A Phase-Difference Approach to EXAFS Analysis of Germanium Polymorphs

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Abstract

Two germanium polymorphs of the diamond type and the ST-12 structure were used to investigate the accuracy of extended X-ray absorption fine structure (EXAFS) analysis with a phase-difference method. This method gives similar accuracies to both conventional curve-fitting and Fourier-transform methods in determining the difference of the first-neighbor distances for these two polymorphs. The number of first-shell atoms of the ST-12 structure was determined to be $4 \cdot 0 \pm 0 \cdot 2$ with the diamond-type phase as a standard. In addition, the first-neighbor coordination of amorphous germanium was analyzed with this method. These results suggest that the phase-difference method is useful for structure analysis of materials and that it is especially useful for structure analyses under high pressure.

1. Introduction

In recent years, local structure analysis utilizing extended X-ray absorption fine structure (EXAFS) has become popular. EXAFS is caused by the interference of an outgoing photo-excited electron from a specified atom with its backscattering component from neighboring atoms. In the single-scattering approximation, the EXAFS oscillation $\chi(k)$ (where k is the wavenumber of the outgoing photoelectron) is expressed by

(Sayers, Stern & Lytle, 1971)

$$\chi(k) = \sum_j \frac{N_j}{|kR_j^2|} |f_j(\pi)| \sin(2kR_j + \delta_j)$$
$$\times \exp(-2R_j/\lambda) \exp(-2\sigma_j^2 k^2), \qquad (1)$$

where N_j is the number of atoms at a distance R_j from the absorbing atom, $|f_j(\pi)|$ is the backscattering amplitude for the jth atom, δ_j is the sum of the phase shifts of the photo-excited electron due to the absorbing and the jth backscattering atoms, λ is the mean free path of the electron and σ_j is the root-mean-square fluctuation of the jth atom relative to the absorbing atom. In the derivation of (1), periodicity of the atomic arrangements is not assumed. Therefore, EXAFS is a useful tool for structural analysis of noncrystalline materials, biological substances which have a large number of atoms per unit cell, *etc.*

EXAFS is also a potentially useful method for the structural analysis of materials under high pressure (Ingalls, Garcia & Stern, 1978; Shimomura, Fukamachi, Kawamura, Hosoya, Hunter & Bienenstock, 1978; Shimomura, Kawamura, Fukamachi, Hosoya, Hunter & Bienenstock, 1980). It should be possible not only to investigate the effect of pressure on the interatomic distances of amorphous materials and liquids but also to obtain important information on new high-pressure structural phases. Powder diffraction is usually used to solve high-pressure structures because it is rare to have single crystals of these phases. However, in general, less information is obtained by powder diffraction methods than by single-crystal techniques, and this limitation is accentuated by the geometrical limitations of the

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scattering angle imposed by high-pressure cells. In this situation, the atomic distances and coordination numbers around specified atoms give valuable information for determining the structure. Furthermore, the local compressibility of materials with complex structures can be determined by EXAFS. However, if diffraction techniques are used, highly precise measurements are required for the diffraction intensities under high pressure.

Before utilizing EXAFS measurements for determining the short-range order under high pressure, two potential problems must be analyzed. One is the limited accuracy with which atomic distances and coordination numbers can be determined by the EXAFS analysis. In order to determine the local compressibility or to solve an unknown structure, accuracies of 0·01 Å in distance and better than 1·0 in coordination number are required. The other is the limitation of transferability of phase shifts associated with the ejection and backscattering of the electron, since there may be different phase shifts at high- and low-pressure phases, owing to changes in atomic arrangement and/or in electronic structure.

For these problems, there are some investigations at normal pressure. A combination of Fourier filtering and curve-fitting techniques is considered to ensure the accuracy of 0·01 Å in distance (Cramer, Hodgson, Stiefel & Newton, 1978), and investigation of Br_2 and some of its compounds indicates the validity of the transferability assumption of phase shifts (Citrin, Eisenberger & Kincaid, 1976). These problems can be conveniently tested by examining various pressure-induced polymorphs of the same materials, when the structures of the polymorphs are known. If the electronic circumstances in the polymorphs are similar, then the transferability assumption of phase shifts may hold, so that the accuracies of both atomic distance and the coordination number can be tested. When the electronic environment is different for each polymorph, the transferability assumption can be tested in combination with the former results.

In this paper, our attention is restricted to the first problem. Let us introduce a phase-difference method which gives the same or better accuracies in determining the atomic distance and coordination number. In this method, the EXAFS of one phase is compared with that of the other and the changes in atomic distance and coordination number are determined from the difference between two profiles. This method has an advantage that those changes can be determined without knowledge of the quantitative value of phase shifts as long as they are transferable.

Let us choose germanium as a test material. Ge with diamond-type structure has been thoroughly investigated by EXAFS analysis and the calculated phase shifts agree well with the experimentally derived phase shifts (Lee & Beni, 1977). Ge shows a structural phase transition from the diamond-type to the β-Sn-type structure at 10 GPa. After releasing the pressure, this phase does not transform directly back to the diamond-type structure but transforms to the ST-12 structure (Kasper & Richards, 1964). As in the diamond-type structure, the ST-12 structure has fourfold coordination. In the ST-12 structure, however, the bond angles vary from 88 to 135° instead of being the 109·3° of the diamond-type structure. The bond lengths are also slightly different. In the ST-12 structure, there are two neighbors at 2·48, one neighbor at 2·486 and one at 2·488 Å, while the first-neighbor bond lengths of the diamond-type structure are all 2·45 Å. Since the ST-12 phase of Ge is a semiconductor, we would expect similar phase shifts for the ST-12 and the diamond-type structural phases of Ge. By comparing the EXAFS profiles of the ST-12 phase with that of the diamond-type phase, we determine the bond lengths and coordination number of the first one. These data were also analyzed by curve-fitting and Fourier-transform techniques for comparison and for discussion of accuracy of a phase-difference method. Amorphous Ge was also taken as one of the polymorphs.

2. Experimental

A Ge sample was prepared in the ST-12 phase with cubic anvil apparatus (Yagi, Ida, Sato & Akimoto, 1975). After verifying the transition to the β-Sn-type structure by X-ray diffraction, the pressure was released. This sample was confirmed, by X-ray powder diffraction, to be a single phase with the ST-12 structure. Each sample of the diamond type and the ST-12 phase was crushed to a fine powder and bonded into thin plates.

The X-ray source used for the EXAFS measurements was beam line IV at Stanford Synchrotron Radiation Laboratory (SSRL). This beam line was equipped with a six-pole wiggler operated at 0·86 T which gave a critical energy of 5·15 keV, when the storage ring was operated at 3·0 GeV and approximately 80 mA (Bienenstock & Winick, 1980). The radiation from this wiggler was monochromatized by a two-crystal Si 220 monochromator in a parallel setting with an energy width of ~2 eV. The intensities of both incident and transmitted beams were monitored by the SSRL arrangement of two ion chambers. The data were collected by a step of ~1 eV near the K absorption edge (-50 to $+30$ eV), ~2 eV in the region from 30 to 300 eV and ~5 eV from 300 to 1000 eV.

3. Results

Fig. 1(a) and (b) shows $\log (I_0/I)$ obtained from measurements on the diamond-type and the ST-12

phases of Ge near the K absorption edge, respectively. These data were analyzed by three methods: (1) a phase-difference approach, (2) a curve-fitting approach and (3) a Fourier-transform approach.

3.1. Phase-difference method

In the phase-difference method we employed, the first-neighbor EXAFS spectra of the two polymorphs are compared in order to obtain the change in the first-neighbor distance. The first-neighbor EXAFS is isolated by Fourier filtering the EXAFS data with an
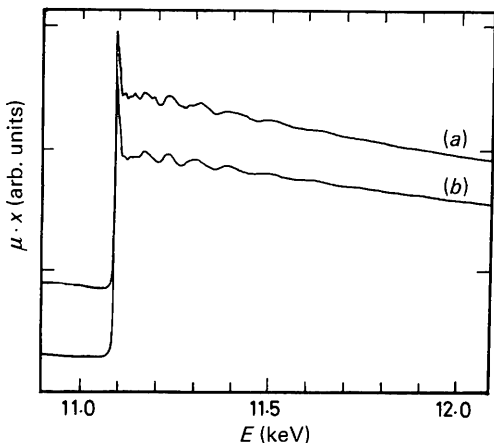

Fig. 1. Experimental log (I_0/I) curves of germanium polymorphs: (a) diamond-type structure; and (b) ST-12 structure. The energy origins are adjusted to be the same for both structures.
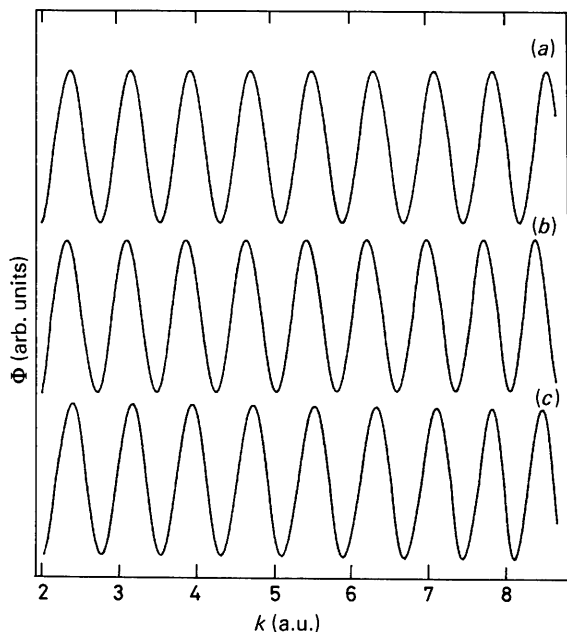

Fig. 2. Normalized first-nearest-neighbor EXAFS to show sine curves for (a) the diamond-type structure, (b) the ST-12 structure and (c) amorphous germanium. The different periods of these curves show the differences of the bond lengths.

appropriate window function around the first-neighbor peak. Both sets of experimental data were processed in this way with a window of between 1·68 and 2·76 Å. A slight change of this window brought little change in the phase of the first-neighbor EXAFS. After Fourier filtering of the data, the amplitude of the first-neighbor EXAFS spectrum was normalized to show a sine function. This process is necessary for comparing the phases of the two polymorphs at an arbitrary wave number k.

The curves thus obtained are

$$\Phi_{\mathrm{dia}} = \sin (2kR_1 + \delta)$$

for the diamond-type structure and

$$\Phi_{\mathrm{ST-12}} = \sin (2kR_2 + \delta)$$

for the ST-12 structure. These curves are shown in Fig. 2(a) and (b). In these relations, R_1 and R_2 are the first-neighbor distances for the diamond-type and the ST-12 phases, respectively. We assume that the phase shifts of the Ge atom and the energy origin E_0 of the photoelectron in the ST-12 phase are the same as in the diamond-type phase. This point will be discussed later.

The value of $\Phi_{\mathrm{ST-12}}$ at the point $k = k_d$ where

$$\Phi_{\mathrm{dia}} = \sin (2k_d R_1 + \delta) = 0$$

is given by

$$\Phi_{\mathrm{ST-12}} = \sin [2k_d(R_2 - R_1)].$$

We can determine a difference between the first-neighbor distances of the ST-12 and diamond phases from this relation regardless of the phase shifts as long as they are transferable. We can obtain a similar relationship by setting $\Phi_{\mathrm{ST-12}} = 0$.

The resultant difference from this analysis is

$$\Delta R = R_2 - R_1 = 0·04 \text{ Å}.$$

This value is in excellent agreement with previous diffraction measurements (Kasper & Richards, 1964) and seems to confirm the transferability of the phase shifts and energy origin E_0 of the photoelectron. To check this result further, we tried another analysis based on curve fitting to obtain the first-neighbor distances.

3.2. Curve fitting with calculated phase shifts

After Fourier filtering the first-neighbor EXAFS, we compared these curves with calculations (Fig. 3) using the phase shifts of Lee, Teo & Simons (1977) and the backscattering amplitude functions of Teo, Lee, Simons, Eisenberger & Kincaid (1977). The imaginary part of the optical potential is 5·8 eV for both phases and the root-mean-square amplitudes of thermal vibration are 0·069 Å for the diamond-type phase and 0·073 Å for the ST-12 phase. We changed the energy origin of the EXAFS until the first-neighbor distance in the diamond-type phase agreed with the known value of

2·45 Å. This was achieved with the origin 8 eV above the absorption edge. In this case, the first-neighbor distance in the ST-12 phase is 2·49 Å, which is in excellent agreement with the phase-difference method. Note, in Fig. 3, that the first-neighbor EXAFS show excellent agreement with calculations which use the same phase shifts for both structural phases. This again suggests that the parameters such as phase shifts and the energy origin are transferable between these structural phases.

3.3. Fourier-transform analysis

In order to confirm the above results and to determine the energy origin difference, we determined the radial distribution function with the usual Fourier-transform
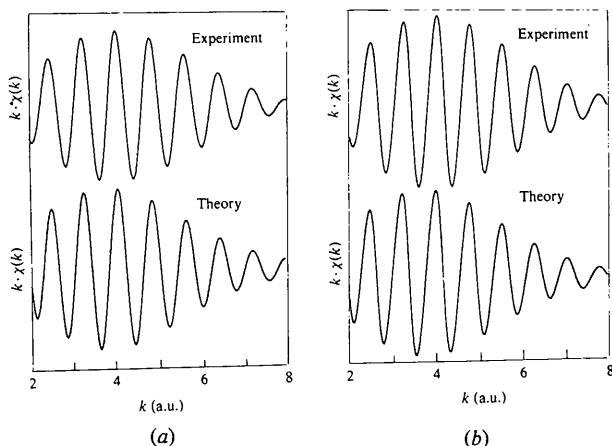

Fig. 3. Curve-fitting results of germanium polymorphs. (a) Comparison between theoretical and experimental curves for the diamond-type structure and (b) for the ST-12 structure of Ge. Theoretical curves are calculated with the same calculated phase shifts and amplitudes.
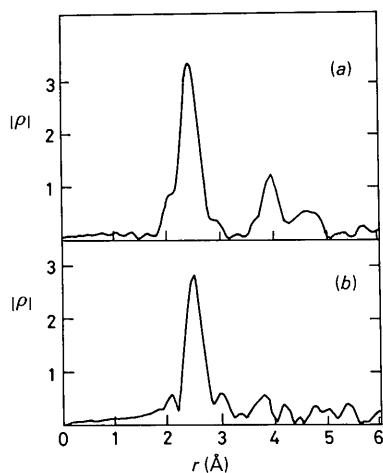

Fig. 4. The amplitudes of the Fourier transform of EXAFS for diamond-type (a) and ST-12 (b) structures. Phase shifts and amplitudes are taken into account in the Fourier transform. The energy origin E_0 is 8 eV above the Ge K absorption edge for the diamond-type structure and 10 eV for the ST-12 structure.

method. The results are shown in Fig. 4. In this case, the energy origin is determined by the Lee & Beni (1977) prescription. That is, the energy origin is changed until the imaginary part and the absolute values of the Fourier transform of the EXAFS spectrum give the same peak. The energy origin of the diamond-type phase is 8 eV above the absorption edge, which is consistent with the curve-fitting results. With the same energy origin, the first-neighbor distance in the ST-12 phase is 2·485 Å. With this origin, the peaks of the imaginary part and the absolute value of the Fourier transform do not agree for the ST-12 results. If the energy origin is varied to satisfy the Lee & Beni criteria, E_0 is 10 eV above the edge and we obtain 2·49 Å for the first-neighbor distance. Thus, unlike the curve-fitting and phase-difference approaches, this technique appears very sensitive to the exact E_0 value.

3.4. Coordination-number determination

From an EXAFS analysis it is possible to determine the first-neighbor coordination number by normalizing the EXAFS oscillation to the absorption coefficient jump at the edge and comparing the magnitude of the EXAFS oscillations between two phases. The coordination number of the ST-12 phase thus obtained is $4·0 \pm 0·2$ assuming that of the diamond phase to be 4·0. In the determination of the coordination number, we should be careful to ensure the homogeneity of the sample thickness. If inhomogeneity exists, a logarithm of the normalized intensity may not be proportional to the absorption coefficient and an erroneous coordination number will be obtained.

4. Discussion

The results of the first-neighbor distances are summarized in Table 1 along with estimated errors in the analysis. The above methods give almost the same difference between the first-neighbour distances for the diamond-type and the ST-12 phases of Ge.

To discuss the errors involved in the above methods, we first estimate the shift of the energy origin of the photoexcited electron. The muffin-tin radius of a Ge atom in the ST-12 structure is larger than that in the diamond-type phase, owing to the expansion of the first-neighbor distance resulting in a higher threshold for absorption (E_0). Since a slight shift of the muffin-tin radius does not affect the core electrons, we will consider only a uniform valence-electron distribution and Coulombic force in estimating this energy shift. The exchange and correlation effects are of second order in this calculation. Under these approximations, the energy shift (ΔE) will be given by

$$\Delta E = \Delta[-Ze^2/r + \rho(r)/r],$$

where Z is the number of valence electrons, e is the

Table 1. *Summary of the present analysis*

	Fourier transform	Curve fitting	Phase difference	Diffraction data
Diamond type	$2 \cdot 45 \pm 0 \cdot 01$ Å	$2 \cdot 45 \pm 0 \cdot 01$ Å	$2 \cdot 45$ Å* c.n. $= 4 \cdot 0$*	$2 \cdot 45$ Å c.n. $= 4 \cdot 0$
ST-12	$2 \cdot 49 \pm 0 \cdot 01$ Å	$2 \cdot 49 \pm 0 \cdot 01$ Å	$2 \cdot 49 \pm 0 \cdot 01$ Å c.n. $= 4 \cdot 0 \pm 0 \cdot 2$	$2 \cdot 49 \pm 0 \cdot 03$ Å† c.n. $= 4 \cdot 0$
Amorphous	NA‡	NA‡	$2 \cdot 47 \pm 0 \cdot 01$ Å c.n. $= 3 \cdot 8 \pm 0 \cdot 2$	$2 \cdot 46 \pm 0 \cdot 03$ Å§ c.n. $= 3 \cdot 85 \pm 0 \cdot 1$§

* Taken as a standard. † Mean value. ‡ Not analyzed. § Shevchick & Paul (1973/4).

electron charge and r is the muffin-tin radius. The electron distribution function in a uniform gas is

$$\rho(r) = (4\pi/3)\rho_0 r^3,$$

with ρ_0 determined by the electron neutrality in an appropriate sphere of radius r_s (a Wigner–Seitz sphere, for example) as

$$\frac{Ze^2}{r_s} = \frac{4\pi}{3} \rho_0 r_s^2.$$

Then, ΔE is expressed by

$$\Delta E = [Ze^2/r^2 + 2Ze^2 r/r_s^3] \Delta r.$$

For Ge, if we put $Z = 4$, $r = 1 \cdot 23$, $r_s = 1 \cdot 76$ Å and the change of bond length $\Delta r = 0 \cdot 04$ Å, $\Delta E = 2 \cdot 6$ eV. This is in qualitative agreement with the shift of the energy origin between the diamond-type and the ST-12 phases of Ge as obtained from the Fourier transform method prescribed by Lee & Beni (2 eV).

The shift of the energy origin in turn gives a change of bond length in the Fourier transform owing to the change of wavenumber k. This change, however, is not large for large k values. The first-order approximation is

$$\Delta r = (\Delta E/2E) r$$

and a ΔE of 2 eV gives a maximum shift of $0 \cdot 01$ Å for $E > 250$ eV above the absorption edge. This suggests that in the phase-difference method sine curves with $k > 8 \cdot 1$ Å^{-1} should be used to minimize the error due to shifts in E_0. This error can also be minimized by comparing the difference in the first-neighbor distance obtained from the relation $\Phi_{dia} = 0$ and from the relation $\Phi_{ST-12} = 0$. The error in Table 1 for the phase-difference method was determined in this way. If the energy shift ΔE cannot be estimated, sine curves for large k should be used to determine the distance changes even though their signal-to-noise ratios become smaller.

The errors in the curve-fitting and the Fourier-transform methods are due to the errors of phase shifts as well as choice of the energy origin. The phase shifts of Lee & Beni include the errors of $0 \cdot 01$ Å or more in the present case (listed in Table 1). In the ST-12 phase, the first-neighbor distances from diffraction data are $2 \cdot 48$ and $2 \cdot 49$ Å with a standard deviation of $0 \cdot 03$ Å

(Kasper & Richards, 1964), which is larger than the error estimated from the EXAFS analysis. In EXAFS, on the other hand, the difference of $0 \cdot 01$ Å in these two bond lengths are not distinguishable. This may be due to the correlation effect of the thermal vibrations of atoms. As pointed out by Eisenberger & Brown (1979) the correlation between two or more atoms should be taken into account in the EXAFS analysis of a disordered system. As far as the present analysis is concerned, however, neglecting these correlations does not lead to serious problems in determining the difference between the first-neighbor distances of the diamond-type and the ST-12 phases of Ge.

We have also analyzed EXAFS data from amorphous Ge by the above methods. The first-neighbor distance was determined to be $2 \cdot 47 \pm 0 \cdot 01$ Å (Fig. 2c) and the coordination number to be $3 \cdot 8 \pm 0 \cdot 2$ from the analysis described in §3.

5. Summary

The errors in the above methods are similar. Therefore, the present phase-difference method gives a convenient way of determining the difference between first-neighbor distances of slightly different structures without a quantitative knowledge of the phase shifts as long as their transferability holds. The agreement of the results for the bond length of the ST-12 phase by three methods means that the transferability between the diamond and the ST-12 phases is well established. This suggests that the transferability holds if the bond nature of polymorphs of the same material is similar.

To investigate the second problem described in the *Introduction*, the phase-difference method will be applied to the determination of bond lengths of the β-Sn-type metallic phase of Ge. The results of this determination will be published in a separate paper.

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A Linear Equation for Products of Normalized Structure Factors. II. Tensor Formalism

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Abstract

New, finite and exact relationships between products of two normalized structure factors, with coefficients which are a function of the squared moduli of structure factors, are presented. The equations allow new linear relationships between the cosine and sine of triple-phase invariants to be set up. The meaning of the new equations is discussed in connexion with the direct calculation of cosines of triple-phase invariants and the results show, for simple one-dimensional model structures, that it is possible to obtain exact solutions.

Introduction

This paper is closely related to two previous ones (Navaza & Silva, 1979; Silva, Tate & Woolfson, 1981), which will be hereafter referred to as papers A and B respectively. In paper A, by means of vector algebra, various relationships between E's were derived, some of them finite and exact. Paper B deals with a new equation involving products of E's which leads to a linear relation between the cosines of triple-phase invariants. One of the results of the present paper is concerned with an equation similar to that derived in paper B, but using in its derivation an extension of the algebra of paper A.

The main equation derived in paper B is

$$\sum_I X(\mathbf{H}_I)E(\mathbf{h}_1 - \mathbf{H}_I)\,E(\mathbf{h}_2 + \mathbf{H}_I) = \lambda E(\mathbf{h}_1)E(\mathbf{h}_2), \quad (1)$$

where the X's satisfy

$$\sum_I X(\mathbf{H}_I) \exp\,[2\pi i \mathbf{H}_I \cdot (\mathbf{r}_i - \mathbf{r}_j)] = \lambda, \quad \text{for } i,j = 1, \ldots, N, \quad (2)$$