

## EXAFS study of intermetallics of the type $RGe_2$ ( $R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er$ and $Y$ ) Part II: Determination of Ge-R distances

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**Abstract.** The extended x-ray absorption fine structure (EXAFS) associated with the Ge  $K$  x-ray absorption discontinuity in pure germanium and in the intermetallics  $RGe_2$  ( $R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er$  and  $Y$ ) has been studied. The Ge-R distances in these compounds have been determined by comparing the experimental phase shifts with the theoretical ones. The Ge-R distances in the compounds  $TbGe_2$ ,  $HoGe_2$  and  $ErGe_2$  are being reported for the first time in this work.

**Keywords.** EXAFS; rare earth intermetallics; phase shifts; bond lengths.

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### 1. Introduction

In an earlier communication (Chourasia *et al* 1985; hereafter referred to as paper I) we have reported an EXAFS study of the Ge  $K$  absorption discontinuity in the compounds of the type  $RGe_2$  ( $R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er$  and  $Y$ ). We have shown how the Ge-Ge distances could be determined from the analysis of the EXAFS data. In the present paper we report the Ge-R distances in these intermetallics from our EXAFS study. In paper I, the Ge-Ge distances were determined taking polycrystalline germanium as the model compound in accordance with the procedure given by Stearns (1982). Since for the present analysis no model compound is available, the analysis for the determination of the Ge-R distances has been carried out by comparing the experimental phase shifts with the theoretical phase shifts computed by us using the data given by Teo and Lee (1979).

### 2. Experimental

The experimental technique for recording the EXAFS, which were obtained at room temperature, has been described in detail in paper I. The experimental phase shifts were obtained by Fourier-filtering the second peak, which corresponds to the rare earth atoms as the backscatterers, in the Fourier transform of  $k^3\chi(k)$ . For this purpose a NAG LIBRARY program CO6FCF was used. A combination of CO6FCF and CO6GCF was used for inverse transforming the data. The Fourier transform was taken in the

*r*-space. The data processing was done using a program developed by us for this purpose on a DEC 1090 computer.

### 3. Results and discussion

As mentioned in paper I the  $RGe_2$  compounds have the  $C_c$  ( $\alpha$ - $ThSi_2$ ) type of crystal structure. According to Grigorii and Bondarev (1969) these compounds form a framework of covalently bonded atoms of germanium with the rare earth metal atoms located in the voids of the germanium framework. The coordination number of germanium in this structure is nine. The nearest neighbours of each germanium atom are three other germanium atoms followed by six rare earth atoms. Thus the first coordination shell of each germanium atom is made up of two sub-shells, the first one containing 3 Ge atoms and the second one 6 rare earth atoms.

The EXAFS associated with the Ge *K* discontinuity in  $ErGe_2$  obtained by us is shown in figure 1. In figure 2 is shown the normalized EXAFS  $\chi(k)$  in this compound. Similar curves were obtained for the other  $RGe_2$  compounds.

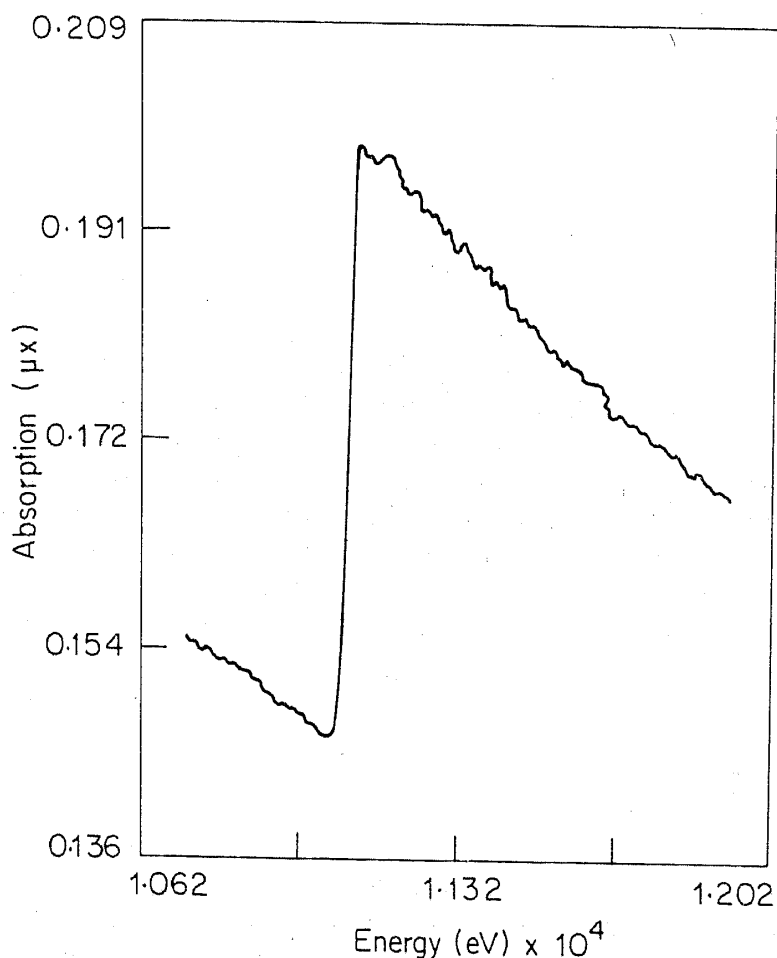


Figure 1. The as-observed *K* absorption discontinuity of germanium in  $ErGe_2$  along with the EXAFS.

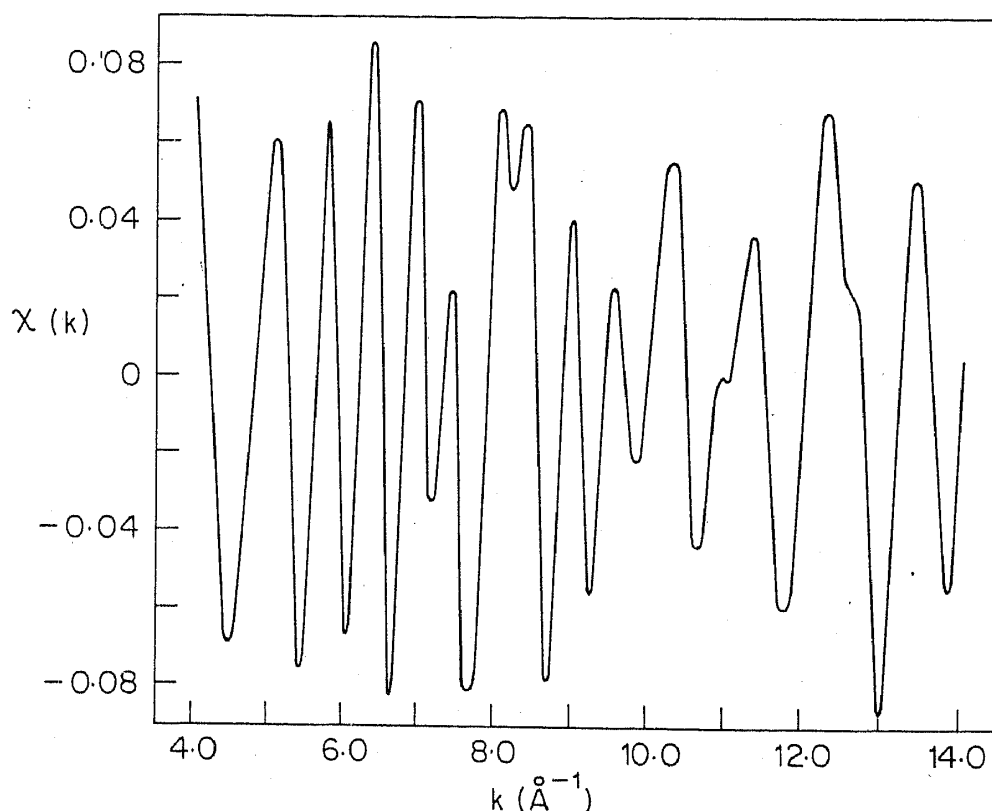


Figure 2. Normalized EXAFS  $\kappa(k)$  for  $\text{ErGe}_2$ .

Rigorous calculations of the theoretical phase shifts for a large number of atoms have been made by Teo and Lee (1979) using Clementi-Roetti as well as Herman-Skillman wave functions. Since Teo and Lee have recommended for the sake of consistency the use of the phase shifts obtained by employing the Herman-Skillman wave functions, we have used these values of the phase shifts given by Teo and Lee. The theoretical phase shifts for the compounds were computed from the expression

$$\phi(k) = \phi_a(k) + \phi_b(k) - \pi \quad (1)$$

where  $\phi_a(k)$  is the phase shift due to the central atom (here germanium) and  $\phi_b(k)$  that due to the neighbouring backscattering atoms (rare earths in our case). The values of  $\phi_b(k)$  for the different rare earth elements were interpolated from the values given for other elements by Teo and Lee. These values of  $\phi(k)$  thus calculated are given in table 1. Using these values of backscattering phase shifts, it has been shown (Teo and Lee 1979; Lee *et al* 1981) that the accuracy for the distance determination is better than 0.5% ( $\sim 0.01 \text{ \AA}$ ).

Theoretical calculation of phase shifts involves certain approximations which also include the ignorance of the chemical bonding between the central and the backscattering atoms. It has been shown by Teo and Lee (1979) and also by Lee *et al* (1981) that the approximations could be taken care of by making  $E_0$  an adjustable parameter. Therefore, to compensate for the total phase shifts obtained from the individual neutral atom phase shifts, we have made  $E_c$  and  $r$  as adjustable parameters while carrying out the matching between the experimental and the theoretical phase shifts. Such a method

Table 1. Total phase shift  $\phi(k)$  in radians vs photoelectron wave vector  $k$  in  $\text{\AA}^{-1}$ .

Backscatterer $k =$	3.7795	4.2519	4.7243	5.1967	5.6692	6.1416	6.6140
	7.0865	7.5589	8.5038	9.4486	10.3935	11.3384	12.2832
	13.2281	14.1729	15.1178				
La	8.8169	8.1972	7.7093	7.3147	6.8799	6.5780	6.4067
	6.2489	6.1520	6.0047	5.6658	5.2056	4.7147	4.2437
	3.7884	3.3096	2.8947				
Ce	8.5429	7.9419	7.3927	7.0406	6.6204	6.2817	6.0920
	5.9205	5.8267	5.7455	5.4767	5.0513	4.6119	4.1475
	3.7107	3.2623	2.8401				
Pr	8.3431	7.7561	7.1598	6.8345	6.4235	6.0549	5.8481
	5.6617	5.5647	5.5312	5.3244	4.9349	4.5392	4.0833
	3.6622	3.3396	2.8136				
Nd	8.2174	7.6399	7.0105	6.6963	6.2892	5.8977	5.6750
	5.4726	5.3661	5.3618	5.2090	4.8564	4.4966	4.0511
	3.6428	3.2915	2.8151				
Sm	8.6226	8.0268	7.4425	7.0073	6.5676	6.1948	5.9481
	5.7006	5.5046	5.4274	5.3587	5.0875	4.7180	4.3065
	3.8916	3.4937	3.1004				
Gd	8.6732	8.0757	7.4901	7.0150	6.5576	6.1658	5.8941
	5.6110	5.3778	5.2682	5.2507	5.0584	4.7353	4.3542
	3.9569	3.5822	3.1996				
Tb	8.7011	8.1018	7.5195	7.0249	6.5568	6.1549	5.8715
	5.5713	5.3230	5.1886	5.1844	5.0321	4.7350	4.3702
	3.9833	3.6196	3.2434				
Dy	8.7308	8.1290	7.5527	7.0389	6.5587	6.1464	5.8519
	5.5350	5.2739	5.1090	5.1099	4.9979	4.7287	4.3809
	4.0055	3.6525	3.2825				
Ho	8.7623	8.1573	7.5897	7.0569	6.5634	6.1404	6.1343
	5.5020	5.2306	5.0294	5.0273	4.9558	4.7165	4.3863
	4.0235	3.6809	3.3171				
Er	8.5351	7.9369	7.4572	6.9713	6.4960	6.0590	5.7477
	5.3936	5.1140	4.8377	4.8047	4.8099	4.6124	4.3036
	3.9654	3.6395	3.2825				
Y	5.2960	4.7998	4.6514	4.5721	4.6021	4.6774	4.4166
	4.0904	3.7989	3.1578	2.5538	1.9749	1.4079	0.9099
	0.4182	-1.0308	-0.5332				

of analysis has been found by many workers (Lee *et al* 1977; Teo *et al* 1977, 1978; Shulman *et al* 1978) to give satisfactory results.

As shown in paper I, the normalized EXAFS  $\chi(k)$  can be written as

$$\chi(k) = -\sum_j A_j(k) \sin [2kr_j + \phi_j(k)], \quad (2)$$

where  $A_j(k)$  is the amplitude for the  $j$ th shell,  $r_j$ , is the average separation of the absorbing atom from the atoms of the  $j$ th shell 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 backscattering. The total phase shift  $\phi_j(k)$  is related to the phase function  $\psi_j(k)$  by

$$\psi_j(k) = 2kr_j + \phi_j(k). \quad (3)$$

The distance  $r_j$  can be determined by comparing  $\phi(k)$  with the theoretical phase shifts. However, the two phase shifts may not match very well due to the uncertainty in the value of the energy zero ( $E_0$ ) of EXAFS which represents the kinetic energy of the outgoing electrons. The matching of the two phase shifts is obtained by varying  $E_c$ , the energy crossover point, *i.e.*, the value of  $E_0$  at which the linear plots of the peak in the Fourier transform of the spectra against  $E_0$  for the different  $k^n$  weighting schemes meet, along with  $r$  by carrying out the least squares fit.

For the matching of the two phase shift curves a program called MINFUN (Humphrey 1962) was used. Figure 3 shows the matching of the experimental and theoretical phase shifts for polycrystalline germanium.

It may perhaps be expected that the experimental phase shift (the solid curve in figure 3) would be perfectly linear since the analysis has been done by choosing  $E_0 = E_c$ . The nonlinearity of the phase shift could be explained by the fact that the matching was done by making  $E_c$  and  $r$  as adjustable parameters and that changing  $E_c$  results in making the phase shift non-linear as has been demonstrated by Stearns (1982). The value of  $r$  determined by matching the two curves was 2.46 Å which agrees with the crystallographically known value 2.45 Å for germanium (Pearson 1964). A similar procedure was adopted for the RGe<sub>2</sub> compounds by varying  $E_c$  and  $r_2$ , the distance

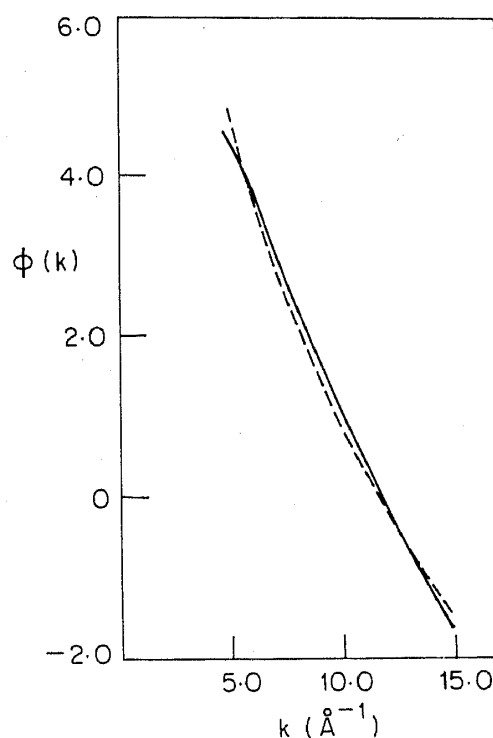


Figure 3. Matching of the experimental phase shifts with the theoretical phase shifts for pure germanium. The solid curve is the experimental one while the dashed curve is the theoretical one obtained from the data given by Teo and Lee (1979).

Table 2. Data on Ge-R distances.

Sample	$\Delta E_c$	Observed $r_2(\text{Å}) \pm 0.01(\text{Å})$	Crystallographic value (Å)
LaGe <sub>2</sub>	-18	3.15	3.14
CeGe <sub>2</sub>	+47	3.13	3.14
PrGe <sub>2</sub>	-12	3.08	3.08
NdGe <sub>2</sub>	+10	3.07	3.07
SmGe <sub>2</sub>	-33	3.02	3.04
GdGe <sub>2</sub>	-1	2.99	3.01
TbGe <sub>2</sub>	-14	2.99	—
DyGe <sub>2</sub>	-9	2.98	2.97
HoGe <sub>2</sub>	-12	2.95	—
ErGe <sub>2</sub>	-2	2.94	—
YGe <sub>2</sub>	+13	2.99	2.98

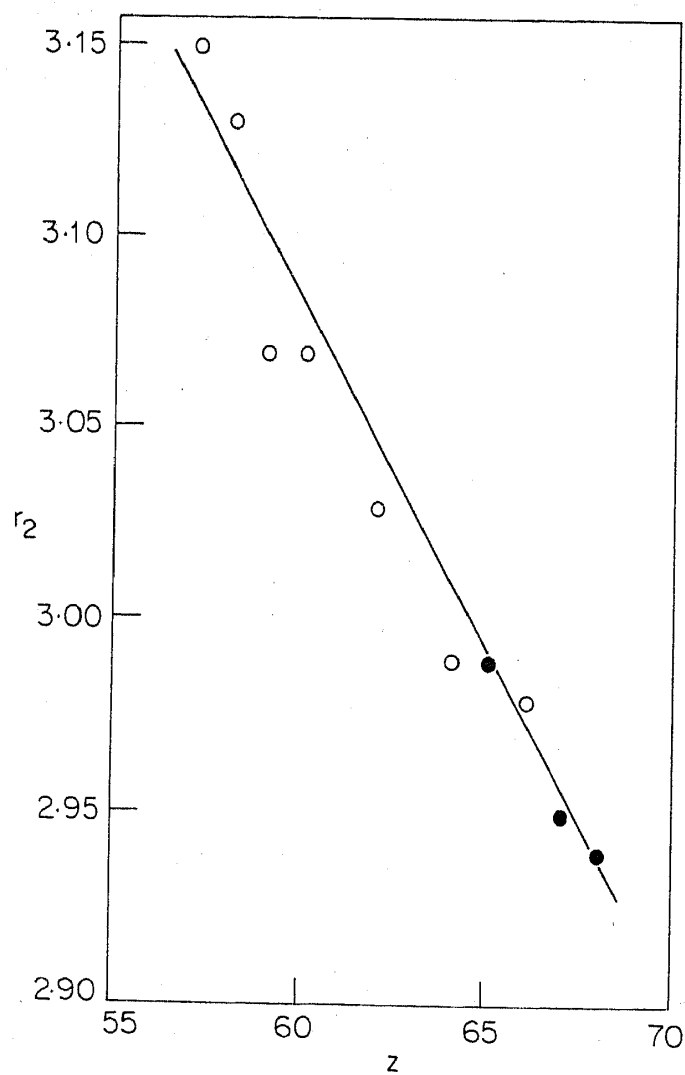


Figure 4. Variation of the Ge-R distance ( $r_2$ ) in the RGe<sub>2</sub> compounds with the atomic number ( $Z$ ) of the rare earth metals. The solid points represent the data obtained for the first time by us.

between the central germanium atom and its rare earth neighbours. The values of  $\Delta E_c$  and  $r_2$  which gave the best fit between the experimental phase shifts and the theoretical ones are given in table 2. The Ge-R distances in the compounds  $TbGe_2$ ,  $HoGe_2$  and  $ErGe_2$  are being reported for the first time in this work. Table 2 also gives the crystallographic values of the Ge-R distances for the compounds for which such data are available. It is observed that there is a very good agreement between our values and the crystallographic values. It is also observed from this table that  $r_2$  decreases as the atomic number  $Z$  of the rare earth atom increases. In figure 4 is shown the variation between  $r_2$  and  $Z$ .

Sekizawa (1966) expressed doubts about the phases of the compounds  $HoGe_2$  and  $ErGe_2$ . For the compound  $HoGe_2$  he indicated the possibility of the existence of another phase besides the  $RGe_2$  phase. Our EXAFS study shows the existence of only one phase ( $RGe_2$ ) in this compound. The existence of any other phase would have shown itself in the Fourier transform of the EXAFS data. The compound  $ErGe_2$  has been shown by Sekizawa (1966) to crystallise in an unknown phase. Our EXAFS analysis indicates that this compound also crystallises in the  $RGe_2$  phase as do the other compounds of the  $RGe_2$  family.

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