Pressure dependence of the Curie temperature of Co_2TiAl

E. DiMasi and M. C. Aronson
The Harrison M. Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan 48109-1120

B. R. Coles
Imperial College, London SW 7 2AZ, United Kingdom

(Received 13 October 1992; revised manuscript received 28 December 1992)

Electrical-resistivity measurements at temperatures between 1.2 and 300 K and pressures up to 12 kbar have been used to determine that the pressure dependence of the Curie temperature T_C of the ferromagnetic Heusler alloy Co_2TiAl is -0.7 K/kbar. Analysis of the pressure dependence of T_C in the Stoner-Wohlfarth theory of weak itinerant ferromagnetism reveals the important role of spin fluctuations in this material. Strong ferromagnetic ordering exists only in a limited range of nearest-neighbor cobalt-cobalt spacing in itinerant ferromagnets whose only potentially magnetic species is Co. Observation of the lack of correlation between Curie temperature and intermoment cobalt spacing is combined with the results of high-pressure measurements to identify cobalt Heusler alloys as examples of weak itinerant ferromagnets in which spin fluctuations are generically expected to make a significant contribution.

INTRODUCTION

Band ferromagnetism is an important phenomenon exhibited by many transition-metal compounds, but developing a complete theoretical description has been limited because direct information about electronic structure and the electron-electron interactions is difficult to obtain from experimental sources. As these properties depend sensitively on the unit cell volume, magnetic measurements at high pressures can provide valuable information about the complicated mechanisms underlying itinerant electron ferromagnetism.[1]

Intermetallic compounds of cobalt are particularly interesting. They exhibit a diverse array of magnetic properties, which often differ from those of analogous compounds containing other transition metals such as nickel or iron.[2] In particular the cobalt-based Heusler alloys Co_2XY have received attention.[3–5] Ferromagnetic ordering, present in most of these compounds, involves itinerant Co $3d$ electrons, which are considerably affected by the neighboring atoms. This is to be contrasted with the properties of the Heusler alloys X_2MnY (where X is not Co), in which essentially localized moments on the Mn atoms are not strongly dependent on the characteristics of the X and Y atoms.[6]

In this paper we present the pressure dependence of the Curie temperature of Co_2TiAl determined by electrical resistance measurements. The experimental results are analyzed in the Stoner-Wohlfarth theory of weak itinerant ferromagnetism, and the importance of the contribution of spin fluctuations is discussed.

EXPERIMENTAL DETAILS AND RESULTS

Polycrystalline specimens were prepared by arc melting the constituent elements in an Ar atmosphere. Platinum wire leads were attached to the as-cast samples either by spot welding or silver epoxy. The four-point resistance was measured with a current source and lock-in amplifier. Hydrostatic pressure was provided by a beryllium-copper liquid clamp cell[7] with 1:1 n-pentane-isoamyl alcohol as the pressure transmitting medium. Pressure was determined inductively from the superconducting transition temperature of lead.[8]

Figure 1 shows the sample resistivity over the entire temperature range for pressures up to 5.8 kbar. Curves have been offset along the vertical axis for clarity. The resistance is linear at high temperatures, and decreases near 115 K indicating a ferromagnetic phase transition, which has been observed previously at atmospheric pressure.[6] Below this transition the resistance is metallic, although the precise T dependence at low temperatures has not been determined as the residual resis-

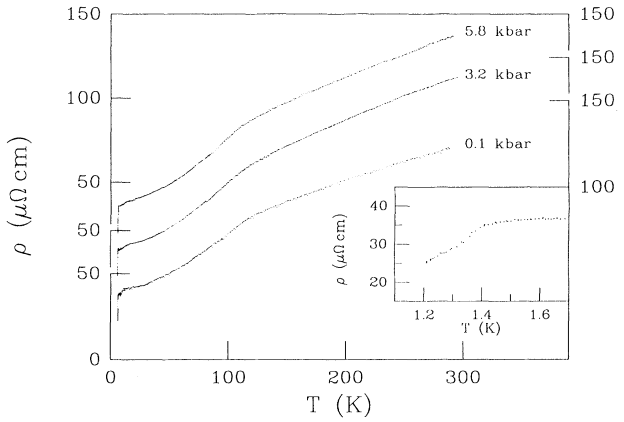

FIG. 1. Resistivity of Co_2TiAl at 0.1, 3.2, and 5.8 kbar for sample with epoxied leads. Curves have been offset along the vertical axis for clarity. Inset: expansion of the superconducting transition at 0.1 kbar.

 ©1993 The American Physical Society

tivity is very large. The decrease in resistance at 5 K has been observed only in samples with epoxied leads and thus is taken not to be intrinsic to Co_2TiAl. A sharp drop in the resistance at 1.48 K indicates a superconducting transition (inset Fig. 1).

At all temperatures the resistivity is only weakly pressure dependent. The pressure dependences of the Curie temperature T_C and superconducting transition temperature T_S are shown in Figs. 2(a) and 2(c), respectively. As shown in Fig. 2(b) the Curie temperature is determined by linearizing the measured resistivity in temperature intervals ≈ 60 and 30 K wide above and below the transition. The Curie temperature is identified as the intersection of extrapolations from the linear regions, and decreases slightly with pressure, at a rate of $dT_C/dP = -(0.7 \pm 0.2)$ K/kbar. The pressure dependence of the Curie temperature of Co_2TiAl has previously been measured inductively, yielding $dT_C/dP = +0.6$ K/kbar.[9]

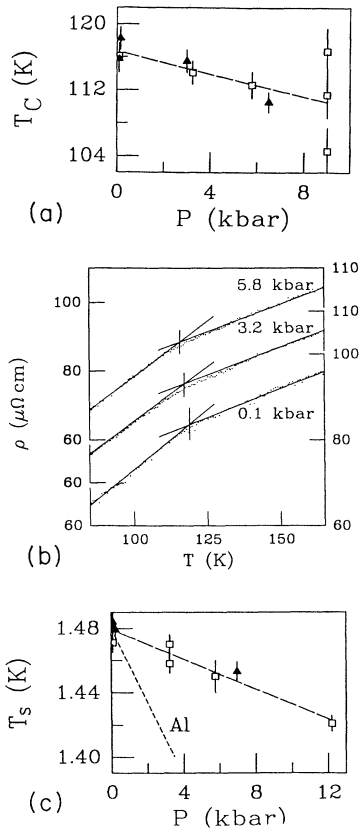

FIG. 2. (a) Pressure dependence of Curie temperature: sample leads attached by spot welding (▲) or silver epoxy (□). The dashed line is a linear fit to data, giving $dT_C/dP = -(0.7 \pm 0.2)$ K/kbar. (b) Expansion of the resistivity curves about the ferromagnetic transition, showing intervals linearized for the determination of T_C. (c) Pressure dependence of the superconducting transition temperature, with a linear fit to the data yielding $dT_S/dP = -(4.6 \pm 0.1)$ mK/kbar (— — —). A line with the slope corresponding to the pressure dependence of the superconducting transition temperature of Al (Ref. 12) (- - - - -) is shown for comparision.

Since studies of $Co_2Ti_{1-x}Al_{1+x}$ for $|x| \leq 0.25$ have shown that the magnetic properties of these compounds are strongly dependent on stoichiometry,[6,10,11] and it has been further noted[1] that for some materials metallurgical inhomogeneities can lead to an anomalous pressure dependence of the Curie temperature, we believe that the difference between our results and those previously reported likely arises from compositional differences. This point will be further addressed below.

The superconducting transition temperature T_S, similarly defined by linear extrapolation about the transition, is also found to be weakly depressed by pressure, with $dT_S/dP = -(4.6 \pm 0.1)$ mK/kbar [Fig. 2(c)]. The appearance of superconductivity in this ferromagnetic alloy is unusual; a more likely explanation is the presence of nonstoichiometric regions in the sample, and there are several clear candidates. One is elemental Al, whose superconducting transition temperature is 1.14 K, similar to that of our samples. However, its pressure dependence has been observed[12] to be $dT_S/dP = -0.02$ K/kbar, much larger than our observations, and we rule out this possibility. We have used energy dispersive x-ray analysis (EDS) to determine that the composition of the grain boundaries differs from that of the bulk. The primary feature is that the boundary regions have essentially no aluminum, while the ratio of titanium to cobalt is approximately the same as that in the bulk. It is reasonable to attribute the superconductivity in our samples to a Co-Ti binary phase localized in the grain boundaries. We consider the possibilities among the known binary phases of Co and Ti. The compound Co_2Ti occurs in two structure types which have both been observed to order magnetically below about 40 K,[13,14] and we discount these possibilities. More likely potentially superconducting phases are CoTi and Co_3Ti, which have been observed to be paramagnetic down to 4.2 K,[15,16] and Ti_2Co,[17] the magnetic properties of which have, to the best of our knowledge, not been investigated. While it is possible that the ferromagnetism and superconductivity we find in our samples may be related, the morphological information obtained by EDS analysis underscores the likelihood that the superconductivity is not intrinsic to Co_2TiAl, and we proceed under this assumption.

We have investigated the magnetization of Co_2TiAl in fields up to 55 kOe. We found the saturation magnetization to be 19.0 emu/g and the Curie temperature to be 124.5 K, here defined from the magnetization by extrapolation about the steeply descending part of the magnetization vs temperature curve. These values are in agreement with previous observations,[3,6,9,11] indicating that our samples have similar stoichiometry to those studied previously. Graphs of M^2 vs H/M (Arrott plots) were found to be straight and parallel for temperatures below T_C. Together with the low Curie temperature, these magnetic measurements indicate that Wohlfarth's theory of weak itinerant electron ferromagnetism is an appropriate starting point for describing the magnetic properties of Co_2TiAl.[18] In the next section we will combine our measurements of magnetization and dT_C/dP to obtain an estimate for the electron-electron correlation strength in this weak itinerant ferromagnet.

DISCUSSION

The theory of weak itinerant electron ferromagnetism has been applied to a number of intermetallic ferromagnets containing cobalt.[9,19–22] The pressure dependence of the Curie temperature of a weak itinerant ferromagnet is given by

$$\frac{dT_C}{dP} = \frac{5}{3}\kappa T_C\left(1 - \frac{a}{T_C^2}\right), \tag{1}$$

where

$$\frac{a}{T_C^2} = \frac{\frac{1}{2}(I/I_b)\bar{I}}{\bar{I}-1}. \tag{2}$$

Here I_b is the bare electron interaction, I the effective interaction, and (I/I_b) lies between 0 and 1 and when small indicates a strongly correlated system. The Stoner term $\bar{I} = IN(\epsilon_F)$, where $N(\epsilon_F)$ is the density of states at the Fermi level, must be determined independently to estimate electron correlations from the pressure dependence of T_C. The compressibility κ is taken to be equal to that of Cu_2MnAl, 9.1×10^{-4} kbar^{-1}.[9]

In the theory of weak itinerant ferromagnetism the zero-temperature magnetization may be written

$$M^2(H, T=0) = M^2(0,0) + \left[\frac{2N(\epsilon_F)\mu_B^2}{(\bar{I}-1)}M^2(0,0)\right] \times \frac{H}{M(H, T=0)}, \tag{3}$$

where M is the magnetization per atom. Thus from the slope and intercept of the low-temperature Arrott plot an experimental estimate of the ratio $N(\epsilon_F)/(\bar{I}-1)$ may be obtained.[18,23] Lacking an independent measurement of $N(\epsilon_F)$, we take the value of 0.96 eV^{-1} obtained from recent band structure calculations performed in the symmetrized augmented plane wave method.[24] We find $\bar{I} = 1.02$, a reasonable value intermediate between that of the strongly ferromagnetic nickel ($\bar{I} = 1.2$) and the very weak $ZrZn_2$ ($\bar{I} = 1.01$).[23] The Stoner term $\bar{I}$ can be calculated directly from the spin polarized density of states as well. From the theoretical band structure[24] the result is $\bar{I} = 1.7$, unreasonably high for this low-T_C magnet. However, it must be noted that the direct calculation of $\bar{I}$ from the density of states is expected to be much more sensitive to the details of the reported band structure than is the value of $N(\epsilon_F)$.

We combine the theoretical value for $N(\epsilon_F)$ with our experimental magnetization and dT_C/dP, and from Eqs. (1) and (2) we find $(I/I_b) = 0.18$. This value indicates electron correlations as strong as those of Co, for which estimates of (I/I_b) range from 0.14 to 0.24.[25] We believe this value to be unphysical, as weak ferromagnets with Curie temperatures comparable to that of Co_2TiAl typically have $(I/I_b) \gtrsim 0.5$.[19] If we instead take (I/I_b) to be in the range 0.3–0.5, closer to the values reported for other weak ferromagnets, the magnitude of the negative pressure dependence of T_C thus predicted is from 1.6 to 2.8 K/kbar, stronger than that observed by a factor of 2–4. Assuming that our estimate of $N(\epsilon_F)$ is accurate, then, the observed dT_C/dP is smaller than would be expected for Co_2TiAl to be consistent with the Stoner-Wohlfarth theory. These results imply the presence of magnetic excitations in Co_2TiAl unaccounted for by Stoner theory, a conclusion similarly reached by previous workers,[9] who found dT_C/dP to be positive and greater than the first term in Eq. (1).

Fluctuations of the magnetization at finite temperatures provide such an additional excitation. Inoue and Shimizu[26] have described the pressure dependence of the Curie temperature in a model which includes spin fluctuations as well as Stoner excitations. Equation (1) is consequently modified to become

$$\frac{dT_C}{dP} = \frac{5}{3}\kappa T_C\left(1 - \frac{(I/I_b)\alpha + \eta F(\xi_c^2)}{T_C\partial(\chi_0^{-1})/\partial T_C + F(\xi_c^2)}\right) \tag{4}$$

in which $F(\xi_c^2)$ should be neglected to neglect spin fluctuations and return to Wohlfarth's model. Here α is a molecular field coefficient proportional to I, ξ^2 is the average of the square of the fluctuating magnetic moments per unit volume, and $F(\xi_c^2)$ is an expansion in ξ^2 of the inverse susceptibility, taken at the Curie temperature. The susceptibility unenhanced by spin fluctuations is χ_0, and η contains the pressure dependence of an exchange stiffness constant.

Since T_C is low for Co_2TiAl, the spin fluctuation term $F(\xi_c^2)$ should dominate in the denominator of the second term of Eq. (4). In this case, taking the parameter η to be roughly of order unity, neglecting $F(\xi_c^2)$ will lead to a larger magnitude of negative dT_C/dP. While we have insufficient information to determine $F(\xi_c^2)$ experimentally, it is qualitatively clear that spin fluctuations substantially reduce the pressure dependence of the Curie temperature of Co_2TiAl. The implication, then, is that for Co_2TiAl, spin fluctuations and Stoner excitations are of comparable importance in determining dT_C/dP. Since the two contributions are so closely balanced in Co_2TiAl, it is reasonable to expect that if either or both are sensitive to small variations in composition, internal strain, or microstructure, then the overall magnitude and even the sign of dT_C/dP may well be sample dependent, explaining the difference between our results and those of Ref. 9.

The systematics of magnetism in cobalt intermetallics is interesting, and not yet well understood. Several simple parametrizations have been applied with some success to certain families of materials. It has been shown that high Curie temperatures are associated with high molar fraction of Co for $CaCu_5$-type Y- and Th-Co intermetallics.[20] Heusler alloys of composition Co_2XY have been investigated and some correlation between cobalt moment and electronegativity of the X atoms was found.[27] The mechanism of Co $3d$ band filling from more electropositive neighboring atoms was also discussed by Coles,[2] who pointed out that in order to overcome such band filling the cobalt-cobalt spacing in such materials should exceed that of pure Co (2.5 Å) in order for ferromagnetism to exist.

Correlation between intermoment spacing and the existence of magnetic ordering has been observed for several types of intermetallic d- and f-electron systems whose

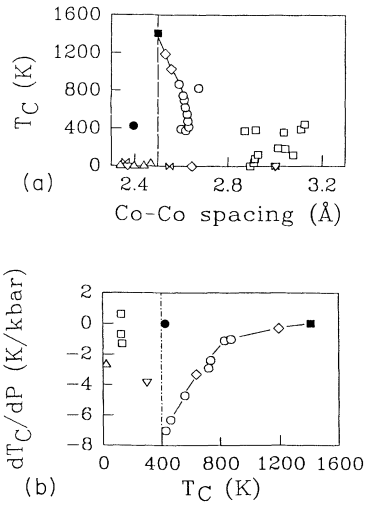

FIG. 3. Cobalt-cobalt spacing vs Curie temperature T_C (a) and T_C vs dT_C/dP (b) for intermetallic materials whose only potentially magnetic species is Co. Lines in the figure are guides for the eye. In (a) the dashed line marks the abrupt boundary at 2.5 Å between strongly magnetic systems and those in which the magnetism has been suppressed. Solid lines indicate the dependence of T_C upon Co-Co spacing in the region 2.5–2.7 Å. In (b) the solid lines indicate the monotonic decrease of dT_C/dP with decreasing Curie temperature T_C, while for materials with $T_C \lesssim 400$ K (dot-dashed line) dT_C/dP deviates from this trend. □: Heusler alloys Co_2XY and related compounds (Refs. 3, 4, 9, and 30); △: Laves compounds RCo_2 with $R = Y$, Lu, and Zr (Refs. 31–34); ▽: YCo_3, Y_3Co_2, Y_9Co_7 (Refs. 2 and 20); ○: RCo_5 and RCo_4B with R=Th, Y, La, Lu (Refs. 20, 21, and 35–38); ◇: R_2Co_7 and R_2Co_{17} with R=Y, Th (Refs. 20, 39, and 40); ⋈: Co_2Ti, CoTi, Co_3Ti (Refs. 13, 15, and 16); ●: Co_2B (Ref. 22); ■: Co.

magnetic moment bearing species are V, Cr, Mn, Ce, U, Np, and Pu.[28,29] Combining high-pressure measurements with such materials studies provides a powerful means of testing the importance of chemical pressure effects on electronic structure, and the investigation of relationships between the lattice constant and magnetic characteristics is expected to complement the results of pressure investigations.

Figure 3(a) shows the relationship between nearest-neighbor cobalt-cobalt spacing and Curie temperature for a number of itinerant magnets whose only potentially magnetic element is Co. For some materials, a weighted average over more than one neighbor has been used. We identify three qualitatively different regions of this plot. The lack of strong magnets with Co-Co spacing below 2.5 Å is striking. Note that only one material with a substantial Curie temperature, Co_2B, has a lattice spacing less than that of pure cobalt. Rather than presenting an exception to Coles' rule of thumb, it satisfies it also as boron is less electropositive than cobalt.

As the figure shows, R-Co magnets which have Co-Co spacing in the range 2.5–2.7 Å and $T_C \gtrsim 400$ K show a strong dependence of T_C upon the intermoment spacing. An exception in this region is Co_3Ti, a paramagnet with Co-Co spacing of 2.55 Å. The cobalt atoms in this material are twelvefold coordinated,[16] and it is possible that with such a high number of near neighbors the cobalt atoms may share electrons in covalent bonds. Such electron sharing might be expected to suppress magnetism is much the same way as electron transfer from electropositive neighbors would, suggesting that Co_3Ti may appropriately be grouped with the nonmagnetic compounds with spacings less than 2.5 Å. The dependence of T_C upon spacing observed between 2.5 and 2.7 Å is absent in the more widely spaced low-T_C Heusler alloys. It has been noted previously that Co magnets with $T_C \lesssim 400$ K depart from trends followed by the stronger magnets for which the Wohlfarth formalism for the pressure dependence works very well.[20] This is borne out by Fig. 3(b) as well, which illustrates the strong dependence of dT_C/dP on T_C for materials having high Curie temperatures, and the tendency for weaker magnets to be less strongly pressure dependent than one would expect from extrapolation from the high-T_C magnets. In the weaker magnets, then, both Co-Co spacing and dT_C/dP point to a deviation from the simple band filling behavior encountered in the high-T_C materials. These low-T_C magnets which depart from trends in spacing and dT_C/dP are good candidates for the study of the effects of spin fluctuations.

SUMMARY

We have reported electrical resistivity measurements of Co_2TiAl at temperatures between 1.2 K and room temperature and at pressures up to 12 kbar. We have determined the pressure dependence of the Curie temperature to be $dT_C/dP = -0.7$ K/kbar, and have shown that in this material spin fluctuations substantially decrease the pressure dependence of T_C. A weakly pressure dependent superconducting transition has been observed at $T_S = 1.48$ K, with $dT_S/dP = -4.6$ mK/kbar, and is attributed to a Co-Ti binary phase localized in the grain boundaries. The correlation between nearest-neighbor cobalt-cobalt spacing and the presence of ferromagnetic ordering has been investigated for a number of materials in which the only potentially magnetic species is Co. We illustrate that the materials having Curie temperatures $\lesssim 400$ K which do not exhibit a dependence of T_C on intermoment spacing are also only weakly affected by pressure. Spin fluctuations are expected to make an important contribution to the magnetic interactions in these weak itinerant ferromagnets.

ACKNOWLEDGMENTS

We wish to acknowledge S. B. Roy for providing the samples, and to thank Jason Cooley for technical assistance. The assistance of Bill Spiegelberg of Brush-Wellman, Inc., for providing special high-pressure materials is gratefully acknowledged.

[1]D. Wagner and E. P. Wohlfarth, J. Phys. F **11**, 2417 (1981).
[2]B. R. Coles and A. K. Chhabra, J. Magn. Magn. Mater. **54–57**, 1039 (1986).
[3]P. J. Webster and K. R. A. Ziebeck, J. Phys. Chem. Solids **34**, 1647 (1973).
[4]K. R. A. Ziebeck and P. J. Webster, J. Phys. Chem. Solids **35**, 1 (1974).
[5]S. Ishida, S. Sugimara, S. Fujii, and S. Asano, J. Phys.: Condens. Matter **3**, 5793 (1991); A. K. Grover, S. K. Dhar, E. V. Sampathkumaran, L. C. Gupta, and S. K. Malik, Solid State Commun. **30**, 141 (1979).
[6]J. V. Yakhmi, I. K. Gopalakrishnan, and A. K. Grover, Phys. Status Solidi A **85**, K89 (1984).
[7]J. D. Thompson, Rev. Sci. Instrum. **55**, 231 (1984).
[8]M. J. Clark and T. F. Smith, J. Low Temp. Phys. **32**, 495 (1978).
[9]T. Kanomata, K. Shirakawa, and T. Kaneko, J. Phys. (Paris) Colloq. **49**, C8-143 (1988).
[10]K. Endo, K. Ooiwa, A. Shinogi, M. Date, and K. Hiramoto, J. Magn. Magn. Mater. **31-34**, 75 (1983).
[11]A. Shinogi, J. Phys. Soc. Jpn. **54**, 400 (1985).
[12]D. U. Gubser and A. W. Webb, Phys. Rev. Lett. **35**, 104 (1975).
[13]T. Nakamichi, Y. Aoki, and M. Yamamoto, J. Phys. Soc. Jpn. **28**, 590 (1970).
[14]T. Nakamichi, Y. Aoki, and M. Yamamoto, J. Phys. Soc. Jpn. **25**, 77 (1968).
[15]Y. Aoki, T. Nakamichi, and M. Yamamoto, J. Phys. Soc. Jpn. **27**, 1455 (1969).
[16]Y. Aoki, J. Phys. Soc. Jpn. **28**, 1451 (1970).
[17]P. Duwes and J. L. Taylor, Trans. AIME **188**, 1173 (1950); K. F. Kelton, P. C. Gibbons, and P. N. Sabes, Phys. Rev. B **38**, 7810 (1988).
[18]D. M. Edwards and E. P. Wohlfarth, Proc. R. Soc. London, Ser. A **303**, 127 (1968).
[19]E. P. Wohlfarth and L. C. Bartel, Phys. Lett. **34A**, 303 (1971).
[20]M. Brouha and K. H. J. Buschow, J. Phys. F **3**, 2218 (1973).
[21]M. Brouha and K. H. J. Buschow, J. Phys. F **5**, 543 (1975).
[22]H. Kadomatsu, F. Ishii, and H. Fujiwara, J. Phys. Soc. Jpn. **47**, 1078 (1979).
[23]E. P. Wohlfarth, in *Magnetism: Selected Topics*, edited by S. Foner (Gordon and Breach, New York, 1976), p. 66.
[24]S. Ishida, S. Akazawa, Y. Kubo, and J. Ishida, J. Phys. F **12**, 1111 (1982).
[25]M. Shimizu, J. Phys. Soc. Jpn. **44**, 792 (1978); M. Shimizu, J. Magn. Magn. Mater. **15-18**, 615 (1980).
[26]J. Inoue and M. Shimizu, Phys. Lett. **112A**, 81 (1985).
[27]K. H. J. Buschow and P. G. van Engen, J. Magn. Magn. Mater. **25**, 90 (1981); P. G. van Engen, K. H. J. Buschow, and M. Erman, *ibid.* **30**, 374 (1983).
[28]H. H. Hill, Nucl. Metall. **17**, 2 (1970); H. H. Hill (unpublished).
[29]L. R. Edwards and L. C. Bartel, Phys. Rev. B **5**, 1064 (1972), and references therein.
[30]J. G. Booth and R. G. Pritchard, J. Phys. F **5**, 347 (1975).
[31]K. Yoshimura and Y. Nakamura, Solid State Commun. **56**, 767 (1985).
[32]K. Murata, K. Fukamichi, H. Komatsu, T. Sakakibara, and T. Goto, J. Phys.: Condens. Matter **3**, 2515 (1991).
[33]E. Piegger and R. S. Craig, J. Chem. Phys. **39**, 137 (1963).
[34]P. C. Riedi, J. G. M. Armitage, and R. G. Graham, J. Appl. Phys. **69**, 5680 (1991).
[35]A. S. van der Goot and K. H. J. Buschow, Phys. Status Solidi A **5**, 665 (1971).
[36]L. Nordström, O. Eriksson, M. S. S. Brooks, and B. Johansson, Phys. Rev. B **41**, 9111 (1990).
[37]N. M. Hong, J. J. M. Franse, N. P. Thuy, and T. D. Hien, J. Phys. (Paris) Colloq. **49**, C8-545 (1988).
[38]T. T. Dung, N. P. Thuy, N. M. Hong, and T. D. Hien, Phys. Status Solidi A **106**, 201 (1988).
[39]K. H. J. Buschow, J. Appl. Phys. **42**, 3433 (1971).
[40]Q. Johnson, G. S. Smith, and D. H. Wood, Acta. Crystallogr. B **25**, 464 (1969).