Anharmonicity and thermal expansion in crystalline germanium

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K-edge EXAFS has been measured in c-Ge from 10 to 600 K. The first-shell contribution has been analyzed by the cumulant method. A resolution better than 10^{-3} Å in the relative values of the 1st cumulant has allowed an accurate study of thermal expansion. For the first time the ratio between perpendicular and radial correlation terms has been experimentally evaluated and low temperature quantum effects in the 3rd cumulant have been observed.

1. Introduction

The direct extraction of thermodynamical parameters, like thermal expansion, from EXAFS spectra is complicated by the effects of thermal vibrations normal to the bond direction and the spherical nature of the photoelectron wave and its mean free path.

Let R be the distance between the centres of the thermal ellipsoids of absorber and backscatterer atoms, whose variation with temperature gives the thermal expansion. The instantaneous interatomic distances r are distributed according to a *real* unidimensional distribution $\rho(r)$, whose cumulants will be denoted by C_i^*. EXAFS samples an *effective* distribution $P(r,\lambda) = \rho(r)\exp(-2r/\lambda)/r^2$ (λ is the photoelectron mean free path), whose cumulants will be denoted by C_i.

The three quantities R, C_1^* and C_1 are connected, to first order, through the equation (Dalba *et al.*, 1998)

$$C_1 = \underbrace{R + \frac{\langle \Delta u_\perp^2 \rangle}{2R}}_{C_1^*} - \frac{2\langle \Delta u_\parallel^2 \rangle}{R}\left(1 + \frac{R}{\lambda}\right) \quad (1)$$

where $\langle \Delta u_\parallel^2 \rangle$ and $\langle \Delta u_\perp^2 \rangle$ are the radial and perpendicular components, respectively, of the average relative thermal displacement of absorber and backscatterer atoms: $\langle \Delta u^2 \rangle = \langle \Delta u_\parallel^2 \rangle + \langle \Delta u_\perp^2 \rangle$ The *radial* component (MSRD) corresponds to a good approximation to the 2nd cumulant, $\langle \Delta u_\parallel^2 \rangle \simeq C_2$, and can be obtained from experimental data, while the *perpendicular* component $\langle \Delta u_\perp^2 \rangle = C_\perp$ cannot be experimentally obtained without an independent knowledge of R.

Low temperature quantum effects, which are currently taken into account in the 2nd cumulant (MSRD), are in principle present also in the 3rd cumulant (Frenkel & Rehr, 1993), and can affect the experimental determination of its absolute values.

To study anharmonicity effects on a thermodynamically well known system, EXAFS measurements have been made on c-Ge in the temperature range from 10 to 600 K and the 1st-shell contribution has been analyzed by a purely phenomenological approach, minimizing theoretical inputs.

The attention has been focused on two topics: a) the correlation of atomic vibrations normal to the bond direction, b) quantum effects on the 3rd cumulant.

2. Experiment and data analysis

EXAFS measurements have been done at the beam line D42 of LURE (Orsay, France). Electron-beam energy and average current were 1.8 GeV and 200 mA, respectively. The monochromator was a Si (331) channel-cut crystal. The acquisition time varied from 3 s/step for the low T spectra to 6 s/step for the high T spectra. At least two spectra were measured at each temperature.

The edge positions of all spectra have been aligned to within 0.1 eV. The atomic background has been subtracted through a multi-step cubic-spline procedure. The 1st-shell contribution, singled out by Fourier filtering, has been analyzed by the cumulant method in single scattering approximation, taking the 10 K spectra as reference for backscattering amplitude, phaseshifts and anelastic terms. The result of the analysis is the temperature dependence of the first three cumulants of the effective distribution: $\Delta C_i(T) = C_i(T) - C_i(10 \text{ K})$, $i=1,2,3$. The odd cumulants are shown in Fig. 1.
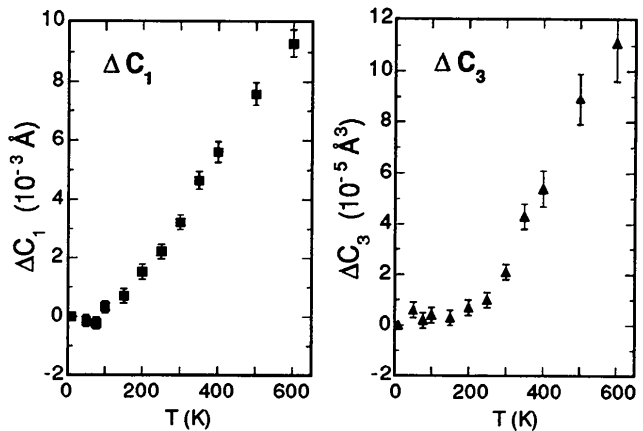

Figure 1
Temperature dependence of the first and third cumulants of the effective distribution. The values are relative to the 10 K spectrum.

3. Thermal expansion and correlation of vibrations

Let us consider the relation between thermal expansion ΔC_1 measured by EXAFS and the XRD thermal expansion ΔR. The two quantities are connected through Eq. 1. Absolute values $C_2 = \langle \Delta u_\parallel^2 \rangle$, to be inserted into Eq. 1, were obtained by the well established technique of fitting an Einstein model to the T dependence of the experimental relative values ΔC_2; the best fitting Einstein frequency was $\nu = 7.55$ THz.

Using the approximate relation

$$C_1^* \simeq C_1 + \frac{2C_2}{C_1}\left(1 + \frac{C_1}{\lambda}\right) \quad (2)$$

the relative values ΔC_1^* were then obtained; the value of λ was varied from 6 to 12 Å (see below). The values ΔC_1^* of the real distribution could now be compared with the XRD thermal expansion ΔR (Touloukian *et al.*, 1977). Using the relation

$$C_1^* = R + C_\perp/2R \quad (3)$$

the relative values $\Delta C_\perp$ ($C_\perp = \langle \Delta u_\perp^2 \rangle$) were thus obtained directly from experiment.

To get absolute values $C_\perp$ an Einstein model was fitted to the T dependence of $\Delta C_\perp$; the best fitting frequency was $\nu = 2.93$ THz. The ratio $\langle\Delta u_\perp^2\rangle/\langle\Delta u_\parallel^2\rangle$ between perpendicular and radial correlation terms was finally calculated as a function of temperature and is shown in Fig. 2 for different values of λ.

On the ground of symmetry considerations, one can show that for the first neighbours in a lattice with the diamond structure (Nielsen & Weber, 1980):

$$\frac{\langle\Delta u_\perp^2\rangle}{\langle\Delta u_\parallel^2\rangle} = 2 + 12\frac{\langle u_x(0)\,u_y(1)\rangle}{\langle\Delta u_\parallel^2\rangle} \qquad (4)$$

To calculate $\langle u_x(0)\,u_y(1)\rangle$ one must know the peculiar vibrational properties of the crystal. A calculation has been done for c-Si by Nielsen and Weber on the basis of a bond charge model, and the resulting ratio is shown in Fig.2. The agreement with the ratio for c-Ge is satisfactory, particularly at low temperatures. The residual discrepancies could depend on the lower reliability of our high-T data: if the Einstein fit to $\Delta C_\perp$ were done only below 300 K, lower absolute values of $C_\perp$ would be obtained. Besides, the actual value to be attributed to the first shell mean free path is questionable. Finally, one cannot exclude an intrinsic difference between the dynamics of Si and Ge.
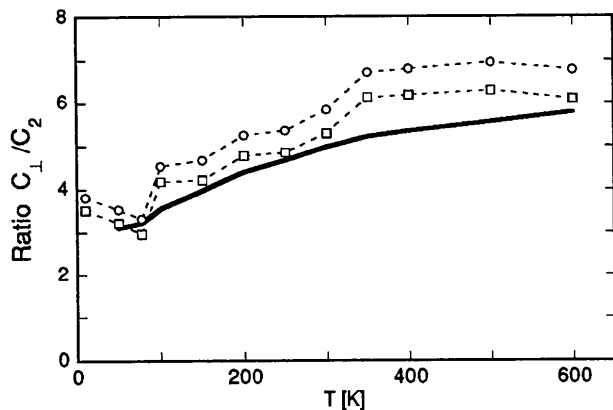

Figure 2
Ratio between perpendicular and radial correlation terms for c-Ge determined from EXAFS, with $\lambda = 6$ Å (circles) or 12 Å (squares). The continuos line is the ratio calculated for c-Si by Nielsen and Weber (1980).

4. Third cumulant

In first-order classical approximation, a T^2 dependence is expected for the 3rd cumulant, and has actually been found in previous studies on AgI (Dalba et al., 1995) and CdSe (Dalba et al., 1998). In the present case of Ge, on the contrary, the 3rd cumulant exhibits a flat constant behaviour at low temperatures (Fig.1). In view of the relatively high Debye temperature of Ge, this behaviour has been attributed to a deviation from the classical approximation.

To get absolute values of C_3, a T^2 parabola (dotted line in Fig.3) has been fitted to the experimental ΔC_3 values only for $T > 200$ K. Non-zero absolute values of C_3 of the order of 1×10^{-5} Å^3 are in this way obtained at 0 K. Our results are consistent with the quantum statistical model suggested by Frenkel & Rehr (1993), again best fitting the T dependence of experimental data above 200 K (continuous line in Fig.3).

In classical approximation, for a *constant effective potential*, the first three cumulants are connected through the equation

$$\Delta C_1 = C_3/2\,C_2. \qquad (5)$$

If quantum effects are taken into account in calculating the absolute values not only of C_2 but also of C_3, Eq.5 is satisfactorily fulfilled for c-Ge in all the temperature range. This means that the temperature dependence of C_1 is entirely due to the asymmetry of the effective potential.

In the cases of AgI (Dalba et al., 1995) and CdSe (Dalba et al., 1998), on the contrary, the growth of $C_3/2C_2$ was significantly stronger than that of ΔC_1. Correspondingly, a shift of the minimum of the potential was observed, which exactly compensated the discrepancy.
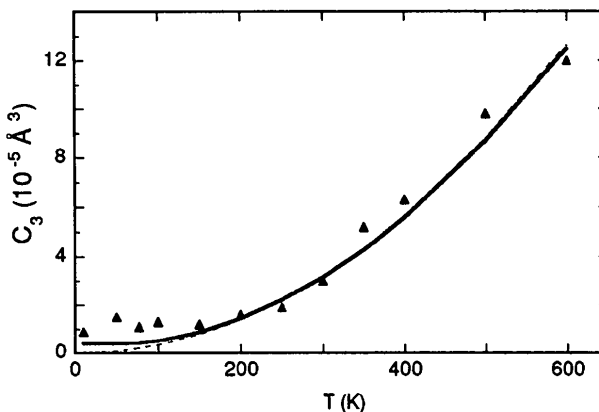

Figure 3
Absolute values of the 3rd cumulant (triangles) obtained by fitting a T^2 parabola (dotted line) to the experimental values above 200 K. The continuos line is from the model of Frenkel & Rehr (1993).

5. Conclusions

A resolution better than 10^{-3} Å in the 1st cumulant values allowed an accurate study of the 1st-shell thermal expansion in c-Ge.

A procedure has been devised to obtain the perpendicular correlation term $\langle\Delta u_\perp^2\rangle$ from the comparison between EXAFS and XRD thermal expansion. The ratio $\langle\Delta u_\perp^2\rangle / \langle\Delta u_\parallel^2\rangle$ experimentally determined for c-Ge is comparable to the ratio calculated for c-Si through a bond charge vibrational model.

A low-temperature quantum deviation from the classical T^2 law has been for the first time experimentally observed on the 3rd cumulant. The deviation is consistent with theoretical calculations. The comparison between ΔC_1 and $C_3/2C_2$ shows that the minimum of the effective potential has a negligible T dependence, contrary to what appens for AgI and CdSe.

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