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MEAN SQUARE RELATIVE DISPLACEMENTS OF NEAREST NEIGHBOUR ATOMS IN Ge

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NOTKESTRASSE 85 · 2 HAMBURG 52

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Abstract

From EXAFS spectra of crystalline and amorphous Ge we have determined the mean square relative displacements σ^2 of nearest and next nearest neighbour atoms in the temperature range 80 K to 400 K. A strong correlation of the nearest neighbour motion is observed for c-Ge. This correlation decreases in a-Ge. The results are compared with calculations performed within the Debye approximation. The structural parameters of a-Ge are consistent with a continuous random network approach.

classification numbers: 61.40, 63.50, 78.70

The thermally induced motions of close lying atoms are well known to be correlated, i.e. part of the atomic vibrations are in phase. With increasing interatomic distance this correlation decreases. Up to now only few informations are available about the mean square relative displacements σ^2 of nearest neighbours and the magnitude of the correlation. Systematic studies have been performed on the extended X-ray absorption finestructure (EXAFS) above the K-edges of atoms in polycrystalline metals (Cu,Co) and cubic binary compounds (RbCl, SrS, SrF_2 $SrCl_2$)(Böhmer and Rabe 1979). It has been shown that in these cases the temperature dependence of σ_T^2 of nearest neighbours is adequately described by a Debye model which considers the in phase motion of the atoms. The Debye model certainly has to be modified for solids with strong covalent bonds. To test the range of application of this model we have measured the absorption spectra above the K-edges of Ge in the crystalline and amorphous state (c-Ge and a-Ge) at various temperatures and determined the mean square relative displacements of nearest and second nearest neighbours from the EXAFS.

The measurements have been performed at the Deutsches Elektronen-Synchrotron (DESY). The synchrotron radiation was monochromatized with a channel-cut Si(220) crystal. The intensities incident onto and transmitted by the samples have been monitored by two ionization-chambers. The spectral resolution amounts to 3 eV at 11.5 KeV The spectra have been measured at 900 steps between 10.9 keV and 12.2 keV. Details about the experimental setup are published elsewhere (Rabe et al 1979). The amorphous sample has been prepared as a homogeneous film by vacuum evaporation at room temperature on to an Al substrate under a pressure of 10^{-6} mbar. The crystalline sample has been powdered from polycrystalline material. The transmission spectra of both samples have been measured at 80 K, 300 K and 400 K.

From the absorption coefficient the oscillating part above the edge (EXAFS) has been extracted by a procedure described by Martens et al 1978. This EXAFS is caused by a superposition of the outgoing photoelectron wave with parts of it backscattered from the neighbouring atoms. It can be expressed as a function of the wavenumber $k = (2m/\hbar^2(h\nu - E_o))^{1/2}$ by

$$1) \qquad \chi(k) = \sum_i A_i(k) \sin(2kR_i + \Phi_i(k))$$

where R_i is the mean distance of the i-th coordination sphere from the central atom and Φ the k-dependent phaseshift of the electron wave. Assuming a symmetric pair distribution function fluctuations of the interatomic distance around R_i are introduced in the amplitude function $A_i(k)$ by a Debye Waller like factor with mean square relative displacements σ^2 ($A(k) \sim \exp(-2\sigma^2 k^2)$). The variation of R_i with temperature can be neglected in A(k). The errors introduced by this assumption are small compared to other uncertainties in the data evaluation. Interatomic distances are extracted from the total phase

of each term in eq.1 (Rabe 1979, Martens et al 1978).

The initial step in the evaluation of interatomic distances and mean square relative displacements is a Fouriertransform of $\chi(k)$ to real space. The magnitude of this Fouriertransform i.e. the radial structure function $|F(r)|$ for c-Ge and a-Ge are shown in Fig.1. These $|F(r)|$ have been calculated from the spectra measured at 80 K and 400 K. In c-Ge we can identify three maxima which are attributed to the first three shells of Ge atoms surrounding the central atoms in accordance with the results of Stern et al (1975). In a-Ge we observe only contributions to EXAFS from the nearest neighbours in agreement with Hayes and Hunter (1977). This result is in contrast to earlier investigations of Sayers et al (1971) where additional contributions to $|F(r)|$ at larger distances might be caused by artificial structures in $\chi(k)$ at larger k values.

The essential procedure applied in this work for the determination of structural parameters is a transform over a limited range in real space back to k-space (Martens et al 1978). For the first shell this range has been indicated in Fig.1. The resulting finestructure represents the contribution of a single shell of scattering atoms $\chi_i(k)$ to the total finestructure $\chi(k)$. From $\chi_i(k)$ the total phase and the envelope function A(k) have been calculated. A comparison of the total phases of a-Ge and c-Ge yields a difference in the nearest neighbour distance $R_a - R_c = 0.003$ Å ± 0.003 Å at 80 K. This result is in agreement with the results of Sayers et al (1971) who found the nearest neighbour distance to be the same in both cases. From X-ray diffraction data of a-Ge a nearest neighbour distance increased up to 0.07 Å has been found (Tauc 1974) which is in contrast to our results. It should be noted that we find a change of the nearest neighbour distance in a-Ge and c-Ge in the range 80 K to 300 K of less than 0.005 Å. This value is consistent with the value expected from the thermal expansion of bulk c-Ge for which one obtains an increase of the nearest neighbour distance of 0.0023 Å (AIP Handbook 1963).

To discriminate the static structural against thermal vibrational disorder we have determined the mean square relative displacements σ_i^2 at various temperatures. Changes of σ_i^2 for the same pairs of atoms with temperature can simply be extracted from a plot vs.k of

2) $$\Delta\sigma^2 = \sigma^2_{T_1} - \sigma^2_{T_2} = (2k^2)^{-1} \ln(A_{T_1}(k)/A_{T_2}(k))$$

As mentioned above effects due to thermal lattice expansions are small compared to other uncertainties and therefore have been neglected in this analysis. All values of $\Delta\sigma^2$ between 80 K and 400 K for the first two shells in c-Ge and the first shell in a-Ge are compiled in Table 1A. The indicated errors are the deviations of $\Delta\sigma^2$ from a constant value over the whole k-range. Differences of σ^2 between first and second shell in c-Ge and the first shells in a-Ge and c-Ge have been determined from the slope of $\ln(A_1(k)/A_2(k))$ plotted versus k^2. These values are compiled in Table 1B. Finally we have determined the absolute value of σ^2 at 80 K for the nearest neighbours in c-Ge. For this calculation we have used the backscattering amplitude of Ge calculated by Teo and Lee (1979). An overall scaling factor and the mean square relative displacement have been varied to give a best fit to the experimental data, resulting in $\sigma^2 = 0.0019 \pm 0.0003$ Å^2. Combining these results we have absolute values for σ^2 of the nearest neighbours in a-Ge and c-Ge and the second nearest neighbours in c-Ge. The temperature dependence of the σ^2 are shown in Fig.2.

The thermal disorder of the first two shells in c-Ge shows significant differences. Only small changes over the whole temperature range are observed for the first shell (σ_1^2). This behaviour shows the strong correlation of the atomic motions. A much stronger increase with temperature is observed for the second scattering shell (σ_2^2). This mean square relative displacement is mainly introduced by a dynamical distortion of the tetrahedrous bond angle. At low temperatures σ_2^2 approaches σ_1^2. This means that the displacement correlation function of nearest and next nearest neighbours i.e. the difference of correlated motion and uncorrelated motion of individual atoms approaches a similar value for both shells.

For the nearest neighbours in a-Ge we find larger values of σ^2 over the whole temperature range compared to c-Ge. In this case σ^2 represents the sum of a static and a dynamic contribution. A standard deviation $(\sigma^2)^{1/2}$ of 0.06 Å for the nearest neighbour distance has been reported by Shevchik and Paul (1972) from X-ray diffraction experiments performed at room temperature. This value is sightly smaller than our value (0.082 Å). Whether these differences are due to different sample preparations techniques or due to uncertainties in the experimental results is not evident. On the other hand both the value of $(\sigma^2)^{1/2}$ determined by Shevchik and Paul and our value for the nearest neighbours are significantly smaller than the result of Grigorovici et al. (1968) who obtained a value of 0.12 Å.

One could argue that the differences of σ^2 for the first shells in a-Ge and c-Ge at least give an estimate of the contribution of the static mean square relative displacement σ_s^2 to the total disorder in a-Ge. Extrapolating both σ^2 curves to T = o one obtaines a standard deviation of $(\sigma_s^2)^{1/2}$ = 0.05 ± 0.01 Å. This value is significantly larger than the result of Polk (1971) who calculated a value of 0.03 Å.

It is interesting to note that the slope of the experimental σ^2 for a-Ge is larger than that of the first shell in c-Ge. This does not necessarily mean that the force constants differ in both cases. Due to unsaturated bonds further apart from the central atom the nearest neighbour correlation is weakened, leading to the increased temperature dependence of σ^2.

The fact that no contribution from the second nearest neighbours is observed is in contrast to the microcrystal approach (Light and Wagner 1968) from which contributions of at least the second nearest neighbours would be expected. From our data we can conclude that the tetrahedron angle in a-Ge is distorted by at least 10°. This value is in excellent agreement with the continuous network model of Polk (1971) who calculated average angle deviations of 10° and with experimental values of Shevchik and Paul (1972) who determined a distortion of 10°.

We have compared our experimental results with correlated mean square relative displacements calculated within the Debye approximation (Beni and Platzman 1976, Böhmer and Rabe 1979). The results for the first two scattering shells obtained with a Debye temperature between 308 K and 296 K in the temperature range 80 K to 400 K (Ludewig 1973) are included in Fig.2. Compared to the experimental values of both the nearest and next nearest neighbours the calculations yields higher values and a much stronger increase of σ^2 with temperature in c-Ge. This fact clearly shows that the correlation is strongly underestimated by this model in the case of covalent bonds. As can be seen from inspections of Fig.2 and Table 1 the experimental σ^2 for the second shell in c-Ge follow the calculated values for the first shell within the experimental errors over the whole temperature range. Certainly this coincidence is introduced accidentally by the choice of crystal parameters (lattice constant, Debye wavenumber, Debye temperature) which had to be used in the calculation so that no physical significance should be attached to this fact.

Additionally Fig.2 shows the temperature dependence of twice the uncorrelated motion $(2\,\sigma_\infty^2)$ calculated from the Debye model. The result shows that in all cases the uncorrelated motion exceeds the experimental values. These differences should be taken into account when high precision structural parameters are extracted from diffraction experiments. In X-ray diffraction the correlated motion of atom pairs shows up in the thermal diffuse scattering intensity. A similar effect is observed in low energy electron diffraction (Pendry 1974). For lack of better information in most of these experiments the uncorrelated mean square displacements of atoms in the bulk are used to account for the temperature dependent damping of the coherently diffracted beam intensity. The quantitative knowledge of the correlation of atomic motion derived from EXAFS may be used for the interpretation of diffraction pattern intensities in LEED and X-ray diffraction.

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Figure captions

Fig. 1: Magnitude of the Fourier transform of $\chi(k)$ of c-Ge and a-Ge.

Fig. 2: Experimental values of σ^2 for c-Ge(I) (x-x-x), c-Ge(II) (+-+-+), and a-Ge(I) (o-o-o). The temperature dependence of σ^2 calculated within the Debye approximation are included for the nearest (———) and next nearest (—.—.) neighbours and for uncorrelated atoms (- - -).

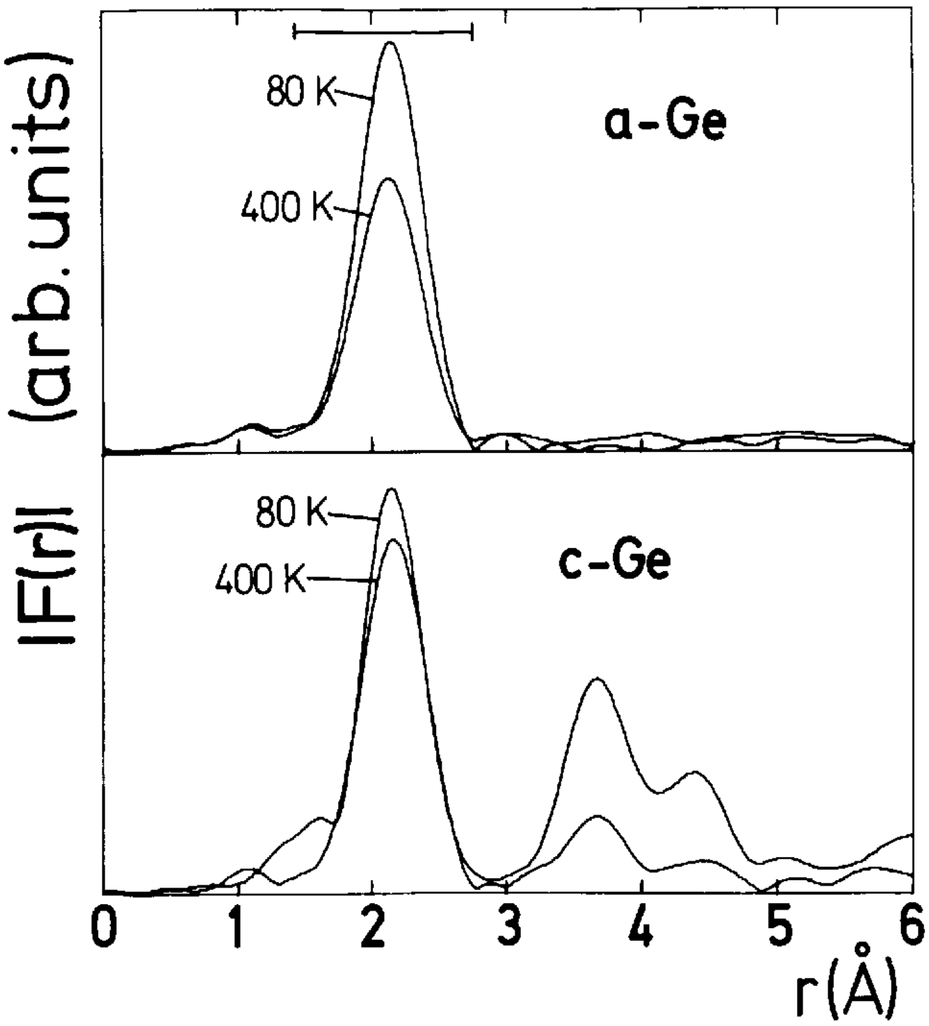
$\Delta\sigma^2$ $[10^{-2}$ Å$^2]$

		80/300 K	80/400 K	80 K
A	c-Ge (I)	0.04 ± 0.02	0.07 ± 0.02	
	c-Ge (II)	0.45 ± 0.02	0.63 ± 0.05	
	a-Ge (I)	0.22 ± 0.02	0.28 ± 0.02	
	Debye (I)	0.2099	0.3368	
	Debye (II)	0.3520	0.5427	
	Debye (∞)	0.5147	0.7777	
B	a-Ge (I) - c-Ge (I)			0.26 ± 0.02
	a-Ge (I) - c-Ge (II)			0.21 ± 0.03
	c-Ge (II) - c-Ge (I)			0.05 ± 0.03

Table 1:

A) Experimental and calculated variation of the mean square relative Displacements σ^2 with temperature for the nearest (I) and next nearest (II) neighbours in c-Ge and a-Ge.

B) Differences of σ^2 for a-Ge(I), c-Ge(I), and c-Ge(II) at 80 K


|F(r)| (arb. units)
80 K
400 K
a-Ge
80 K
400 K
c-Ge
0
1
2
3
4
5
6
r(Å)

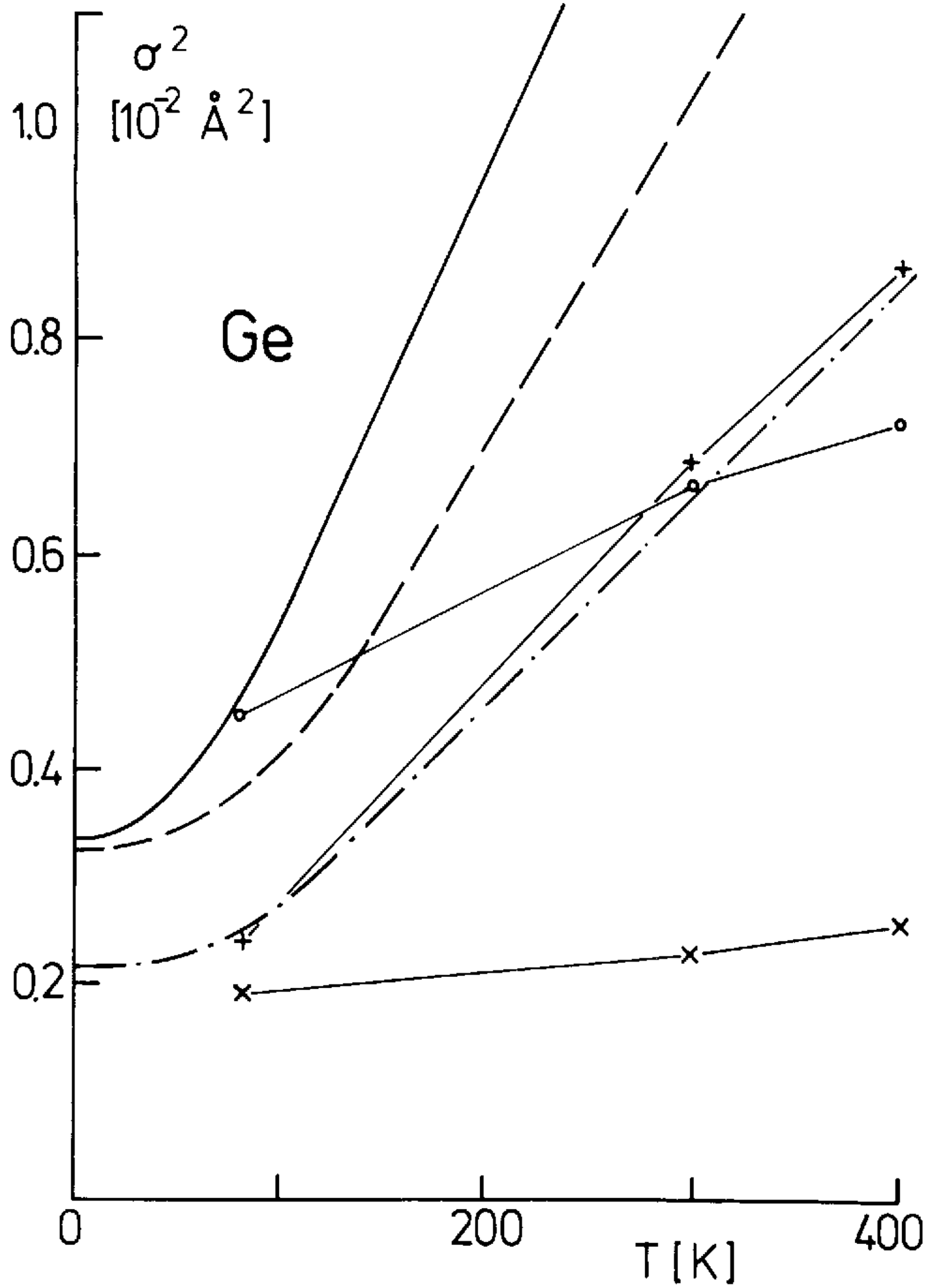

σ²
[10⁻² Å²]
1.0
0.8
0.6
0.4
0.2
Ge
0
200
400
T [K]

Fig. 2