

The metamagnetic phase of the cubic Laves phase transition-metal compounds

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 2209

(<http://iopscience.iop.org/0953-8984/8/13/012>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.208

The article was downloaded on 13/05/2010 at 16:16

Please note that [terms and conditions apply](#).

The metamagnetic phase of the cubic Laves phase transition-metal compounds

H Yamada[†], K Terao[†], S Takagi[†], H Mitamura^{‡§}, T Sakakibara[‡] and T Goto[§]

[†] Department of Physics, Faculty of Science, Shinshu University, Matsumoto 390, Japan

[‡] Department of Physics, Faculty of Science, Hokkaido University, Sapporo 060, Japan

[§] ISSP, University of Tokyo, Tokyo 106, Japan

Received 8 December 1995

Abstract. Electronic structures of d electrons under magnetic fields for the transition-metal compounds with the cubic Laves phase structure are calculated in the self-consistent tight-binding approximation. The induced moments as a function of magnetic field are obtained for AB₂ compounds with various numbers of d electrons, n_A and n_B , on the constituent transition-metal elements A and B. Ferromagnetic and paramagnetic phases are obtained on the plane of n_A and n_B , by performing calculations at more than 50 points on this plane. In a narrow range along the boundary between the two phases a metamagnetic phase is found. The critical fields of the metamagnetic transition are calculated in this range. The calculated results are qualitatively in good agreement with the observed values for Hf(Fe, Co)₂, Y(Fe, Co)₂ and Y(Co, Ni)₂.

1. Introduction

A Laves phase compound, as a typical intermetallic, consists of two kinds of atom A and B, where the composition ratio is one half—namely, AB₂. The A atom is an early transition-metal element (including rare-earth and actinide elements). On the other hand, the B atom is a late transition-metal element, e.g., Fe, Co or Ni. Magnetic properties of these compounds, especially of rare-earth and 3d-transition-metal compounds with the cubic Laves phase structure, have been studied intensively.

YFe₂ is ferromagnetic with a Curie temperature of 540 K and YNi₂ is paramagnetic in the ground state. On the other hand, YCo₂ shows curious magnetic behaviours. This compound is paramagnetic without any magnetic field at low temperature. Under an extremely high magnetic field above 700 kOe, it becomes ferromagnetic [1]. That is, YCo₂ shows a metamagnetic transition (MT) from the paramagnetic state to the ferromagnetic one. Such a metamagnetic transition is attributed to the electronic structure of itinerant d electrons in YCo₂. A sharp peak of the density-of-states (DOS) curve exists very close to the Fermi level for this compound, as shown by the band calculation [2]. This sharp peak of the DOS is responsible for the MT and also for the anomalous temperature dependence of the paramagnetic susceptibility observed [3, 4].

The pseudo-binary compounds Y(Fe, Co)₂ [5] and Hf(Fe, Co)₂ [6] show also a MT at low temperature. They are ferromagnetic in Fe-rich composition. With increasing Co concentration, they become suddenly paramagnetic at a certain critical concentration and subsequently the MT occurs in a narrow concentration range. The critical field H_c of the MT increases with increasing Co concentration and the MT disappears at Co-rich compositions.

Mitamura *et al* [7] have recently observed the critical field of the MT for $Y(\text{Co}_{1-x}\text{M}_x)_2$ at $x \leq 0.03$, where $\text{M} = \text{Ni}, \text{Fe}$ or $\text{Fe}_{0.5}\text{Ni}_{0.5}$. They have found that the values of H_c for $\text{M} = \text{Ni}$ and Fe increase and decrease, respectively, with increasing x . This result is naturally understood from the band picture of metamagnetism. A partial substitution of Ni (Fe) for Co in YCo_2 shifts the Fermi level to the higher- (lower-) energy side, because the average number of d electrons increases (decreases). Then, for $\text{M} = \text{Ni}$ and Fe , higher and lower fields are needed to turn the system magnetic, as the position of the Fermi level goes far from and close to the sharp peak of the DOS, respectively. This fact is also confirmed by the observed result for H_c for $\text{M} = \text{Fe}_{0.5}\text{Ni}_{0.5}$, which is almost constant at $x \leq 0.02$. That is, the average number of d electrons of $\text{Fe}_{0.5}\text{Ni}_{0.5}$ is the same as that of Co, and then H_c is considered to be almost constant at any concentration x . These experimental facts suggest that the B atom in YB_2 can be treated as a virtual atom with the average number of d electrons of Fe, Co and Ni [7, 8].

The aim of the present paper is to evaluate the metamagnetic phase for the cubic Laves phase transition-metal compounds. The electronic structures of d electrons are calculated in the self-consistent tight-binding approximation under the magnetic field H . Our method for the band calculation is given in section 2. The induced moments $M(H)$ as a function of H are calculated for AB_2 compounds with various numbers of d electrons, n_A and n_B , of the constituent virtual atoms A and B. When the Landau energy is expanded up to the term in M^6 , $M(H)$ is given by the magnetic equation of state

$$H = aM + bM^3 + cM^5$$

and the Landau coefficients a , b and c can be estimated by fitting the calculated $M(H)$ with this form of the equation of state [9]. The calculated results for a , b and c are given in section 3. In section 4, the metamagnetic phase, together with the ferromagnetic and paramagnetic phases, is obtained on the plane of n_A and n_B , by performing calculations at more than 50 points on this plane. The critical fields of the MT are also evaluated in section 4. Our conclusions and a discussion are given in section 5.

2. The method of the band calculation

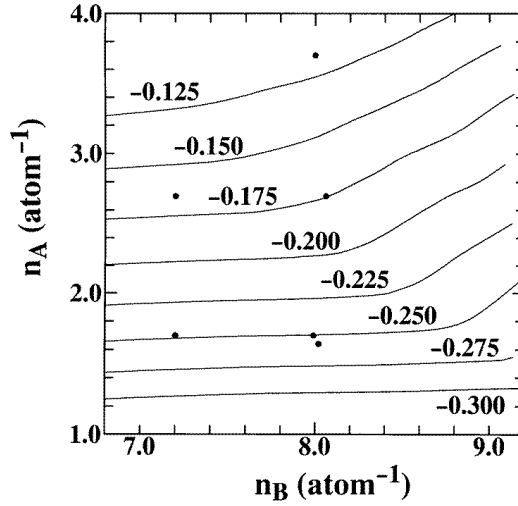
The method of numerical calculations on the electronic structure of d electrons for an AB_2 compound in the present paper is the same as that used in [10]. The hopping integrals of d electrons are estimated in the Andersen–Jepsen–Pettifor formalism [11, 12, 13]. That is, the hopping integrals, $dd\sigma$, $dd\pi$ and $dd\delta$, defined by Slater and Koster [11], are determined for A–A and B–B pairs by using a useful simple formula proposed by Pettifor [12], where the effective-mass parameters of the d band and the Wigner–Seitz radii are made use of as are the calculated values for metals given by Andersen and Jepsen [13]. In the case of the A–B atom pairs, use is made of the geometrical average of the values for the A–A and B–B atom pairs which are corrected by the R^{-5} -law, where R is the atomic distance [10].

The main aim of the present paper is to calculate the magnetic phase diagram of the cubic Laves phase transition-metal compounds. The calculated results depend not only on the numbers of d electrons, n_A and n_B , but also on the band parameters and lattice constant. However, our aim is to discuss the magnetic phases on the plane of n_A and n_B . Then, the band parameters, the effective masses of the d band and the Wigner–Seitz radii, and the lattice constant for YCo_2 used in [10] are made use of, as representatives, for all AB_2 compounds in the present paper.

On the other hand, the site energies of the A and B atoms can be determined so as to give self-consistent values of n_A and n_B in the following way. In the Hartree–Fock

Table 1. The values of n_A and n_B per atom estimated previously for transition-metal compounds with cubic Laves phase structure [14].

	YFe ₂	YCo ₂	LuFe ₂	LuCo ₂	ZrFe ₂	ZrCo ₂	HfFe ₂	HfCo ₂	NbCo ₂
n_A	1.70	1.64	1.70	1.70	2.70	2.70	2.70	2.70	3.70
n_B	7.20	8.02	7.20	7.99	7.20	8.06	7.20	8.06	8.00

**Figure 1.** Calculated values of n_A and n_B for some values of ϵ_B in Ryd. Closed circles show those estimated previously [14].

approximation for the multi-band Hubbard Hamiltonian, the site energy is given by [2]

$$V_i^p = \epsilon_i + U_i n_i^p \quad (1)$$

in the paramagnetic state without a magnetic field, where $i = A$ and B and ϵ_i is the unperturbed site energy on the atom i without the intra-atomic Coulomb integral U_i , and n_i^p is the number of d electrons per spin on the atom i , i.e., $n_A^p = n_A/2$ and $n_B^p = n_B/2$. The value of ϵ_A is taken to be zero as an origin of the energy. The value of ϵ_B is determined so as to get the values of n_A and n_B self-consistently. Figure 1 shows the calculated values of n_A and n_B for some values of ϵ_B shown on each curve. The values of n_A and n_B estimated previously [14] for various transition-metal compounds are listed in table 1. They are also shown by closed circles in figure 1.

The calculated DOS curves for $\epsilon_B = -0.15$, -0.20 , -0.25 and -0.30 Ryd are shown in figures 2(a), 2(b), 2(c) and 2(d), respectively. D_A and D_B denote the local DOSs of d electrons on the A and B atoms. The numbers of d electrons, n_A and n_B , are shown in the lower portion in each figure. The two characteristic peaks of the DOSs for YFe₂ and YCo₂ [10] can be seen at, say, about -3.40 and -3.55 eV in figure 2(d). These peaks become broad when the absolute value of ϵ_B decreases. This is because the hybridization between the d states of A and B atoms becomes strong [14].

In the magnetized state under the magnetic field H the site energy is written as [2]

$$V_{i\sigma} = V_i^p - \sigma \mu_B H + U_i (n_{i-\sigma} - n_i^p) \quad (2)$$

where $n_{i-\sigma}$ is the number of d electrons with spin $-\sigma$ on the atom i .

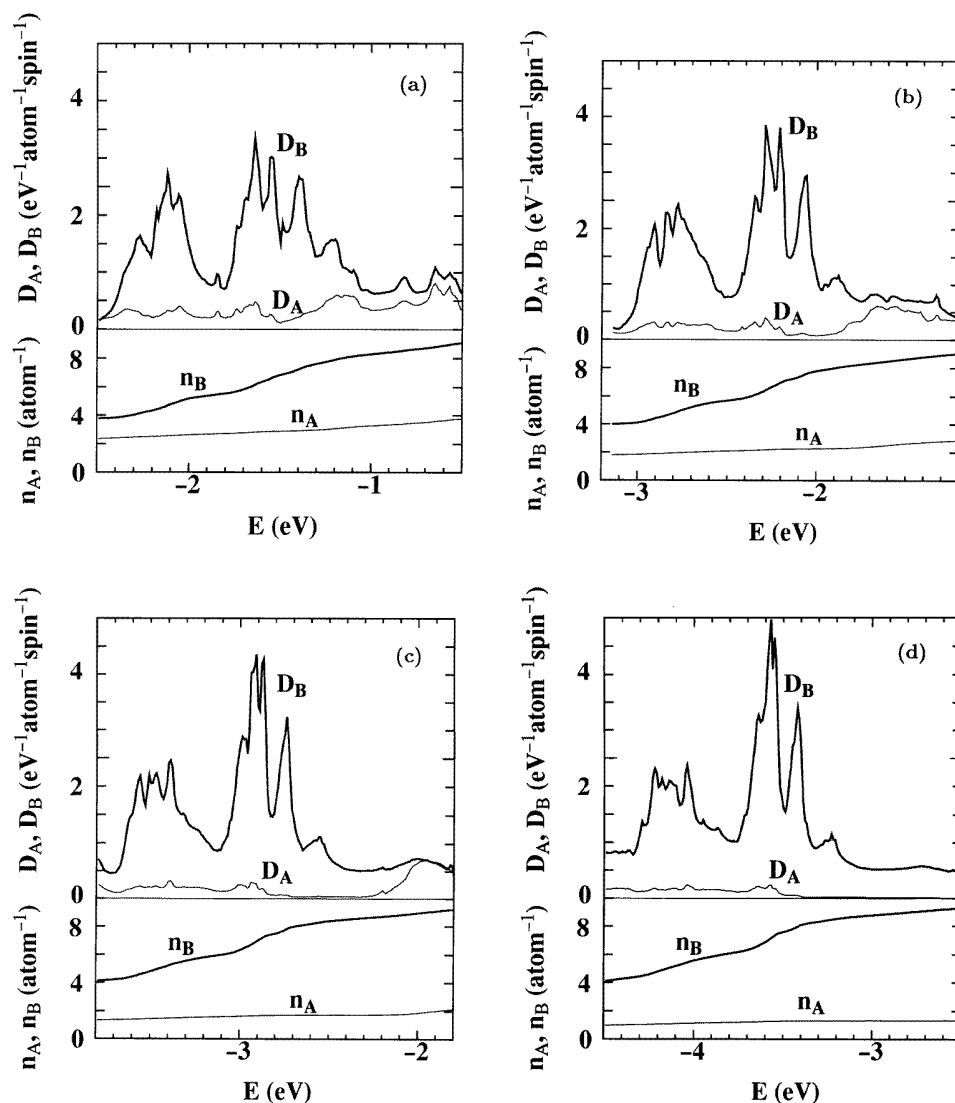


Figure 2. Calculated local DOSs of d electrons on the A and B atoms, D_A and D_B , and the numbers of d electrons, n_A and n_B , for $\epsilon_B = -0.15$ Ryd (a), $\epsilon_B = -0.20$ Ryd (b), $\epsilon_B = -0.25$ Ryd (c) and $\epsilon_B = -0.30$ Ryd (d).

For all AB_2 compounds in the present paper the values of U_A and U_B are taken as 30 and 44 mRyd, respectively, as estimated for YCo_2 in [2]. The position of the Fermi level is determined so as to give the total number of d electrons $n_A + 2n_B$ per formula unit. The calculations for $n_{A\uparrow}$, $n_{A\downarrow}$, $n_{B\uparrow}$ and $n_{B\downarrow}$ are repeated until they are obtained self-consistently within an accuracy of less than 10^{-5} per atom. That is, the accuracy of the site energies $V_{i\sigma}$ is less than 10^{-2} mRyd.

The total moment $M(H)$ per formula unit is given by

$$\{n_{A\uparrow} - n_{A\downarrow} + 2(n_{B\uparrow} - n_{B\downarrow})\}\mu_B.$$

3. The magnetization curve and Landau coefficients

The calculations of the magnetization curve $M(H)$ have been carried out at more than 50 points on the plane of n_A and n_B shown in figure 1. At the left-hand side on the n_A and n_B plane, $M(H)$ is finite at $H = 0$ and increases slightly with increasing H . That is, the ferromagnetic state is stable. On the other hand, at the right-hand side on the plane, $M(H)$ is zero at $H = 0$ and increases with increasing H . That is, the paramagnetic state is stable. Near the boundary between the ferromagnetic and paramagnetic states, three self-consistent solutions of $M(H)$ are obtained in some range of H ; one is the unstable solution and other two are the stable or metastable solution (see figure 1 of [2]).

The calculated $M(H)$ can be interpolated by using the Landau coefficients. When the Landau energy is expanded up to the order of M^6 as

$$E(M) = \frac{1}{2}aM^2 + \frac{1}{4}bM^4 + \frac{1}{6}cM^6 \quad (3)$$

where a , b and c are expansion coefficients, the magnetic equation of state is written as

$$H = dE(M)/dM = aM + bM^3 + cM^5. \quad (4)$$

By using the calculated values of $M(H)$ we can plot M^2 as a function of H/M —so-called Arrott plots. The plotted curve can be interpolated in the form of

$$H/M = a + bM^2 + cM^4$$

and the values of a , b and c are estimated by the method of least squares. The values of a , b and c estimated thus can reproduce the magnetization curve very well as shown for example in figures 1 and 2 of [15].

The contour lines of the estimated values of the Landau coefficients a , b and c are shown in figures 3(a), 3(b) and 3(c), respectively. Closed circles denote the values of n_A and n_B for YCo_2 and ZrCo_2 or HfCo_2 listed in table 1. The values of a , b and c are found to depend strongly on n_B , but not so much on n_A . This is because the main part of the DOS near the Fermi level is constructed of the 3d states of the B atoms, as seen in figure 2. Then the dominant contribution to the total energy $E(M)$ or the Landau coefficients a , b and c comes from the 3d states of the B atoms. The values of a and c increase monotonically with increasing n_B , while b decreases. The $b = 0$ curve in figure 3(b) is almost the same as that for $a = 0$ in figure 3(a). However, they are a little different from each other. On the $a = 0$ curve the value of b is negative and small.

When $a < 0$ the ferromagnetic state is stable. However, even if $a > 0$, the ferromagnetic state becomes stable when $b < 0$, $c > 0$ and $ac/b^2 < 3/16$ [16]. This is because $E(M)$ given by (3) may have two minima at $M = 0$ and finite M . When $a > 0$, $b < 0$, $c > 0$ and $ac/b^2 < 3/16$, the minimum energy at the finite M is lower than that at $M = 0$ and the ferromagnetic state becomes stable. This condition is satisfied only in a very narrow range along the line $a = 0$, as shown in the next section.

4. The magnetic phase diagram and critical field of the MT

In the previous section, we obtained the values of the Landau coefficients a , b and c as functions of n_A and n_B . Thus we can obtain the value of ac/b^2 , which is a characteristic quantity of the metamagnetism [9]. The metamagnetic transition occurs when $a > 0$, $b < 0$, $c > 0$ and $3/16 < ac/b^2 < 9/20$ [16]. In figure 4, the contour lines of ac/b^2 are shown on the plane of n_A and n_B . Closed circles denote the values of n_A and n_B for YCo_2 and ZrCo_2 or HfCo_2 listed in table 1. The metamagnetic phase appears in the region surrounded by

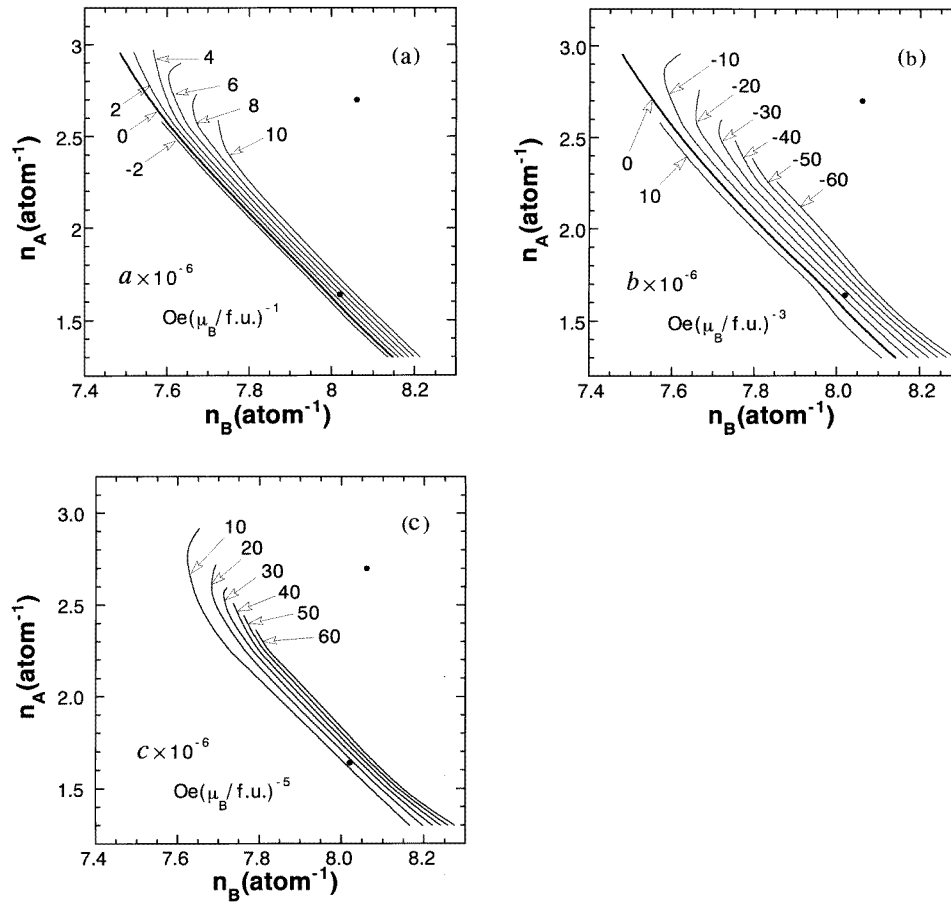


Figure 3. Contour lines of the Landau coefficients a , b and c in (a), (b) and (c), respectively. The numbers on the curves denote the values of $a \times 10^{-6} \text{ Oe}(\mu_{\text{B}}/\text{f.u.})^{-1}$, $b \times 10^{-6} \text{ Oe}(\mu_{\text{B}}/\text{f.u.})^{-3}$ and $c \times 10^{-6} \text{ Oe}(\mu_{\text{B}}/\text{f.u.})^{-5}$. Closed circles show the values of n_{A} and n_{B} for YCo_2 and ZrCo_2 or HfCo_2 given in table 1.

$ac/b^2 = 3/16$ and $9/20$, where $a > 0$, $b < 0$ and $c > 0$. The value of ac/b^2 increases monotonically with increasing n_{B} from 0 to $9/20$. It is also found that the value of ac/b^2 increases with increasing n_{A} . The boundary between the ferromagnetic and paramagnetic phases is shown by the curve for $ac/b^2 = 3/16$. The ferromagnetic phase with $a > 0$, $b < 0$, $c > 0$ and $ac/b^2 < 3/16$ exists certainly in a very narrow range surrounded by the curves for $a = 0$ and $ac/b^2 = 3/16$, as well as in the region where $a < 0$.

The metamagnetic phase appears in a narrow range of n_{B} for any n_{A} as shown in figure 4. When $n_{\text{A}} = 1.64$, for example, the metamagnetic state is stable for $7.98 < n_{\text{B}} < 8.14$. Then, the critical concentration between the ferromagnetic and paramagnetic (metamagnetic) states for $\text{Y}(\text{Fe}_x\text{Co}_{1-x})_2$ is derived at $x = 0.049$, by making use of the values of $n_{\text{Co}} = 8.02$ and $n_{\text{Fe}} = 7.20$ shown in table 1. This is found to be close to the observed result [5], considering that the concentration dependences of the lattice constant and band parameters were neglected in this paper. Similar calculations are carried out for $\text{Zr}(\text{Fe}_x\text{Co}_{1-x})_2$ and $\text{Hf}(\text{Fe}_x\text{Co}_{1-x})_2$ and it is found that the critical concentration is $x = 0.43$ and the

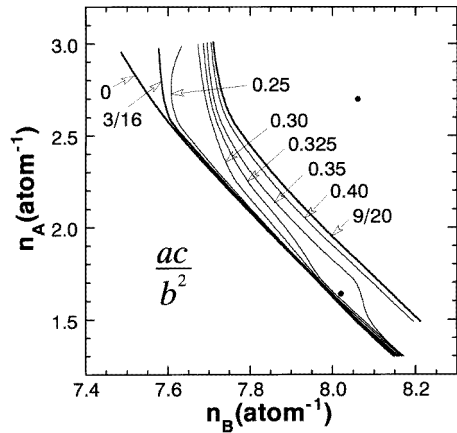


Figure 4. Contour lines of ac/b^2 . The numbers on each curve denote the values of ac/b^2 . The metamagnetic phase is stable in the region between $ac/b^2 = 3/16$ and $ac/b^2 = 9/20$. Closed circles show the values of n_A and n_B for YCo_2 and $ZrCo_2$ or $HfCo_2$ given in table 1.

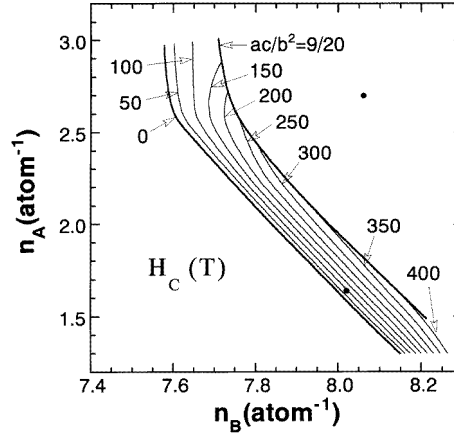


Figure 5. Estimated values of H_c . The thick curve for $H_c = 0$ is that for $ac/b^2 = 3/16$ in figure 4. Another thick curve for $ac/b^2 = 9/20$ denotes the metamagnetic phase boundary. Closed circles show the values of n_A and n_B for YCo_2 and $ZrCo_2$ or $HfCo_2$ given in table 1.

metamagnetic phase appears for $0.43 < x < 0.64$ for these two compounds. This result is also close to the observed one for $Hf(Fe, Co)_2$ [6], although the lattice constant and band parameters for all compounds AB_2 are fixed to the values for YCo_2 . For $Zr(Fe, Co)_2$, however, a spin-glass or mictomagnetic phase is said to appear in this concentration range [17]. On the other hand, the metamagnetic phase appears over a relatively wider range of n_A when n_B is constant. For example, $(Y_{1-x}Zr_x)Co_2$ is found to be in a metamagnetic phase for $x < 0.25$, by making use of the values $n_Y = 1.64$ and $n_{Zr} = 2.70$ shown in table 1.

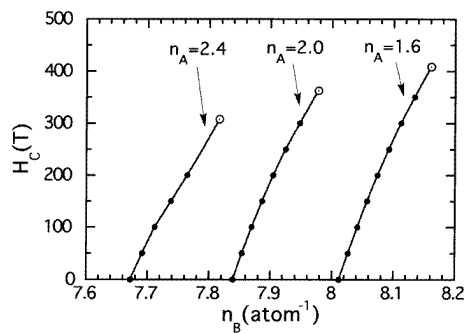


Figure 6. Calculated values of H_c as a function of n_B for some values of n_A . Closed circles show calculated values and open circles denote the metamagnetic phase boundary.

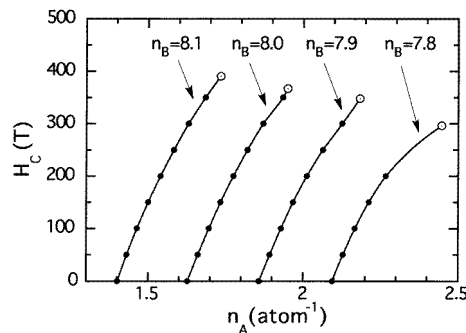


Figure 7. Calculated values of H_c as a function of n_A for some values of n_B . Closed circles show calculated values and open circles denote the metamagnetic phase boundary.

The critical field H_c in the quasi-static process is obtained by using the values of a , b and c estimated in the previous section and Maxwell's rule. Figure 5 shows the calculated values of H_c on the plane of n_A and n_B . Closed circles denote the values of n_A and n_B listed in table 1. It is found that H_c increases monotonically with increasing n_B when n_A is

constant. This is explicitly shown in figure 6 for $n_A = 1.6, 2.0$ and 2.4 . These results are qualitatively consistent with the concentration dependence of H_c observed for $\text{Hf}(\text{Fe}, \text{Co})_2$ [6] and for $\text{Y}(\text{Fe}, \text{Co})_2$ and $\text{Y}(\text{Co}, \text{Ni})_2$ [7], where H_c increases with increasing average number of 3d electrons. However, quantitative agreements are not obtained as mentioned in the next section. The open circles in figure 6 denote the values of H_c at the boundary of $ac/b^2 = 9/20$.

On the other hand, the value of H_c is also found to increase with increasing n_A when n_B is constant. In figure 7, H_c is shown as a function of n_A for some values of n_B . The open circles denote the values of H_c at the boundary of $ac/b^2 = 9/20$. This result suggests that the value of H_c for $(\text{Y}_{1-x}\text{Zr}_x)\text{Co}_2$ and $(\text{Y}_{1-x}\text{Hf}_x)\text{Co}_2$ increases with increasing x , because the average number of d electrons n_A of (Y, Zr) and (Y, Hf) increases. The value of dH_c/dn_A is found, from figures 6 and 7, to be about half of dH_c/dn_B .

5. Conclusions and discussion

In the present paper the electronic structures of d electrons for AB_2 compounds with cubic Laves phase structure in a magnetic field have been calculated. The induced moments on the constituent A and B atoms were calculated for various numbers of d electrons on the A and B atoms, n_A and n_B . The magnetic phase diagram has been evaluated by using the Landau coefficients a , b and c estimated at more than 50 points on the plane of n_A and n_B . It has been found that the metamagnetic phase appears certainly in a narrow range along the boundary between the ferromagnetic and paramagnetic phases.

The critical field of the metamagnetic transition has also been calculated as a function of n_A and n_B . It has been shown that the value of H_c increases monotonically with increasing n_A and n_B . This result is qualitatively consistent with the observed ones for $\text{Hf}(\text{Fe}_{1-x}\text{Co}_x)_2$ [6], $\text{Y}(\text{Fe}_{1-x}\text{Co}_x)_2$ and $\text{Y}(\text{Co}_{1-x}\text{Ni}_x)_2$ [7], because the average number of d electrons n_B on the virtual atoms of (Fe, Co) and (Co, Ni) increases with increasing x . However, the value of dH_c/dx estimated from the $n_A = 1.6$ curve in figure 6 is about 38 T, which is about four or five times larger than the observed dH_c/dx for $\text{Y}(\text{Co}_{1-x}\text{Fe}_x)_2$ and $\text{Y}(\text{Co}_{1-x}\text{Ni}_x)_2$ for $x < 0.03$. This discrepancy is due to the fact that the constituent A and B atoms in the present paper are treated as virtual atoms with the average number of d electrons and other alloying effects are not taken into account at all. Moreover, in the present paper, the lattice constant and band parameters for all of the AB_2 compounds are fixed to the values for YCo_2 .

Figure 7 shows that H_c increases with increasing n_A . As pointed out in the last section, this result suggests that the value of H_c for $(\text{Y}_{1-x}\text{Zr}_x)\text{Co}_2$ and $(\text{Y}_{1-x}\text{Hf}_x)\text{Co}_2$ increases with increasing x , because the average number of d electrons n_A on the virtual atoms of (Y, Zr) and (Y, Hf) increases with increasing x . From the values of n_A and n_B shown in table 1 and the phase diagram shown in figure 4, the metamagnetic phase for these pseudo-binary compounds is predicted to appear for $x < 0.25$ approximately. The estimated value of dH_c/dx is about 15 T, although this value will be reduced very much by the alloying effects. High-field measurements are desired for these compounds.

References

- [1] Goto T, Fukamichi K, Sakakibara T and Komatsu H 1989 *Solid State Commun.* **72** 945
- [2] Yamada H and Shimizu M 1985 *J. Phys. F: Met. Phys.* **15** L175
- [3] Lemaire R 1966 *Cobalt* **33** 201
- [4] Burzo E, Gratz E and Pop V 1993 *J. Magn. Magn. Mater.* **123** 159

- [5] Yoshimura K, Yoshimoto Y, Mekata M, Sakakibara T and Goto T 1987 *J. Magn. Magn. Mater.* **70** 147
- [6] Sakakibara T, Goto T and Nishihara Y 1988 *J. Physique Coll.* **49** C8 263
- [7] Mitamura H, Sakakibara T, Goto T and Yamada H 1995 *J. Magn. Magn. Mater.* **140–144** 821
Mitamura H 1995 *PhD Thesis* Hokkaido University
- [8] Yamada H and Shimizu M 1989 *J. Phys.: Condens. Matter* **1** 2597
- [9] Yamada H 1993 *Phys. Rev. B* **47** 11 211
- [10] Yamada H, Inoue J, Terao K, Kanda S and Shimizu M 1984 *J. Phys. F: Met. Phys.* **14** 1943
- [11] Slater J C and Koster G F 1954 *Phys. Rev.* **94** 1498
- [12] Pettifor D G 1977 *J. Phys. F: Met. Phys.* **7** 613
- [13] Andersen O K and Jepsen O 1977 *Physica B* **91** 317
- [14] Yamada H 1988 *Physica B* **149** 390
- [15] Yamada H 1995 *Physica B* **211** 161
- [16] Shimizu M 1982 *J. Physique* **43** 155
- [17] Muraoka Y, Shiga M and Nakamura Y 1979 *J. Phys. F: Met. Phys.* **9** 1889