

# Pressure dependence of the Curie temperature of intermetallic compounds of iron and rare-earth elements, Th, and Zr

M. Brouha and K.H.J. Buschow

Philips Research Laboratories, Eindhoven, Netherlands

(Received 28 August 1972)

The pressure dependence of the Curie temperature ( $T_c$ ) of several intermetallic compounds of iron has been determined by means of the temperature dependence of the electrical resistivity at various pressures. Pressures up to 40 kbar were applied. The value of  $dT_c/dp$  was observed to be negative in the compounds  $R_2Fe_{17}$  ( $R = \text{Pr, Nd, Er, and Th}$ ),  $Y_6Fe_{23}$ ,  $Er_6Fe_{23}$ ,  $ErFe_3$ ,  $Th_2Fe_7$ ,  $ThFe_3$ ,  $CeFe_2$ , and  $ZrFe_2$ . The Curie temperature of the compound  $ThFe_4$  is pressure independent within experimental error. In the compounds  $RFe_2$  ( $R = \text{Gd, Ho, Er, and Y}$ ), the value of  $dT_c/dp$  was found to be positive. The experimental data are discussed in terms of Friedel's semilocalized model and the collective electron model.

## I. INTRODUCTION

The magnetic properties of rare-earth transition intermetallics have been studied extensively in recent years.<sup>1,2</sup> Whereas the Curie temperature ( $T_c$ ) of rare-earth cobalt and nickel compounds decreases with decreasing concentration of the 3d element, an increase of this quantity is observed in rare-earth iron compounds. This behavior has tentatively been explained in terms of a changing coupling energy between the magnetic moments, with the use of a partially localized description of the 3d moments.<sup>2</sup>

More direct information concerning the magnetic properties of the 3d electrons in the rare-earth iron compounds can be obtained by studying the influence of pressure on the Curie temperature. Previously, this pressure dependence of  $T_c$  had been studied only for a few R-Fe compounds ( $YFe_2$ ,  $Y_6Fe_{23}$ ,  $Y_2Fe_{17}$ ) at relatively low pressures (up to 4.5 kbar).<sup>3</sup> In the present investigation the pressure dependence of  $T_c$  has been studied with pressures up to 40 kbar on several samples of each of the series of compounds  $R_2Fe_{17}$ ,  $R_6Fe_{23}$ ,  $RFe_3$ , and  $RFe_2$ . To account for the possible influence of the valence electron concentration, we have also investigated several intermetallic compounds between iron and the elements Th and Zr.

## II. EXPERIMENTAL

The samples were prepared from 99.9% pure starting materials by arc melting. In order to obtain single-phase material, most of the samples were vacuum-annealed at temperatures ranging from 800 to 1100 °C. After annealing, the absence of foreign phases was verified by x-ray diffraction. The pressure was generated in a piston-cylinder device of the type described by Kennedy and La Mori.<sup>4</sup> Nearly all the measurements were carried out with boron-nitride and pyrophyllite as pressure-transmitting media. The Curie temperature was determined from the temperature-resistance curve. The temperature was measured with a chromel-alumel thermocouple. The resistance was obtained from four terminal measurements. Pressure was adjusted to the proper level by measuring the ram pressure with a Heise-Bourdon tube pressure gauge, which was calibrated on a bismuth sample mounted in the same way. On some samples the pressure was also applied using the Teflon cell technique with a mixture of *n*-pentane and isopentane as pressure-transmitting fluid. The pressure was recorded by noting the change in the resistance of a calibrated manganin coil during the

measurements. More details concerning the pressure equipment are given elsewhere.<sup>5</sup>

The shift of the Curie temperature is determined by comparison of the various resistance-temperature curves. In Fig. 1 an example is given of the variation of the temperature dependence of the electrical resistivity  $\rho(T)$  when studied at different pressures. It is seen that the ferromagnetic Curie temperature ( $T_c$ ) of the compound  $ZrFe_2$ , which shows up as a break in the  $\rho$ -vs- $T$  curve, gradually shifts to lower temperatures as the pressure is increased. The pressure dependence of ( $T_c$ ) for the other compounds was determined in a similar way. The Curie temperatures determined from the resistivity data at normal atmospheric pressure are gathered in Table I. These values are seen to agree closely with those obtained from measurements of the temperature dependence of the magnetization, also shown in Table I.

In Fig. 2 the pressure dependence of  $T_c$  is given for some of the Laves-phase compounds  $RFe_2$ , which constitute the compounds poorest in Fe content in the various binary R-Fe systems. For  $R = \text{Gd, Ho, Er, and Y}$ , the Curie temperature increases with pressure, whereas in  $CeFe_2$  and  $ZrFe_2$  it decreases.

The Curie temperature of the compounds with the highest Fe content, i.e., the compounds of composition  $R_2Fe_{17}$ , was observed to decrease very strongly with pressure (Fig. 3). A survey of the pressure dependence of  $T_c$  is given for all Er-Fe compounds in Fig. 4 and for all Th-Fe compounds in Fig. 5. It is seen that an increasing Curie temperature is accompanied by a change in slope  $dT_c/dp$  from negative values to pressure-independent or positive values.

The present data are only in partial agreement with those reported by Givord *et al.*<sup>3</sup> for applied pressures up to 4.5 kbar. For the compounds  $Y_2Fe_{17}$ ,  $Y_6Fe_{23}$ , and  $YFe_2$ , the values of  $dT_c/dp$  are  $-9.8 \text{ K/kbar}$ ,  $+0.1 \text{ K/kbar}$ , and  $+5.0 \text{ K/kbar}$ , respectively. The first of these compounds has a value which is in line with the results shown in Fig. 3. For  $Y_6Fe_{23}$ , we observed a value of about  $-4 \text{ K/kbar}$ , which therefore differs from the one mentioned above not only in magnitude but also in sign. It can be seen from Fig. 2 that the present value for  $YFe_2$  is also different, being about one order of magnitude smaller than the value reported in Ref. 3. The same values for  $Y_6Fe_{23}$  and  $YFe_2$  ( $-4 \text{ K/kbar}$  and  $+0.6 \text{ K/kbar}$  were found using the transformer method<sup>6</sup> in the Teflon cell.

NOV 15 1973



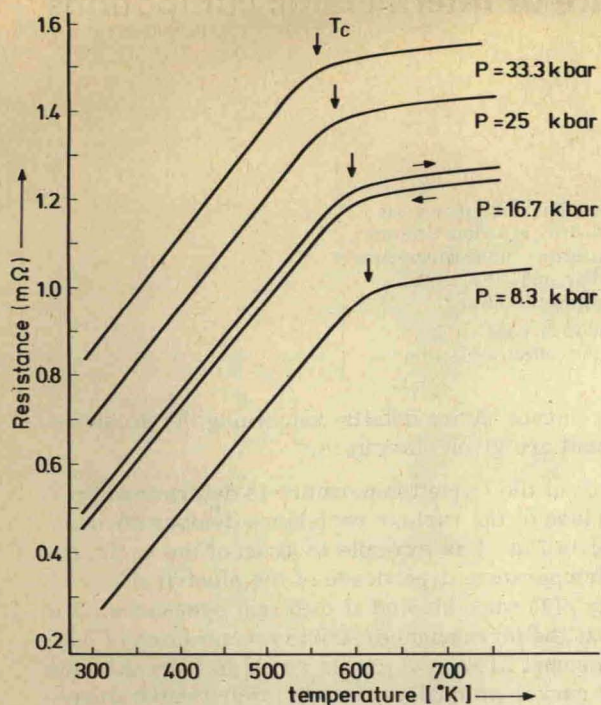


FIG. 1. Temperature dependence of the electrical resistivity at various applied pressures for  $\text{ZrFe}_2$ . Except for  $p = 16.7$  kbar, the curves are given for increasing temperature only. The resistance scale corresponds to the upper curve at  $p = 16.7$  kbar. The other curves have been given an arbitrary vertical displacement.

### III. DISCUSSION

In compounds of rare-earth elements with Ni, Co, and Fe, the magnetic moment per 3d atom decreases with decreasing concentration of the 3d element.<sup>1,2</sup> This is also the case with the Curie temperature of the nickel and cobalt compounds.<sup>1,2</sup> The rare-earth iron compounds, however, behave quite remarkably, as their Curie temperature increases with decreasing Fe content. This behavior has tentatively been explained by means of a semilocalized model<sup>7-9</sup> (the Friedel model).

The average distance between the 3d atoms tends to

TABLE I. Curie temperatures of various intermetallic compounds of iron as determined by measurements of the temperature dependence of the resistivity ( $\rho$ ) and the magnetization ( $\sigma$ ).

Compound	$T_c(\rho)$	$T_c(\sigma)$
$\text{GdFe}_2$	803	785
$\text{HoFe}_2$	608	612
$\text{ErFe}_2$	591	590
$\text{YFe}_2$	545	545
$\text{CeFe}_2$	229	230
$\text{ZrFe}_2$	628	625
$\text{PrFe}_{17}$	294	290
$\text{Nd}_2\text{Fe}_{17}$	330	326
$\text{Th}_2\text{Fe}_{17}$	286	295
$\text{ThFe}_5$	676	680
$\text{Th}_2\text{Fe}_7$	568	570
$\text{ThFe}_3$	432	425
$\text{Er}_2\text{Fe}_{17}$	308	310
$\text{Er}_5\text{Fe}_{23}$	498	495
$\text{ErFe}_3$	559	555
$\text{ErFe}_2$	591	590

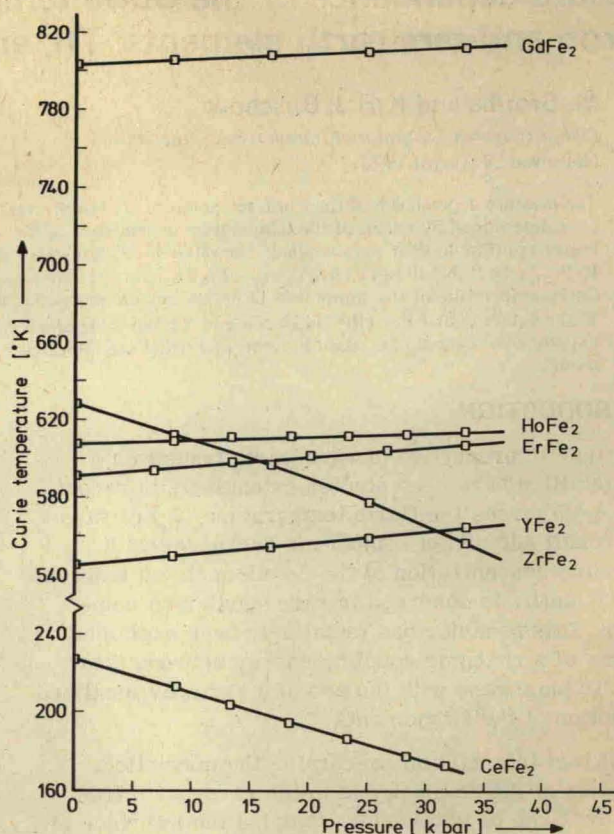


FIG. 2. Pressure dependence of the Curie temperature ( $T_c$ ) for various Laves-phase compounds.

larger values when the 3d content is decreased. It is very likely that in the case of the iron compounds this results in a more positive (ferromagnetic) coupling between the moments. The coupling energy depends not only on the distances between the 3d atoms but also on the Fermi wave vector  $k_M$  of the 3d band, measured to the nearest band extremum. On the assumption that an applied pressure brings about a negligible  $s$ - $d$  or  $d$ - $s$  electron transfer in the R-Fe compounds, the quantity  $k_M$  can be considered as remaining roughly unaffected. If the increase in  $T_c$  in the series  $\text{R}_2\text{Fe}_{17}$ ,  $\text{R}_6\text{Fe}_{23}$ ,  $\text{RFe}_3$ , and  $\text{RFe}_2$  is the result of increasing Fe-Fe distances, one would expect a negative value for  $dT_c/dp$ , at least for the first three members of this series. This is indeed observed experimentally (see Fig. 3). The positive pressure derivative of  $T_c$  observed for most of the  $\text{RFe}_2$  compounds (Fig. 2) probably means that the optimal Fe-Fe distances for large positive moment couplings occur in between those of the compounds  $\text{RFe}_3$  and  $\text{RFe}_2$ . Because the elements Ce, Zr, and Th have one more valence electron than the normal rare-earth elements, it is very likely that the value of  $k_M$  in their iron compounds is smaller than the value of the corresponding R-Fe compounds, at least if it is assumed that part of the valence electrons go into the 3d band. The optimal Fe-Fe distances would then be larger than in the R-Fe compounds, and from this point of view it is understandable that  $T_c$  of  $\text{CeFe}_2$  and  $\text{ZrFe}_2$  still shows a negative pressure dependence (Fig. 2). It is surprising, however, that the maximum value of  $T_c$  in the Th-Fe



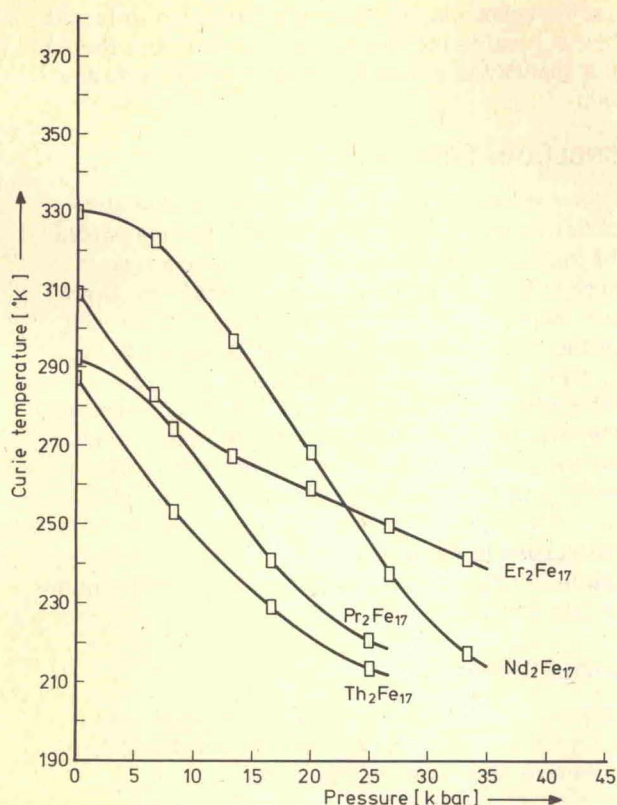


FIG. 3. Pressure dependence of the Curie temperature for compounds of composition  $R_2Fe_{17}$ .

system occurs already at a relatively large Fe content (see Table I). If this maximum of  $T_c$  for  $ThFe_5$  is likewise to be considered the result of the dependence of the magnetic moment coupling energy on the Fe-Fe distance, a positive value for  $dT_c/dp$  should be observed for  $Th_2Fe_7$  and  $ThFe_3$ , which is in obvious disagreement with the experimental results.

In the following, we will investigate whether the collective electron model is able to give a more satisfactory account of the experimental data. Using Heine's<sup>10</sup> result that the  $3d$  bandwidth  $W$  varies with the distance  $r$  between two  $3d$  atoms in proportion to  $r^{-5}$ , and the assumption that the number of  $3d$  electrons in the band remains constant under pressure, it can be shown that the following relation holds<sup>11-14</sup>:

$$\frac{\partial T_c}{\partial P} = \frac{5}{6} \kappa [2T_c - B/T_c], \quad (1)$$

$$B = \frac{U_{eff} T_F^2}{\bar{U} U} \quad (2)$$

$$U_{eff} = \frac{U}{1 + \gamma U W^{-1}}$$

$$\bar{U} = U_{eff} N(E_F); \quad \gamma = \frac{1}{2} W \int_{E_F}^W [N(E)/E] dE,$$

$$T_F^2 = \frac{6}{k_B \pi^2} \left[ \frac{N'(E_F)^2}{N(E_F)} - \frac{N''(E_F)}{N(E_F)} \right]^{-1}.$$

In these expressions  $\kappa$  represents the compressibility,  $U$  is the bare intraatomic Coulomb repulsion,  $T_F$  is the degeneracy temperature,<sup>15</sup> and  $N(E_F)$ ,  $N'(E_F)$ , and  $N''(E_F)$  are the density of states at the Fermi surface

and the first and second derivatives, respectively. The special form given above for  $B$  is due to Edwards and Bartel.<sup>13</sup> The quantity  $\gamma$  is independent of the bandwidth. A glance at Fig. 4 shows that relation (1) is in qualitative agreement with experiment: In compounds with low Curie temperatures the term  $-B/T_c$  dominates, making  $dT_c/dp$  negative, whereas in compounds with high Curie temperatures the  $T_c$  term dominates and  $dT_c/dp$  is positive. It is gratifying that relation (1) can also describe qualitatively the experimental data of the Th-Fe system shown in Fig. 5, where the lowest and highest values for  $T_c$  do not correspond to the highest and lowest Fe concentrations, respectively. Satisfactory agreement also exists with respect to the compounds shown in Figs. 2 and 3: It is clear that the compounds  $R_2Fe_{17}$  with low  $T_c$  shown in Fig. 3 should have a negative pressure dependence. Regarding the compounds  $RFe_2$  shown in Fig. 2, we note that a positive value for  $dT_c/dp$  is expected for all compounds except  $CeFe_2$ , which, because of its low  $T_c$ , should show a negative pressure dependence.

An unexpected behavior is shown by the compound  $ZrFe_2$  which, in spite of its high  $T_c$ , has a negative value of  $dT_c/dp$ . It is possible that the value for  $B$  appearing in Eq. (1) is significantly larger in  $ZrFe_2$  than in the other compounds mentioned above, so that the term  $-B/T_c$  is dominant even for high values of  $T_c$ . A high value of  $B$  could for instance be the result of a larger bandwidth, since  $U_{eff}$  [Eq. (2)] as well as  $T_F$  ( $\sim W$ ) depend on this quantity. A comparison of the magnetic properties of the compounds  $ZrFe_2$  and  $RFe_2$

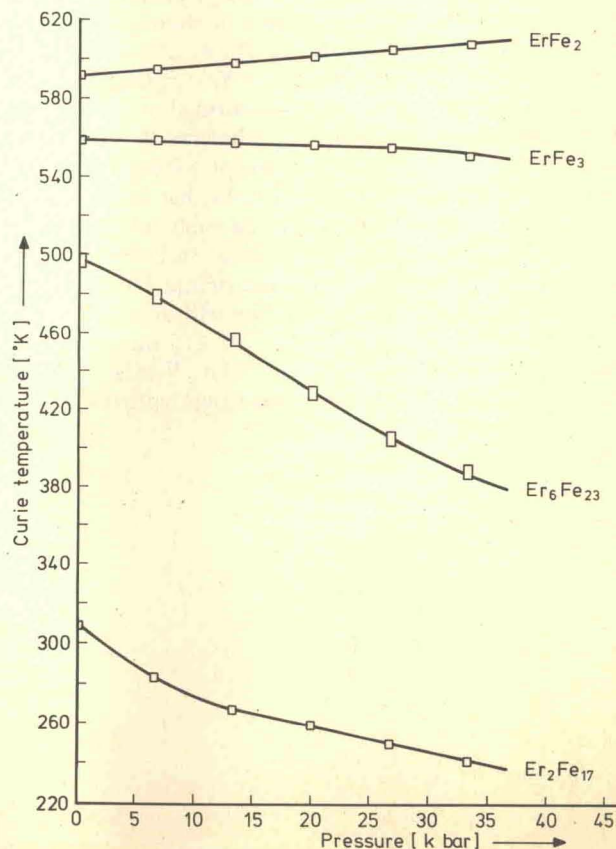


FIG. 4. Pressure dependence of the Curie temperature for erbium iron compounds.



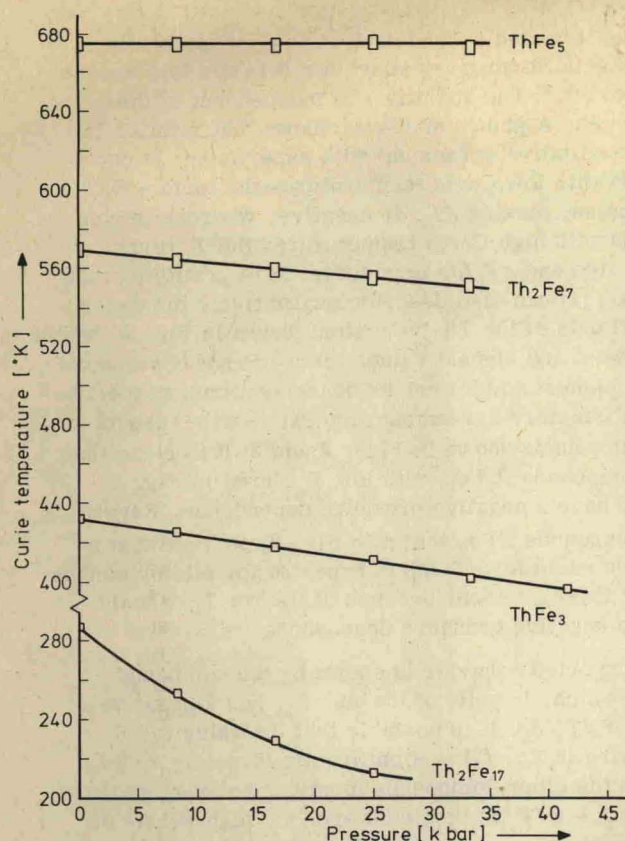


FIG. 5. Pressure dependence of the Curie temperature for thorium iron compounds.

does in fact give some indications that  $U_{\text{eff}}$  in  $\text{ZrFe}_2$  is larger; the dependence of the magnetic moment per  $3d$  atom on concentration is different in  $\text{ZrFe}_{2-2x}\text{Co}_{2x}$  from that found in  $\text{YFe}_{2-2x}\text{Co}_{2x}$ . In the series  $\text{YFe}_{2-2x}\text{Co}_{2x}$  the magnetic moment per  $3d$  atom passes through a maximum upon replacement of Fe by Co, whereas the magnetic moment per  $3d$  atom decreases continuously in the series  $\text{ZrFe}_{2-2x}\text{Co}_{2x}$ .<sup>1,16</sup> This suggests that in the rare-earth compound each of the two  $3d$  subbands (of one spin direction) is unsaturated and that in  $\text{ZrFe}_2$  the unsaturated character is restricted primarily to a subband of one spin direction. Together with the fact that the magnetic moment per Fe atom (i.e., the number of holes) is larger in the case of  $\text{ZrFe}_2$ ,<sup>17</sup> this indicates that in this compound the exchange splitting

between the subbands of either spin direction is larger. A higher  $U_{\text{eff}}$  value for  $\text{ZrFe}_2$  then follows from the fact that this quantity is a direct measure of the exchange splitting.

#### IV. CONCLUDING REMARKS

It has been shown in Sec. III that the collective electron model is able to explain well the pressure derivatives of the Curie temperature of rare-earth iron compounds. Subject to certain assumptions concerning the band shape, it is also possible to explain the variation of the Curie temperature in the sequence  $\text{R}_2\text{Fe}_{17}$ ,  $\text{R}_6\text{Fe}_{23}$ ,  $\text{RFe}_3$ ,  $\text{RFe}_3$ . The difficulties connected with the applicability of this model to the compounds under investigation become clearly apparent, however, if one tries to explain the drastic difference in Curie temperature (but not in moment) between pure Fe and  $\text{R}_2\text{Fe}_{17}$ .<sup>1,2</sup> The explanation of this feature presents less difficulties in the semilocalized model, where it is possible to take negative or antiferromagnetic interactions into account as well.

#### ACKNOWLEDGMENTS

The authors would like to thank A. G. Rijnbeek and R. Kuipers for their work and assistance in making these high-pressure measurements possible.

- <sup>1</sup>K. N. R. Taylor, *Adv. Phys.* **20**, 552 (1971).
- <sup>2</sup>K. H. J. Buschow, *Phys. Status Solidi A* **7**, 199 (1971).
- <sup>3</sup>D. Givord, F. Givord, and R. Lemaire, *J. Phys. (Paris)* **32**, C1-688 (1971).
- <sup>4</sup>G. C. Kennedy and P. N. La Mori in *Progress in Very High Pressure Research*, edited by F. P. Bundy, W. R. Hibbard, and H. M. Strong (Wiley, New York, 1961).
- <sup>5</sup>M. Brouha and A. G. Rijnbeek, *Rev. Sci. Instr.* (to be published).
- <sup>6</sup>L. Patrick, *Phys. Rev.* **93**, 384 (1954).
- <sup>7</sup>J. Friedel, G. Leman, and S. Olszewski, *J. Appl. Phys. Suppl.* **32**, 325 (1961).
- <sup>8</sup>J. Friedel, *J. Phys. Radium* **23**, 501 (1962).
- <sup>9</sup>P. Lederer and A. Blandin, *Philos. Mag.* **14**, 363 (1966).
- <sup>10</sup>V. Heine, *Phys. Rev.* **153**, 673 (1967).
- <sup>11</sup>N. D. Lang and H. Ehrenreich, *Phys. Rev.* **168**, 605 (1968).
- <sup>12</sup>E. P. Wohlfarth, *J. Phys. C* **2**, 68 (1969).
- <sup>13</sup>L. R. Edwards and L. C. Bartel, *Phys. Rev. B* **5**, 1064 (1972).
- <sup>14</sup>M. Shiga, *Solid State Commun.* **7**, 559 (1969).
- <sup>15</sup>D. M. Edwards and E. P. Wohlfarth, *Proc. R. Soc. A* **303**, 127 (1968).
- <sup>16</sup>K. Kanematsu, *J. Phys. Soc. Jap.* **31**, 1355 (1971).
- <sup>17</sup>K. H. J. Buschow and R. P. van Staple, *J. Phys. (Paris)* **32**, C1-672 (1971).