EXAFS study of intermetallics of the type RGe$_2$ (R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er and Y) Part I: Determination of Ge-Ge distances

A R CHOURASIA, V D CHAFEKAR*, S D DESHPANDE
and C MANDE
Department of Physics, Nagpur University, Nagpur 440 010, India
* Department of Physics, Indian Institute of Technology, Kanpur 208 016, India

Abstract. A study of the EXAFS associated with the K x-ray absorption discontinuity of germanium in pure germanium and in the rare-earth germanides RGe$_2$ (where R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er and Y) has been carried out. The Ge-Ge distances have been obtained in these compounds. Considering the phase obtained from the EXAFS of germanium as model and assuming chemical transferability of phase to the RGe$_2$ system, the bond lengths in these compounds have been determined. The values obtained by us for the RGe$_2$ compounds (R = La, Ce, Pr, Nd, Sm, Gd, Dy and Y) agree with those obtained earlier by crystallographic methods. The bond lengths for the compounds TbGe$_2$, HoGe$_2$ and ErGe$_2$ are also being reported.

1. Introduction

It is well known (Bonnelle and Mande 1982; Bianconi *et al* 1983) that the x-ray absorption discontinuities are accompanied on their high energy side by a fine structure which extends to a few hundred eV and even up to a few thousand eV in certain cases. The study of this structure, which is now called EXAFS (extended x-ray absorption fine structure), provides valuable information about local structure in all types of materials (Lytle *et al* 1975, 1982; Stern *et al* 1975; Stern 1978; Eisenberger and Kincaid 1978; Lee *et al* 1981). In the present paper we report an EXAFS study of pure germanium and the compounds of the type RGe$_2$ (R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er and Y) undertaken to determine the average bond distances between the germanium-germanium atoms. Amongst these compounds, the structure data on the compounds TbGe$_2$, HoGe$_2$ and ErGe$_2$ have not yet been reported.

2. Method of EXAFS analysis

The basic scheme for EXAFS data analysis was outlined by Stern (1974), Lytle *et al* (1975) and Stern *et al* (1975). Since then various refinements and extensions have been added to the original scheme. The methods of analyzing EXAFS data include Fourier transform techniques (Stern 1974; Lytle *et al* 1975; Stern *et al* 1975), the ratio method (Stern *et al*

1975), maximum entropy spectral estimation (Labhardt and Yuen 1979), beat analysis (Martens *et al* 1977), least squares fitting procedures in either wave number (k) or coordinate (r) space using theoretical or empirical back-scattering functions (Hayes *et al* 1976; Lee *et al* 1981), and hybrids of these. Recently it has been shown by Stearns (1982) that at a particular value of the energy $E_0 = E_c$ for which the peak position in the Fourier transform is independent of the weighting factor k^n, the phase shift is a linear function of k. Making use of this linearity the bond length in any unknown material could be evaluated without inverse Fourier transforming the data, with the help of the known bond distance in a model compound which is chemically similar to the unknown material. The method proposed by Stearns has the advantage that it provides much cleaner data for selection of single peaks for back transformation than those generated at other E_0 values, reducing the errors in EXAFS data analysis. However, in Stearn's method there lies an uncertainty (of the order of 2π) in the k-independent part of the phase shift. In the present work, we have basically used Stearn's method with the simple modification that we have inverse Fourier-transformed the data to remove the uncertainty in the phase shifts.

The rare earth intermetallic RGe_2 compounds have interesting magnetic and superconducting properties (Compton and Matthias 1959; Jaccarino *et al* 1960; Williams *et al* 1962; Gorsard *et al* 1962; Matthias *et al* 1963). They have a crystal structure of the α-$ThSi_2$ type (Gladyshevskii 1964; Sekizawa 1966). In this structure the germanium atoms form zigzag chains passing through prisms of rare earth atoms parallel to the X and Y axes at different heights. The projections of the chains are directed towards one another; the distance between the germanium atoms in the projection equals that between the germanium atoms in the chain, *i.e.* a three-dimensional framework of germanium atoms is created. The nearest neighbours of each germanium atom in these compounds are three other germanium atoms with distances close to d_{Ge-Ge} in the germanium structure (2·45 Å). Thus the only difference in the chemical environment of the germanium atoms in pure germanium and the compounds is that while in the pure material each Ge atom is surrounded by 4 Ge neighbours, in the compounds each Ge atom is surrounded by 3 Ge neighbours. We have therefore chosen polycrystalline germanium as the model system in the present study.

3. Experimental procedure

The compounds of the family RGe_2 were prepared by arc melting of the mixture of component metals in stoichiometric proportion. The rare earth metals were of 99·9 % purity, while the polycrystalline germanium used was ultrapure. The formation of these compounds was checked by x-ray diffraction technique. The diffractograms showed that the materials were essentially in a single phase, since no lines corresponding to the individual elements were observed. The absorbing screens of pure germanium and the compounds were prepared by spreading uniformly their fine powders on adhesive cellotape.

The x-ray absorption experiments were made using a Seifert x-ray spectrometer equipped with an auto-step scanning mechanism. A sealed x-ray tube with Cu-target operated at 50 kV and 30 mA was used as the source of white radiation. A flat single crystal of $LiF(2d_{200} = 4·026$ Å) was used as the analyser. It may be mentioned here that LiF is a particularly suitable crystal for EXAFS study as shown by Lytle *et al* (1975). The

x-ray intensities were measured using a scintillation counter. The times T and T_0 (preset count mode, 10^5 counts) were noted for each spectrometer position with the absorber in the path of the x-ray beam and without the absorber respectively. The spectra were scanned in steps of $\Delta\theta = 0.005°$. The data processing was done using a program developed by us on a DEC 1090 computer.

4. Procedure for data analysis

When a photon of energy E falls on an atom, an electron is knocked out from an inner shell of binding energy E_0 (if $E_0 < E$). We may then write

$$E = E_0 + \tfrac{1}{2} mv^2. \tag{1}$$

Since the kinetic energy of the electron is large relative to the binding energies in the material, it may be considered as almost free, so that the magnitude of its wave-number k is written as

$$E = E_0 + \frac{\hbar^2 k^2}{2m}. \tag{2}$$

For the sake of normalisation, the EXAFS function $\chi(k)$ is defined by

$$\chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)}, \tag{3}$$

where $\mu(k)$ is the experimentally observed absorption coefficient and $\mu_0(k)$ is its monotonically decreasing portion in the general μ, E curve.

The physical origin of EXAFS is ascribed to the final state interference (Stern *et al* 1975), *i.e.*, the modification of the final states by the presence of the surrounding atoms. The cross-section for absorption of the photons is proportional to the square of the matrix element of the interaction, taken between the initial core state, i, and the excited final state, f. The final state is the result of the outgoing wave and the wave back-scattered by the atoms coordinating the photoexcited atom. Since the initial state, in the present study, the K shell state, is highly localised in the vicinity of a specific nucleus, this matrix element takes into account the final state wave-function in the vicinity of that nucleus. From such considerations Lytle *et al* (1975) gave a semiempirical equation for $\chi(k)$ in terms of the coordination parameters of the absorbing atom as

$$\chi(k) = -\sum_j \frac{N_j}{kr_j^2} f_j(k, \pi) \exp(-2\sigma_j^2 k^2)$$
$$\exp[-2r_j/\lambda_j(k)] \sin[2kr_j + \phi_j(k)]. \tag{4}$$

Here the summation is over the different coordination shells. r_j is the average separation of the absorbing atom from the atom of the jth shell, σ_j is the root-mean-square deviation of that distance, N_j is the number of atoms in the jth shell, $f_j(k, \pi)$ is the back-scattering amplitude of the photoelectron wave from the neighbours, $\lambda_j(k)$ is the energy dependent mean free path and $\phi_j(k)$ is the phase shift of the outgoing electron wave relative to the core state, together with the phase shift resulting from partial back scattering.

Since in the present work we are interested in the average bond distances only, we

may simplify (4) as

$$\chi(k) = -\sum_j A_j(k) \sin\left[2kr_j + \phi_j(k)\right], \tag{5}$$

where $A_j(k)$ is the amplitude function for the jth shell.

The values of the EXAFS function $\chi(k)$ were determined from the raw curves obtained experimentally using the procedure given by Schmückle *et al* (1982). The next step in data analysis is to calculate the Fourier transform of the spectrum. The Fourier transform of the EXAFS data yields a radial-scattering function $R(r)$

$$R(r) = (1/2\pi)^{1/2} \int_{k_{min}}^{k_{max}} k^n \chi(k) \exp(2ikr) \, dk. \tag{6}$$

In the above expression, following Lytle *et al* (1975), $\chi(k)$ has been multiplied by the factor k^n, where n is the weighting factor equal to 1, 3 or 5, so as to reduce the k dependence from the amplitude function $A_j(k)$ in (5). The limits k_{min} and k_{max} of the integral are the minimum and maximum values of k at which experimental data are obtained. When a Fourier transform is taken over a finite range of variables, as in (6) a termination error is introduced into the function resulting from the transform. This error leads to a set of ripples propagating through the transformed function and contributes significantly to broadening of the peaks (Sayers 1971). A correction for the termination error is made by multiplying $\chi(k)$ by a Hanning window function (Via *et al* 1979) of the form

$$(\tfrac{1}{2})\left\{1 - \cos 2\pi\left[(k - k_{min})/(k_{max} - k_{min})\right]\right\}, \tag{7}$$

in the region of k values corresponding to the first and last 10% of the range investigated. As a result, $\chi(k)$ assumes a half-cosine bell shape terminating at zero at k_{min} and k_{max}. This treatment of the data is helpful in minimising the termination ripples that have a period equal to $\sim 2\pi/k$.

A difficult problem in EXAFS analysis is the experimental determination of the E_0 value, the zero energy defined by (2). The approximate value of E_0 can be taken as the energy of the inflection point on the absorption edge. It has been shown recently (Stearns 1982) that there exists a critical energy value E_c for each coordination shell for which the corresponding transform peak position is independent of the weighting factor n. The value of E_c, which gives the correct value of E_0, can be obtained from the intersection point of the curves drawn between the values of the peak position for a given coordination shell and those of the energy zero for different values of n. The determination of the correct value of E_0 helps in making the phase shift $\phi(k)$ a linear function of k.

For the correct determination of the phase shift $\phi(k)$, the peak corresponding to the shell of interest is inverse Fourier-transformed into k space. Considering a range of r values from $r' - \Delta r$ to $r' + \Delta r$ encompassing a peak, we can write for the inverse transform

$$k^n \chi(k) = (2\pi)^{1/2} \int_{r'-\Delta r}^{r'+\Delta r} R(r) \exp(-2ikr) \, dr. \tag{8}$$

Retaining only the positive r values in the Fourier transform, we see that the resulting EXAFS function is a complex quantity which can be easily decomposed into the

amplitude function $A(k)$ and the phase function

$$\psi(k) = [2kr + \phi(k)].$$

It has been shown (Lee *et al* 1981) that for sufficiently high photoelectron kinetic energies, the phase shift $\phi(k)$ is almost constant for chemically similar systems. Hence, if $\psi(k)$ is determined for an atom pair (with known distance r_m) in a model system, one can obtain the value of r_u in an unknown system which is chemically similar to the model system.

For the model system, the total phase is

$$\psi_m(k) = 2\,kr_m + \phi, \tag{9}$$

where ϕ is the scattering phase shift.

Using the concept of transferability of phase shift, we may write for the unknown system containing the same atom pair

$$\psi_u(k) = 2\,kr_u + \phi. \tag{10}$$

Hence

$$\psi_m(k) - \psi_u(k) = 2k\,(r_m - r_u). \tag{11}$$

The plot of $[\psi_m(k) - \psi_u(k)]$ as a function of k should, therefore, be a straight line with zero intercept and slope $2\,(r_m - r_u)$. In practice, one can vary the value E_c in such a fashion so as to reduce the intercept of the line to a minimum. The knowledge of r_m then enables the determination of r_u for the same atom pair in different chemically similar compounds.

5. Results and discussion

The EXAFS associated with the K absorption discontinuity of pure germanium is shown in figure 1. The normalized EXAFS $\chi(k)$ obtained by pre-edge fitting and by removing the smooth atomic background is shown in figure 2. Figure 3 shows the Ge K discontinuity in one of the compounds $LaGe_2$. The normalized EXAFS in this compound is shown in figure 4.

The variation of the position of the first peak, which corresponds to the first near neighbour shell in germanium, with E_0 for $n = 1, 3$ and 5 is shown in figure 5. The crossover energy E_c obtained by us for pure germanium is -25 eV which agrees well with the value $(-26\ \text{eV})$ obtained by Stearns (1982). The E_c values obtained in this way for the RGe_2 compounds are given in table 1.

The Fourier transform of $\chi(k)$ at E_c with $n = 3$ for pure germanium is shown in figure 6. The first shell contribution to the EXAFS function $\chi(k)$ is obtained by filtering the curve in figure 6 by using an appropriate smooth filter window function, which is shown by the dashed curve in figure 6. Inverse transformation of the data yields the phase function $\psi(k)$ as explained earlier. The phase function thus obtained for crystalline germanium is taken as the value of $\psi_m(k)$.

That the phase shift $\phi(k)$ obtained at $E_0 = E_c$ is linear can be demonstrated by extracting $\phi(k)$ from $\psi_m(k)$ obtained at $E_0 = E_c$ knowing r. In figure 7 are shown the phase shift curve obtained by us experimentally for pure germanium and the theoretical phase shift curve for pure germanium drawn from the data given by Teo and Lee (1979). It is seen in this figure that the variation of the experimental phase shift with k is linear, while that of the theoretical phase shift is slightly nonlinear.
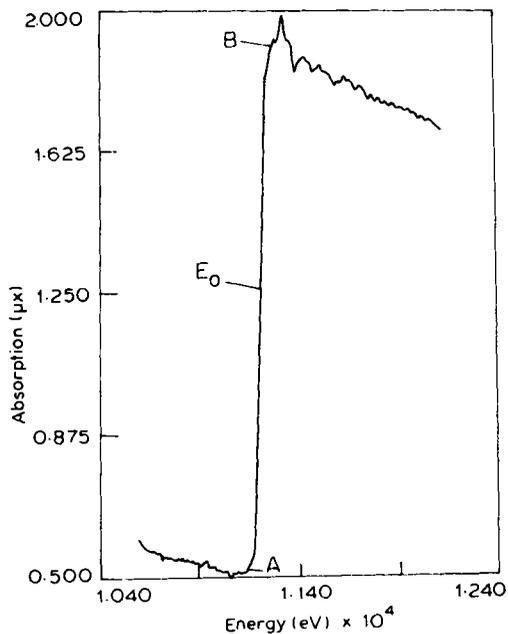
Figure 1. The as-observed K absorption discontinuity of germanium along with the EXAFS. AB is the absorption step.
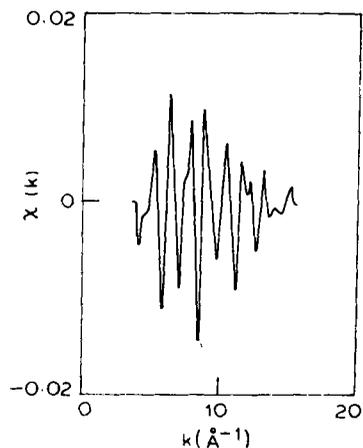

Figure 2. Normalized EXAFS $\chi(k)$ for pure germanium obtained after removing the background as per (3) in the text.
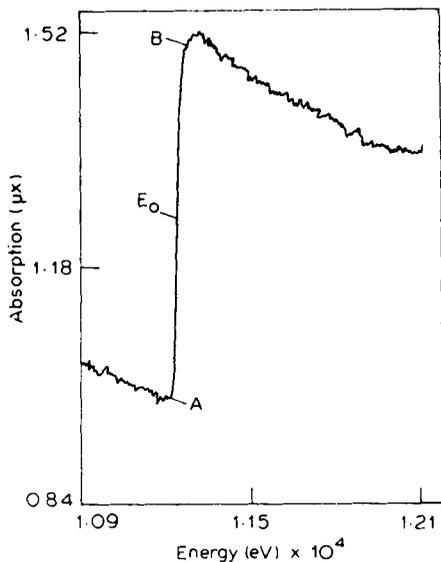

Figure 3. The as-observed K absorption discontinuity of germanium in LaGe$_2$ along with EXAFS. AB is the absorption step.
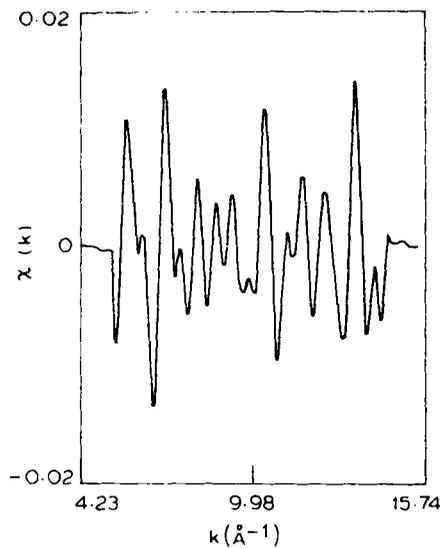

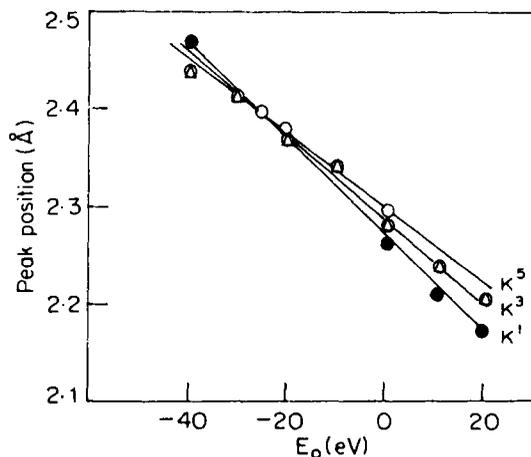**Figure 4.** Normalized EXAFS $\chi(k)$ for LaGe$_2$.

Figure 5. First peak position as a function of E_0 for pure germanium for various wave vector weighting factors k^1, k^3, k^5. The crossover energy $E_c = -25$ eV.

Table 1. Data on bond lengths.

| | | Value of r (Å) | |
| | E_c | Observed | |
Sample	(eV)	± 0.01 Å	Crystallographic
LaGe$_2$	−22	2·40	2·38
CeGe$_2$	−14	2·34	2·35
PrGe$_2$	−6	2·35	2·34
NdGe$_2$	+35	2·32	2·33
SmGe$_2$	+15	2·33	2·30
GdGe$_2$	−24	2·25	2·27
TbGe$_2$	−11	2·25	—
DyGe$_2$	+20	2·24	2·23
HoGe$_2$	+72	2·24	—
ErGe$_2$	+43	2·23	—
YGe$_2$	−35	2·22	2·24

Curves similar to those shown for LaGe$_2$ were obtained for the other RGe$_2$ compounds and from them the values of the phase function $\psi_u(k)$ were obtained. Taking $r_m = 2·45$ Å for crystalline germanium (Pearson 1964), the Ge-Ge distance in the RGe$_2$ compounds was obtained using (11). The values of this distance in the different compounds are given in table 1. Also given in the table are the values obtained crystallographically wherever available. We observe that there is a very good agreement between our values of the Ge-Ge distance and the crystallographic values. As expected, we note that the Ge-Ge distance in these compounds lies close to that in the Ge structure. The Ge-Ge distance in the compounds TbGe$_2$, HoGe$_2$ and ErGe$_2$ is being reported for the first time in this work (table 1).

Several workers (Gladyshevskii 1964; Iandelli and Palenzona 1979) have reported
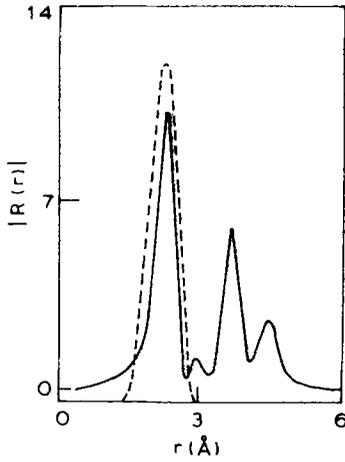
Figure 6. Fourier transform of EXAFS data at E_c $= -25$ eV and $n = 3$ for pure germanium. The dashed curve is the filter window used to isolate the first shell EXAFS.
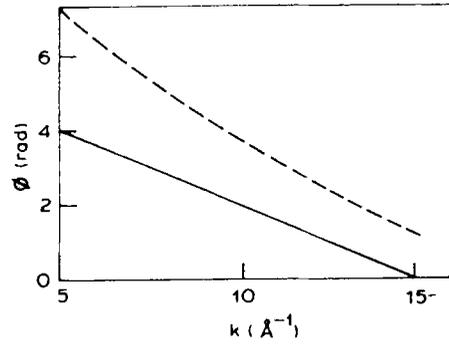
Figure 7. Phase shifts for pure germanium. The solid curve is the experimental one and the dashed curve is the theoretical one obtained from the data given by Teo and Lee (1979).
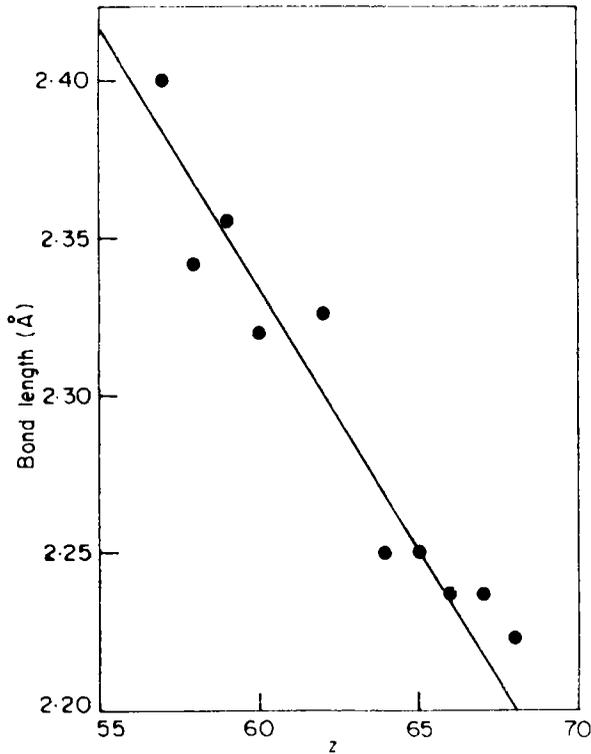

Figure 8. Variation of the Ge-Ge distance (r) in the RGe_2 compounds with atomic number Z of the rare earth metals.

linear relationships with atomic number in properties like heat of formation, molecular volume and effective nuclear charge for the rare earth intermetallics. In figure 8 we have plotted the bond length (Ge-Ge distance, r) against the atomic number (Z) in the rare earth compounds studied by us. We also find a linear correlation between r and Z.

Acknowledgements

References

Bianconi A, Incoòcia L and Stipcich S 1983 *EXAFS and near edge structure* (Berlin: Springer-Verlag)
Bonnelle C and Mande C 1982 *Advances in x-ray spectroscopy* (London: Pergamon Press)
Compton V B and Matthias B T 1959 *Acta Crystallogr.* **12** 651
Eisenberger P and Kincaid B M 1978 *Science* **200** 1441
Gladyshevskii E I 1964 *J. Struct. Chem. (USSR)* **5** 523
Gorsard A C, Jaccarino V and Wernick J H 1962 *J. Phys. Soc. Jpn* **17** 88
Hayes T M, Sen P N and Hunter S H 1976 *J. Phys.* **C9** 4357
Iandelli A and Palenzona A 1979 Crystal chemistry of intermetallic compounds in *Handbook on the physics and chemistry of rare earths* (eds) K A Gschneidner Jr and L Eyring (Amsterdam: North-Holland Publ. Co.) p 1
Jaccarino V, Matthias B T, Peter M, Suhl H and Wernick J H 1960 *Phys. Rev. Lett.* **5** 251
Labhardt A and Yuen C 1979 *Nature (London)* **277** 150
Lee P A, Citrin P H, Eisenberger P and Kincaid B M 1981 *Rev. Mod. Phys.* **53** 769
Lytle F W, Sayers D E and Stern E A 1975 *Phys. Rev.* **B11** 4825
Lytle F W, Sayers D E and Stern E A 1982 *Advances in x-ray spectroscopy* (eds) C Bonnelle and C Mande (London: Pergamon Press) p 267
Martens G, Rabe P, Schwentner N and Werner A 1977 *Phys. Rev. Lett.* **39** 1411
Matthias B T, Geballe T H and Compton V B 1963 *Rev. Mod. Phys.* **35** 1
Pearson W B 1964 *A handbook of lattice spacings and structure of metals and alloys* (London: Pergamon Press)
Sayers D E 1971 Ph.D. dissertation, University of Washington, USA
Schmükle F, Lamparter P and Steeb S 1982 *Z. Naturforsch.* **a37** 572
Sekizawa K 1966 *J. Phys. Soc. Jpn* **21** 1137
Stearns M B 1982 *Phys. Rev.* **B25** 2382
Stern E A 1974 *Phys. Rev.* **B10** 3027
Stern E A 1978 *Contemp. Phys.* **19** 289
Stern E A, Sayers D E and Lytle F W 1975 *Phys. Rev.* **B11** 4839
Teo B K and Lee P A 1979 *J. Am. Chem. Soc.* **101** 2815
Via G H, Sinfelt J H and Lytle F W 1979 *J. Chem. Phys.* **71** 690
Williams H J, Wernick J H, Nesbitt E A and Sherwood R C 1962 *J. Phys. Soc. Jpn* **17** 91