The metamagnetic transition of Hf(Fe,Co)$_2$

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Abstract. Electronic structure of d electrons in pseudo-binary compounds Hf(Fe, Co)$_2$ with the cubic Laves phase structure is calculated in the tight-binding approximation and the virtual crystal approximation. The concentration dependence of the magnetic moment is calculated in the mean-field approximation and good agreement between the calculated and observed results is obtained. It is shown that the metamagnetic transition (MT) occurs in the small concentration range just before the onset of the magnetic moment. The MT of other pseudo-binary compounds Sc(Fe, Co)$_2$, Y(Fe, Co)$_2$ and Lu(Fe, Co)$_2$ is also discussed.

1. Introduction

Recently, the present authors (Yamada and Shimizu 1985, Yamada *et al* 1987a, b) have calculated the electronic structures of d electrons under the magnetic field in ScCo$_2$, YCo$_2$ and LuCo$_2$ with the cubic Laves phase structure and estimated the field dependence of the induced magnetic moment in the mean-field approximation with the effective exchange parameters on Sc, Y or Lu and Co atoms. It has been shown by numerical calculations that there exist two magnetic states with small induced paramagnetic and large spontaneous moments within a finite range of the magnetic field. By comparing the total energies of the two magnetic states, the metamagnetic transition (MT) from the paramagnetic to ferromagnetic state has been shown to occur at the critical magnetic field of 120 T for ScCo$_2$, 89 T for YCo$_2$ and 94 T for LuCo$_2$. The reason why the MT occurs in these compounds is that the Fermi level E_F lies just above a sharp peak of the density-of-states (DOS) curve. This is consistent with the result obtained on the analysis for the temperature dependences of the paramagnetic susceptibility χ (Yamada *et al* 1984, 1985).

   The critical magnetic fields of the MT estimated for ScCo$_2$, YCo$_2$ and LuCo$_2$ are too high to be observed in laboratory but the anomalous field dependence of the susceptibility for YCo$_2$ and LuCo$_2$ (Schinkel 1978) has been explained by the shape of the DOS around E_F. Recently, the MT has been observed in the ternary compounds with Al atoms, Sc(Co, Al)$_2$ (Ishiyama *et al* 1987), Y(Co, Al)$_2$ (Aleksandryan *et al* 1985, Sakakibara *et al* 1986) and Lu(Co, Al)$_2$ (Gabelko *et al* 1987, Sakakibara *et al* 1987). The observed critical fields of the MT depend sensitively on the Al concentration and the extrapolated values to those of pure ScCo$_2$, YCo$_2$ and LuCo$_2$ have been found to be very close to our theoretical values mentioned above. Anyhow, these compounds have

been found to be typical examples of the itinerant electron metamagnet discussed first by Wohlfarth and Rhodes (1962) and in more detail by Shimizu (1982).

On the contrary, for ACo_2 with the IVA group element, Ti, Zr or Hf, as the A atom, the induced paramagnetic moment under the external field is not anomalous because E_F lies on the flat part far above the sharp peak of the DOS (Yamada *et al* 1985). Therefore, neither the MT nor the maximum in the temperature dependence of χ is observed in these compounds ACo_2 (A $\equiv$ Ti, Zr or Hf). However, when some Co atoms in ACo_2 are replaced by Fe atoms, i.e. the pseudo-binary compound of $A(Fe, Co)_2$, the position of E_F comes near to the sharp peak of the DOS which is responsible for the MT, because the number of 3d electrons decreases with increasing Fe concentration, and then the MT may be observed. Very recently, such a MT has in fact been observed for $Hf(Fe, Co)_2$ (Sakakibara *et al* 1989).

For $Hf(Fe_{1-x}Co_x)_2$ with $x < 0.7$, the long-range magnetic ordering was observed at low temperature (van Dongen *et al* 1981). No hyperfine fields were detected on the Fe sites for $x > 0.8$ and this pseudo-binary compound does not show a mictomagnetic or spin-glass behaviour. Sakakibara *et al* (1989) have observed that the spontaneous magnetisation of this compound disappears abruptly at $x = 0.625$–0.65. The induced magnetic moments under the applied magnetic fields up to 40 T were observed near the critical concentration and the MT was found in the small concentration range $0.65 < x < 0.70$.

On the contrary, Yoshimura *et al* (1987) have observed the metamagnetic-like behaviour of the induced magnetic moments at the concentration range $0.93 < x < 0.96$ for $Y(Fe_{1-x}Co_x)_2$. The observed spontaneous magnetisation decreases abruptly near $x = 0.95$. However, large hyperfine fields on Fe sites were observed and the local magnetic moment on Fe atoms seems to exist for all concentrations x (Steiner 1979). Then this compound is said to be in a spin-glass state near the critical concentration. It is not clear whether the anomalous field dependence of the magnetic moment observed by Yoshimura *et al* (1987) is due to the MT or to the spin-glass nature.

In this paper, the concentration dependence of the magnetic moment in the ferromagnetic state and the induced paramagnetic moment under the external magnetic field for the pseudo-binary compound $Hf(Fe, Co)_2$ are calculated. In §2, the method of calculation is described and the calculated results are given in §3. A discussion on the MT for other compounds $A(Fe, Co)_2$ (A $\equiv$ Sc, Y and Lu) is given in §4.

2. Method of calculation

For pseudo-binary compounds such as $Hf(Fe_{1-x}Co_x)_2$, the randomness of the atomic sites of Fe and Co should be taken into account. Yamada *et al* (1987c, d) have recently calculated the concentration dependences of the magnetic moment, the spin susceptibility, the Curie temperature and the low-temperature specific heat coefficient for $Y(Fe, Co)_2$ and $Zr(Fe, Co)_2$ by using the rigid-band model. They showed that the fine structures of the DOS near E_F are responsible for these magnetic properties. Their calculated results obtained using the rigid-band model have been shown to be almost the same as those obtained by using the coherent potential approximation (Tanabe 1988). A combined method of the coherent potential approximation and the recursion method for the calculation of the DOS for pseudo-binary compounds has been proposed recently (Amaral *et al* 1982, 1983, Inoue and Shimizu 1987a, b).
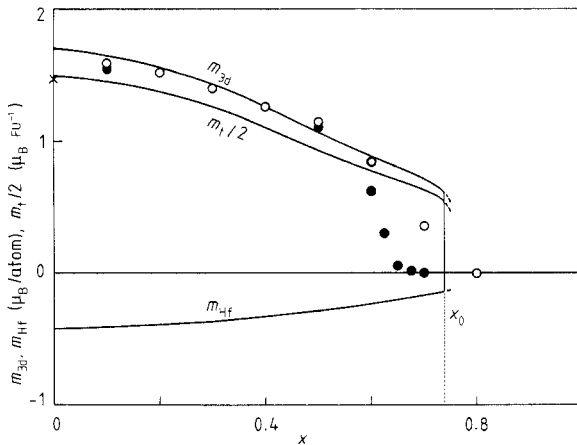
Figure 1. Calculated results of the concentration dependences of m_{Hf}, m_{3d} and $m_t/2$ for Hf(Fe$_{1-x}$Co$_x$)$_2$: $\bigcirc$, values obtained by van Dongen *et al* (1981); $\bullet$, values obtained by Sakakibara *et al* (1989); $\times$, value obtained by Nakamichi *et al* (1970). x_0 denotes the critical concentration.

In this paper the alloying effect is taken into account in the virtual crystal approximation, i.e. the Fe and Co atoms in A(Fe, Co)$_2$ are treated as the virtual atom with averaged values of the band parameters and the average number of 3d electrons of Fe and Co atoms. In these transition-metal compounds AB$_2$, the hybridisation between d states of the A and B atoms plays an important role in their magnetic properties. As we treat the Fe and Co atoms in A(Fe, Co)$_2$ as the virtual atom, then the effect of the hybridisation between d states of the A atom and 3d states of the virtual atom B is taken into account in the present paper.

The DOS for d electrons in Hf(Fe, Co)$_2$ is calculated in the self-consistent tight-binding approximation. In our virtual crystal approximation, the band parameters, i.e. the Wigner–Seitz radii, effective masses and lattice constants in the formalism of Andersen and Jepsen (1977) and Pettifor (1977) are estimated from the linearly interpolated values between those of HfFe$_2$ and HfCo$_2$. The difference between the atomic potentials of 3d and 5d electrons in the paramagnetic state is determined self-consistently so as to fit the calculated numbers of 3d and 5d electrons with those given *a priori*. By using the atomic potentials estimated thus, the local moments m_{3d} on Fe or Co atoms and m_{Hf} on Hf atoms in Hf(Fe, Co)$_2$ are calculated, by using the effective intra-atomic exchange integrals U_{Hf} and U_{Fe} estimated previously (Yamada and Shimizu 1986). The calculated results are shown in § 3.

3. Calculated results

The values of intra-atomic exchange integrals U_{Hf} and U_{3d} on Hf and Fe or Co atoms are adjustable parameters in the present paper and are taken to be 40 mRyd and 62 mRyd, respectively, as estimated previously for HfFe$_2$ (Yamada and Shimizu 1986), so as to obtain the agreement between the calculated total magnetic moment at 0 K and the observed value and by assuming the same ratio between U_{Hf} and U_{Fe} as that calculated for metals in the local spin-density functional formalism (Janak 1977).

In figure 1, the calculated results of the concentration dependence of m_{Hf} and m_{3d} per atom and half the total moment ($m_t/2 = m_{Hf}/2 + m_{3d}$) per formula unit are shown by solid curves. The open circles, the full circles and the cross in figure 1 denote the observed values of $m_t/2$ obtained by van Dongen *et al* (1981), Sakakibara *et al* (1989)
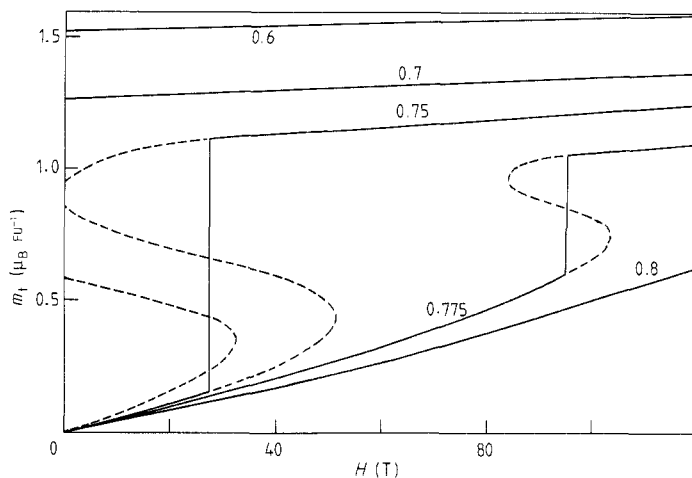
Figure 2. Calculated results of the induced total magnetic moment m_t per formula unit under the external field H for $Hf(Fe_{1-x}Co_x)_2$: the numbers shown on each curve denote the concentrations x; ---, the unstable or metastable states (Shimizu 1982).

and Nakamichi *et al* (1970), respectively. The negative values of m_{Hf} are due to the difference between the strengths of the 3d–5d hybridisation in the majority and minority spin bands, as discussed before (Yamada *et al* 1984, Yamada and Shimizu 1985, 1986).

As seen in figure 1, the calculated critical concentration x_o for the onset of magnetic moment is a little larger than the observed value. If we take a slightly smaller value of the intra-atomic exchange integrals, better agreement between the calculated and observed results will be obtained. The reason why such an abrupt change in m_t appears at x_o is that the position of E_F is close to the sharp peak of the DOS in the paramagnetic state which stabilises the magnetic state, even if the Stoner condition of the appearance of the ferromagnetic state is not satisfied (Shimizu 1964).

The induced moments under the external magnetic field H are estimated as a function of H, by calculating self-consistently the electronic structures for each value of H (Yamada and Shimizu 1985, Yamada *et al* 1987a, b). Here, the same values of U_{Hf} and U_{3d} as used above are made use of. In figure 2, the calculated results of the induced total magnetic moment m_t in $Hf(Fe_{1-x}Co_x)_2$ are shown by the full curves. The number on each curve denotes the concentration x of Co atoms. The induced local moment on a Hf atom is found to be negative; this is due to the difference between the strengths of the 3d–5d hybridisation in the majority and minority spin bands, but the absolute value itself is very small as discussed before (Yamada and Shimizu 1985). Then the induced local moment on a virtual atom of Fe and Co is close to $m_t/2$. The broken curves in figure 2 denote the unstable or metastable states (Shimizu 1982) and the MT can be seen in a small concentration range just above x_o. The calculated results are very similar to the observed results (Sakakibara *et al* 1989) if we take into account the fact that the discontinuous change in m_t will be smeared out by the clustering of atoms or the distributions of the concentration in alloys. However, as the calculated value of x_o is a little larger than the observed value, the concentration x shown in figure 2 corresponds to a slightly larger value than the observed x-value.
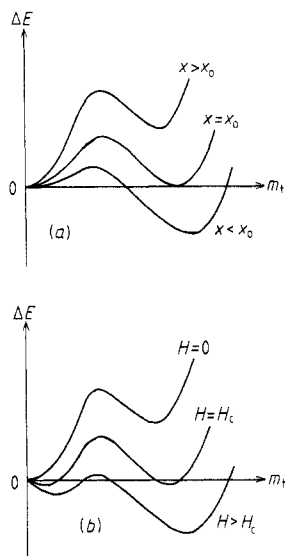
Figure 3. Schematic figures of ΔE as a function of m_t (a) for $x < x_o$, $x = x_o$ and $x > x_o$ at $H = 0$ and (b) for $H = 0$, $H = H_c$ and $H > H_c$ at $x > x_o$.
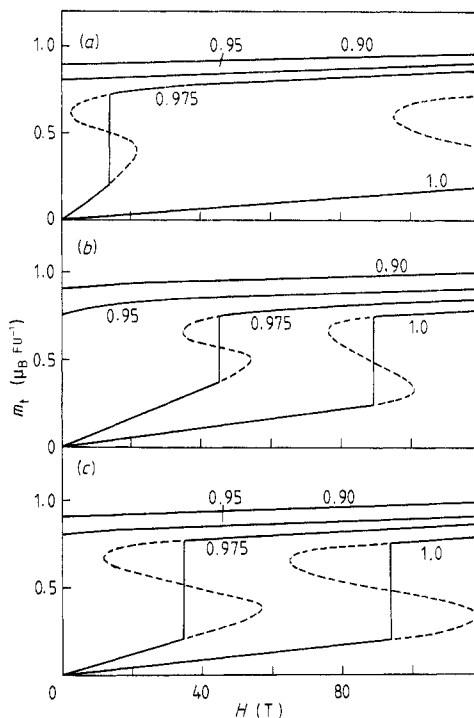

Figure 4. Calculated result of the induced total magnetic moment m_t per formula unit under the external field H for (a) Sc(Fe$_{1-x}$Co$_x$)$_2$, (b) Y(Fe$_{1-x}$Co$_x$)$_2$ and (c) Lu(Fe$_{1-x}$Co$_x$)$_2$: the numbers shown on each curve denote the concentrations x; ———, the unstable or metastable states (Shimizu 1982).

4. Discussion and conclusions

In § 3, the MT has been obtained for Hf(Fe$_{1-x}$Co$_x$)$_2$ only in the small concentration range above x_o. It is noted here that the MT occurs in the small concentration range just before the onset of the magnetic moment. This is easily understood by using the model for the itinerant electron metamagnet discussed by Shimizu (1982). When the difference ΔE between the energies in the magnetic and non-magnetic states has double minima with respect to m_t as shown in figure 3(a) (one minimum is due to the non-magnetic state ($m_t = 0$) and the other is due to the magnetic state ($m_t \neq 0$)), the state with the lower energy is actually stabilised. In the region $x < x_o$, the magnetic state is stable and in the region $x > x_o$ the non-magnetic state is stable. When the external magnetic field is applied for $x > x_o$, the energy of the state with larger m_t decreases rapidly and then at a critical magnetic field H_c it becomes lower than that in the non-magnetic state, as shown in figure 3(b). The value of H_c increases with increasing concentration from x_o, because the difference between the minima of ΔE in the non-magnetic and magnetic states at $H = 0$ becomes large. Therefore the MT can be observed only near the critical concentration for the onset of magnetic moment.

As mentioned in § 1, the MTs for $ScCo_2$, YCo_2 and $LuCo_2$ can occur at extremely high magnetic fields. When some Co atoms are substituted by Fe atoms in these compounds, the critical field H_c is expected to be small, as for $Hf(Fe, Co)_2$ in § 3 but can be observed. This is because the position of E_F is very close to the sharp peak of the DOS which is responsible for the MT. In order to show this fact explicitly, the numerical calculations for the induced moments of $A(Fe, Co)_2$ ($A \equiv Sc$, Y and Lu) are carried out by the same method as used in § 2. Only for $Sc(Fe_{1-x}Co_x)_2$ is the lattice constant assumed to be a constant for all concentrations x because $ScFe_2$ does not have a cubic Laves phase structure but a hexagonal structure. The values of the intra-atomic exchange integrals U_A and U_{3d} determined previously for $ScCo_2$, YCo_2 and $LuCo_2$ (Yamada and Shimizu 1985, Yamada *et al* 1987a, b) are made use of. The calculated results of m_t for $Sc(Fe_{1-x}Co_x)_2$, $Y(Fe_{1-x}Co_x)_2$ and $Lu(Fe_{1-x}Co_x)_2$ are shown as full curves in figures 4(a), 4(b) and 4(c), respectively.

The local induced moments on Sc, Y and Lu are found again to be negative but very small and the induced moment on a virtual atom of Fe and Co is close to $m_t/2$, as for $Hf(Fe, Co)_2$ in § 3. The broken curves in figure 4 denote the metastable or unstable state (Shimizu 1982). The numbers shown on each curve denote the concentrations x of Co atoms.

The magnetic field dependences of the induced moments in figure 4 have not been observed so far except for $Y(Fe, Co)_2$. The calculated results for $Y(Fe, Co)_2$ shown in figure 4(b) are similar to the observed values (Yoshimura *et al* 1987). Although this pseudo-binary compound shows a spin-glass behaviour (Steiner 1979), the observed anomalous field dependence of the induced moment can be explained as the itinerant electron metamagnetism. As the virtual crystal approximation has been used in this paper, the local moments on Fe and Co atoms cannot be distinguished. However, in the actual compound $Y(Fe, Co)_2$, the local moment on Fe atoms may not change its value so much and the local moment on Co atoms may show the MT near $x = x_0$. Then, the total moment m_t near x_0 increases rapidly at H_c as observed by Yoshimura *et al* (1987). The calculated value of x_0 is larger than 0.95 but the observed value is about 0.9 (Steiner 1979, Yoshimura *et al* 1987). The difference between the calculated and observed values of x_0 may be mainly due to the effect of the local environment which is neglected in this paper. The induced magnetic moments in $Sc(Fe, Co)_2$ and $Lu(Fe, Co)_2$ are expected to be observed as shown in figures 4(a) and 4(c) and the observations under high magnetic fields are highly desirable. Moreover, as mentioned in § 1, the peak of the DOS near E_F is responsible both for the MT and for a maximum in the temperature dependence of the paramagnetic susceptibility χ. Then a maximum in the temperature dependence of χ will also be observed for these pseudo-binary compounds near the critical concentration.

In the present paper, the induced magnetic moment under the external field for the pseudo-binary compounds $Hf(Fe, Co)_2$, $Sc(Fe, Co)_2$, $Y(Fe, Co)_2$ and $Lu(Fe, Co)_2$ have been calculated by using the virtual crystal approximation. The MT has been shown to occur in a small concentration range above x_0, which is consistent with experiments for $Hf(Fe, Co)_2$ and $Y(Fe, Co)_2$. It has been shown that the detailed shape of the DOS near E_F plays an important role in these magnetic properties.

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