge spectra of a silver foil (cf. Table I) as determined by EXAFS from 10 to about 950 K is compared to the corresponding XRD data of single-crystalline silver.⁴³

As already mentioned above, despite of the uncertainty of EXAFS analysis, the Ag-Ag distance $R(T)$ is always larger than the distance between the centers of probability functions measured by XRD. As can be seen in Fig. 5, this difference in the distances increases at higher temperatures. This effect was already observed for several crystalline compounds.^{15,16} This difference in bond lengths compared to XRD measurements can be attributed to the influence of thermal vibrations perpendicular to the bond direction of the atom pair treated.^{18,20,24,46} Therefore, the parameter γ has been determined by Eq. (26). That allows the calculation of the quantity $L(T)$ as a result of EXAFS experiments, which can be discussed in relation to the Ag-Ag bond length R_{XRD} .^{21,42} The present investigations of the crystalline Ag lattice yield the value $\gamma=2.2 \pm 0.7$. This result is similar to those obtained by EXAFS spectroscopy¹⁸ and theoretical considerations⁴⁶ of Cu, which shows a fcc structure like that of silver. Fornasini *et al.*¹⁸ estimated for Cu a ratio between 2 and 3 in a tem-

perature range up to 500 K by means of x-ray absorption spectroscopy. The authors explained this behavior by a slight parallel-perpendicular anisotropy that showed a factor of 2.7 in agreement with path-integral Monte Carlo calculations.²⁸ Vila *et al.*⁴⁶ reported a factor between 2.17–2.5 calculated on the basis of density functional theory. For Ag, such calculations are not available, but similar results are expected because it has a fcc structure too.

In Fig. 5, the EXAFS results for $L(T)$ determined for Ag as described in Sec. IV are represented together with the crystallographic distances as determined by XRD. The results in Fig. 5 demonstrates that the EXAFS values fairly well match the XRD curve within the whole temperature range considering the uncertainty of experimentally determined parameters. These results show that the EXAFS measurements allow the determination of the lattice parameters of the silver fcc structure in spite of the constraints of the theoretical model used, e.g., the neglect of cross correlations between parallel and perpendicular vibrations as well as of terms on the order of $(R^0)^{-2}$. Especially, at temperatures near the melting point of the material, such approximations are completely valid.

The results of thermal expansion based on the first cumulants of EXAFS parameters are strongly influenced by the quality of the experiments as well as by the theoretical interpretation of the x-ray absorption process in order to get the $L(T)$ values. Considering the first point, the experiments with pure polycrystalline metal foils such as Ag as used here should give nearly perfect results. However, besides the experimental accuracy, the contributions of the linear terms of the EXAFS phase [see Eq. (11)], the calculation of $L(T)$ from $C_1(T)$ and the effect of the k dependence of the mean free path of electrons with respect to thermal expansion have to be taken into consideration.^{4,13} The second point is related to the shift of C_1 due to the perpendicular relative displacements as discussed before. The precise calculation of this effect requires further investigations and theoretical considerations as mentioned above. In spite of these circumstances, the results of Ag presented here demonstrate that the principal dependence of $L(T)$ within the whole temperature range can be derived by EXAFS experiments under the given assumptions. Therefore, the overall behavior of the thermal expansion can be determined by the first cumulant.

The third and the fourth cumulants should allow description of the anharmonic vibrations of the lattice. The data evaluation showed that the third cumulant C_3 cannot be neglected, whereas the effect of the C_4 values is much less. Without considering C_3 , the data evaluation does not yield the correct temperature dependence of the lattice parameters. The existence of positive values of C_3 could be confirmed by the ratio method also in the low-temperature interval (10–150 K), whereas the fit results showed a larger uncertainty in this range. The evaluation of the third cumulant with regard to the expansion behavior requires the use of a potential function in combination with a statistical approach that will be given in Sec. V B.

Earlier EXAFS analysis of temperature-dependent Ag data in the range between 30 and 360 K by using the cumulant-expansion analysis of Refs. 29 and 30 showed a good agreement between the EXAFS cumulants and lattice

parameters for some certain temperatures. Furthermore, it was also found that the values of C_4 are quite small or can be similarly neglected in our results. Possible corrections due to the vibrational behavior have not been discussed.

B. Third and fourth-order perturbation and potential functions

In the next step, the experimental x-ray absorption data are interpreted by a one-dimensional effective pair potential as displayed by Eq. (14) to describe the thermal expansion behavior. That can be realized by a fit of the parameters K , b , and c on the basis of the experimentally determined cumulants L , C_2 , C_3 , and C_4 or by simultaneously fitting the entire EXAFS spectra within the first coordination shell as represented in the present work. Here, the cumulants were calculated by using the third- and fourth-order quantum perturbation theory because of failures of lower-order perturbation at elevated temperatures for other materials¹¹ and because of our own calculations that used first-order perturbation for Ag. All of these evaluations of EXAFS data demonstrated that low-order perturbation cannot adequately describe the high-temperature range of thermal expansion. The investigations presented here regard the extended temperature range up to 950 K. Therefore, the expected deviations between EXAFS parameters and crystalline distances should be more pronounced. First calculations using the results of temperature-dependent cumulants data to estimate the force constants were already reported.³³

Now, these calculations were simultaneously continued and complemented by the fits of the entire EXAFS scans in real space. Thus, a stronger correlation between the experimental spectra and the potential parameters should be achieved. Third- and fourth-order perturbation terms were considered in the calculation of the cumulants L , C_2 , C_3 , and C_4 .

The data evaluation demonstrates that these different orders of perturbations have to be included to sufficiently describe the experimental cumulants. This is due to alternating signs of higher-order terms as well as different powers with respect to the temperature [see Eqs. (17)–(20)]. However, it can be shown that already the second term of third-order contributions is always rather small and can be neglected.

Hence, the terms up to T^2 for C_1 , up to T^3 for C_2 , and up to T^4 for C_4 have to be considered. In addition, for C_3 [Eq. (19)], it was necessary to also take into account the fourth-order perturbation terms to compensate more or less for the large positive values of the third-order terms. This results in two extra terms, but like before, the second one is insignificant. So all contributions up to T^4 were used for C_3 .

The results in Figs. 5–8 indicate reasonable good agreement of temperature-dependent fitted cumulants L , C_2 , C_3 , and C_4 with the EXAFS cumulants calculated with potential parameters by means of Eqs. (17)–(20) within the uncertainty of the experimental data. Consequently, the third- and fourth-order perturbation theory is sufficient to describe the temperature dependence of EXAFS cumulants and the thermal expansion in a wide temperature range. The use of the theoretical model for the cumulants allows discussion of the differences between lower-order perturbation and the pre-

FIG. 6. Ag-Ag first-shell C_2 values as a function of temperature: (●) EXAFS parameters C_2 fitted by means of FEFF, (—) EXAFS parameters C_2 fitted with pair potential by using the third order QPT [Eq. (18)], (·····) temperature dependence of C_2 calculated with the first order QPT, and (— · —) temperature dependence of C_2 calculated with the second-order QPT.

sented quantum-statistical approach of third- and fourth-order perturbation. The different results of theoretical calculations are given in Figs. 5–9, which demonstrate clear differences, especially, at elevated temperatures. In addition, the calculations indicate a contribution of C_4 that cannot be neglected. However, the corresponding values of C_4 are very small. For that reason, the evaluation of experimental spectra could not give an unambiguous proof for these cumulants.

The presented results clearly demonstrate that only the extension to higher-order perturbation enables the reflection of the complete range of temperature-dependent EXAFS data. The behavior of the theoretically calculated cumulants shows only slight variations with increasing orders of perturbations for $L(T)$ and $C_2(T)$. Therefore, and because of the reasonable agreement with experimental results, it is not necessary as well as not useful to further increase the order of perturbation. Furthermore, it should be considered that such

FIG. 7. Ag-Ag first-shell C_3 values as a function of temperature: (●) EXAFS parameters C_3 fitted by means of FEFF, (—) EXAFS parameters C_3 fitted with pair potential by using the fourth-order QPT [Eq. (19)], (·····) temperature dependence of C_3 calculated with the first order QPT, (— · —) temperature dependence of C_3 calculated with the second-order QPT, and (— — —) temperature dependence of C_3 calculated with the third order QPT.

FIG. 8. Ag-Ag first-shell C_4 values as a function of temperature: (●) EXAFS parameters C_4 fitted by means of FEFF, (—) EXAFS parameters C_4 fitted with pair potential by using the third order QPT [Eq. (20)], (·····) temperature dependence of C_4 calculated with the first order QPT, and (— · —) temperature dependence of C_4 calculated with the second-order QPT.

discussions demand the inclusions of two additional orders in each case because of the alternating signs of terms and the increasing power of temperatures [see Eqs. (17)–(20)]. These effects already cause distinct variations at low-order perturbations for $C_3(T)$ and are more pronounced for $C_4(T)$, as presented in Figs. 7 and 8. This result was obtained before by Yokoyama *et al.*¹¹ for second-order perturbation. For those reasons and because of the accuracy of the C_3 and C_4 data reflecting their relatively small contribution to the EXAFS signal, the use of further developments of perturbation theory does not yield more detailed information.

The next point is the calculation of the thermal expansion coefficient in dependence of the temperature by means of Eq. (23) and using the estimated force constants. The results in Fig. 9 demonstrate that for the whole range of temperature,

FIG. 9. Ag-Ag first-shell thermal expansion coefficients as a function of temperature: (■) XRD measurements, (Ref. 43), (●) EXAFS parameters calculated with the classical HT limit [Eq. (22)] by using experimental EXAFS data C_2 and C_3 , (—) EXAFS parameters fitted with pair potential by using the third order QPT [Eq. (23)], (·····) temperature dependence calculated with the first order QPT, and (— · —) temperature dependence calculated with the second-order QPT.

the thermal expansion determined by XRD experiments can be reasonably described by means of third- and fourth-order perturbation. For comparison, the lower-order quantum perturbation results and the classical high-temperature approximation of Eq. (22) that corresponds to the result of classical statistics are also represented. The classical high-temperature approximation data were calculated by means of experimental EXAFS cumulants. These plots show that the first-order quantum perturbation approach sufficiently reflect the low-temperature range up to approximately 100–120 K. The observed deviations at higher temperatures can only be eliminated by third- and fourth-order considerations. The high-temperature limit of the lowest order of classical statistics calculations displays a nearly constant expansion parameter above 400 K and strong differences to the real expansion coefficients in this temperature range. However, these differences can be removed, of course, in the high-temperature range only, by using higher perturbations in classical statistics,⁵ as shown for silver in our previous work.³³

With these results, EXAFS spectroscopy allows the description of the macroscopic and the local thermal expansion of silver or Ag-Ag bonds, respectively, in the extended temperature range as observed here by means of the temperature-dependent first-order cumulants and by an anharmonic potential function calculated with higher cumulants. The comparison of potentials or force constants determined by means of quantum-statistical theory that uses third-order perturbation shows some differences if a fit of the whole scan was applied instead of a fit of EXAFS cumulants for all temperatures.³³ However, there are large differences in force constants in the case of the classical-statistical theory.³¹

The presented discussions and conclusions can be confirmed by results on other materials. So, for RbBr, it could be shown that the quantum case in first-order perturbation can be used for 30 and 125 K.⁷ This is due to the low temperature in which this approximation is still valid. Nevertheless, differences could be already found between XRD results for experiments in the room-temperature range and above if the data were recorded at small intervals of temperature, e.g., for Cu.¹⁸ This indicates the use of higher-order perturbations. The classical high-temperature approximation by means of Eq. (22) has often been used for the estimation of thermal expansion coefficients (see, e.g., Ref. 13). The present results show that this use of cumulants C_2 and C_3 enables to extract the expansion parameters in well-defined temperature ranges only. Earlier investigations of Ag expansion in the high-temperature range by EXAFS³¹ were carried out by using the classical approach of cumulants. Therefore, the whole temperature dependence could not be described. Another possibility to fit the high-temperature range is given by the path-integral method,^{11,26–28} but no results are known for silver crystals from this method.

VI. CONCLUSION

EXAFS investigations are reported concerning the thermal expansion behavior of silver in the range from 10 to about 950 K, where both the ratio method and an EXAFS fitting procedure were applied to reveal the whole tempera-

ture dependence of the mean nearest-neighbor atomic distances, the Debye–Waller factors C_2 and the third- and fourth-order cumulants C_3 and C_4 describing the deviation of the thermal vibrations from harmonicity. The overestimation of the first cumulant in the EXAFS analysis in comparison with real Ag-Ag distances can be attributed to the effect of vibrations perpendicular to the line of atom bonding under investigation. It is shown that this vibrations perpendicular to a given Ag-Ag bond of the fcc lattice gives deviations in the isotropic case. The real temperature dependence of bond lengths can be sufficiently described if this effect has been considered in data evaluation by the parameter $\gamma = 2.2 \pm 0.7$.

The thermal expansion coefficient based on higher cumulants allows description of the extended temperature range between 10 and 952 K if the quantum statistics in third- and fourth-order perturbation is calculated in combination with an anharmonic potential function of the fourth order. Other models that use lower-order perturbations or classical approximations are valid only in limited temperature ranges. The reliability of a potential function derived from EXAFS

experiments is improved when the whole EXAFS scans are included into the fit procedure. Further refinements of the presented EXAFS data evaluation are related to the precision of experimental x-ray absorption results and to the extension of theoretical considerations.

The results for the crystalline silver lattice presented here allow determination of both the local and the macroscopic expansion behaviors. It seems possible to extend such investigations of bulk crystals to composites and nanoscaled materials.

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¹See, for example, *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES*, edited by D. C. Konigsberger and R. Prins (Wiley, New York, 1988), and references therein.

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