Hyperfine fields and electronic structures of the Heusler alloys Co_2MnX (X=Al, Ga, Si, Ge, Sn)

1990 J. Phys.: Condens. Matter 2 8583

(http://iopscience.iop.org/0953-8984/2/43/004)

J. Phys.: Condens. Matter **2** (1990) 8583–8589. Printed in the UK

Hyperfine fields and electronic structures of the Heusler alloys Co_2MnX (X = Al, Ga, Si, Ge, Sn)

S Fujii†, S Sugimura†, S Ishida† and S Asano‡

† Department of Physics, Faculty of Science, Kagoshima University, Kagoshima, 890 Japan.

‡ Institute of Physics, College of Arts and Science, University of Tokyo, Meguro-ku, Tokyo, 153 Japan

Received 16 January 1990, in final form 2 July 1990

Abstract. Hyperfine fields and electronic structures were calculated by the KKR method to investigate the effects of the X atom on the magnetic properties of Co_2MnX. The obtained magnetic moments of Co or Mn sites in Co_2MnX are in good agreement with the experimental ones. Though the obtained hyperfine fields on Co or Mn sites are smaller in absolute value than the experimental ones, their trend is consistent with the experimental one. The hyperfine field on Mn sites is essentially determined by the magnetic moments on Mn sites themselves, but not that on Co sites. The relationship between the Co hyperfine field and the valence electron number of X atoms is discussed in terms of the obtained density-of-state.

1. Introduction

The electronic and magnetic properties of Heusler alloys have been investigated experimentally and theoretically. Webster (1971) investigated the chemical and magnetic structures of the alloys Co_2MnX (X = Al, Ga, Si, Ge, Sn). He reported that the alloys containing the group IVb elements (X = Si, Ge and Sn) have net moments of approximately 5.1 μ_B per molecule with individual moments of 0.75 μ_B and 3.6 μ_B on Co and Mn sites, respectively, and that the alloys containing the group IIIb elements (X = Al and Ga) have net moments of approximately 4.0 μ_B per molecule and correspondingly smaller moments on both Co and Mn sites. The hyperfine fields on Co and Mn sites in Co_2MnX have been measured by NMR (LeDang *et al* (1978) and Kawakami *et al* (1987) for X = Si, Ge, Sn, Ga; Yoshimura *et al* (1985) for X = Al, Ga; Kawakami (1989) for X = Al, Sn). These data show the following trend, as indicated by Kawakami (1989). The Mn hyperfine field H_{hf}(Mn) is linearly related to the Mn magnetic moment, while the Co hyperfine field H_{hf}(Co) is not proportional to the Co magnetic moment itself and decreases with increasing numbers of s and p valence electrons of the atom X.

The mechanism producing the change in magnetic moment and hyperfine field, which results from the difference of an atom X in Co_2MnX, is not yet understood. In this paper, we investigate the mechanism in terms of the density-of-state (DOS) for constituent atoms in Co_2MnX. The band calculations were carried out by the Korringa–Kohn–Rostoker (KKR) method using a muffin-tin potential (Kohn and Rostoker 1954). The exchange-correlation potential was treated by the local-spin-density (LSD) approxi-

0953-8984/90/438583 + 07 $03.50

Table 1. The magnetic moments of constituent atoms in Co_2MnX. The unit is μ_B. The numbers in parentheses are experimental values for magnetic moments (Webster 1971). Lattice parameters used for calculations are listed in the last column (Webster 1971).

	Molecule	Co	Mn	X	a(A)
X = Al	4.09(4.01)	0.70(0.5)	2.83(3.1)	−0.08	5.756
X = Ga	4.14(4.05)	0.68(0.52)	2.89(3.0)	−0.07	5.770
X = Si	5.00(5.07)	1.00(0.75)	3.05(3.6)	−0.06	5.654
X = Ge	5.00(5.11)	0.97(0.75)	3.11(3.6)	−0.05	5.743
X = Sn	5.03(5.08)	0.94(0.75)	3.23(3.6)	−0.06	6.000

mation, which is of the Barth–Hedin form with parameters determined by Janak *et al* (1975). The self-consistency was achieved on 85 points in the irreducible Brillouin zone. The DOS was obtained by the tetrahedral integration method (Rath and Freeman 1975). The lattice parameters used for calculations are listed in table 1.

2. Results of calculations

The obtained magnetic moments of each constituent atom in Co_2MnX (X = Al, Ga, Si, Ge and Sn) are listed in table 1, together with the experimental data. The obtained magnetic moments are in good agreement with the experimental ones. In particular, for the moments per molecule our results agree very well with experimental ones. The table shows that there exists a distinct difference in magnetic moments on Co and Mn sites between two types of alloys, that is, the alloys containing the group IIIb elements (Alloy(IIIb)) have smaller moments on both Co and Mn sites than the alloys containing the group IVb elements (Alloy(IVb)). The difference is discussed in terms of the obtained density-of-state (DOS) in section 3.

The contribution to the hyperfine field from the Fermi contact interaction is written as the following expressions (Watson and Freeman 1961)

$$H = n\mu_B\chi$$

$$\chi = (4\pi/n)\sum\{\rho_\uparrow(0) - \rho_\downarrow(0)\}$$

where n is the number of unpaired electrons, and $\rho_\uparrow(0)$ ($\rho_\downarrow(0)$) is the density of s electrons at the nucleus for the majority spin (minority spin). The obtained hyperfine fields of each constituent atom in Co_2MnX are listed in table 2, together with the experimental data. In table 2, we also list two parts of the hyperfine field, that is, the contribution from valence s electrons (denoted by H_{val}) and the contribution from core s electrons (denoted by H_{core}). Table 2 shows that the present calculation systematically underestimates the hyperfine field. In this regard, Ishida *et al* (1984) have already pointed out that when we adopted the LSD approximation, we evaluated H_{core} to be small. As they have done, we assumed χ_{core} to be −3.1 and −2.5 for Mn and Co in the Heusler alloys and calculated the hyperfine fields. We obtained the result that H_{hf}(Mn) values are much improved but H_{hf}(Co) are little improved. We cannot explain the discrepancy in H_{hf}(Co) between the calculated values and the experimental ones. We suppose that the contribution from the orbital angular momentum is needed for Co sites since the indication that there is an unquenched orbital moment on Co sites has been reported (LeDang *et al* 1978, Ishida *et al* 1983 and Yoshimura *et al* 1985).

Table 2. Hyperfine fields of constituent atoms in Co_2MnX. The unit is kOe. H_{core} and H_{val} are the contributions to the hyperfine fields from the core and valence s electrons. $H_{theo} = H_{core} + H_{val}$. H_{exp} are experimental values; (a) LeDang *et al* 1978, (b) Yoshimura *et al* 1985, (c) Kawakami *et al* 1987 and (d) Kawakami 1989. The last column shows the difference of s electrons between majority and minority spin.

		H_{core}	H_{val}	H_{theo}	H_{exp}	n_s
	Co	−77.3	−61.4	−138.6	$-177^{(d)}$ $-175.1^{(b)}$	−0.008
Co_2MnAl	Mn	−290.8	84.3	−206.5	$-280.5^{(d)}$	0.010
	Al	3.5	−28.0	−24.5		−0.009
	Co	−73.3	−54.9	−128.1	$-171.8^{(c)}$ $-173^{(a)}$	−0.008
Co_2MnGa	Mn	−292.6	87.2	−205.5	$-280.0^{(c)}$ $-280^{(a)}$	0.010
	Ga	1.6	−26.6	−25.0		−0.005
	Co	−101.2	30.3	−70.9	$-145.0^{(c)}$ $-146^{(a)}$	0.004
Co_2MnSi	Mn	−305.2	83.9	−221.3	$-335.9^{(c)}$ $-337^{(a)}$	0.010
	Si	3.3	9.8	13.1		−0.000
	Co	−99.6	23.5	−76.1	$-140.2^{(c)}$ $-141^{(a)}$	0.003
Co_2MnGe	Mn	−311.1	84.6	−226.5	$-339.4^{(c)}$ $-339^{(a)}$	0.010
	Ge	2.1	65.6	67.7		0.003
	Co	−96.9	−4.8	−101.7	$-156.0^{(c)}$ $-155^{(a)}$	−0.001
Co_2MnSn	Mn	−324.6	103.3	−221.3	$-344.1^{(c)}$ $-352^{(a)}$	0.013
	Sn	2.7	−41.7	−39.1		−0.004

As mentioned above, there appears to be a systematic underestimation of the hyperfine field. However, there is no discrepancy between our results and experimental ones concerning the sign of the hyperfine field and the tendency of the absolute value. Furthermore, since our data are divided into two parts, H_{core} and H_{val}, it is convenient to discuss the influence of neighbouring magnetic atoms on the hyperfine fields. For these reasons, it is worthwhile to investigate the relationship between hyperfine fields and electronic structures on the basis of our data. Before discussing the subject, we make some comments on the obtained hyperfine fields. The signs of H_{core} of Co and Mn sites are negative for all of the alloys and the values of H_{core} are linearly related to their own magnetic moments. This is consistent with our expectation. The sign of H_{val} on Mn sites is positive and its value is almost the same for all of the alloys. The sign of H_{val} on Co sites is negative for Alloy(IIIb) and positive for Alloy(IVb) except for Sn. These facts indicate that the mechanism determining H_{val} is different for Co and Mn sites. Furthermore, there is a different influence of the neighbouring magnetic atoms on the H_{val} of Co atoms between Alloy(IIIb) and Alloy(IVb).

Incidentally, the hyperfine field is determined from the charge density of s electrons at the nucleus. However, table 2 shows that the sign of the s-electron polarization, that

is, the difference of s electrons between majority and minority spins (denoted by n_s), is not only identical with the sign of H_{val} for all of the alloys but also n_s is linearly related to H_{val}. This enables us to discuss the hyperfine fields in terms of the obtained DOS. In the next section, we discuss this subject.

3. Discussion

Before we discuss the relationship between the hyperfine fields and the obtained DOS, we consider the difference in magnetic moments on Co and Mn sites between alloys containing the group IIIb elements and those containing IVb elements in terms of the obtained DOS. We show the DOS of Co_2MnX (X = Al, Ga, Si, Ge and Sn) in figure 1 and figure 2. Figure 1 shows the DOS of d bands for Co and Mn and figure 2 shows the DOS of s and p bands for constituent atoms in Co_2MnX. As seen from these figures, the magnetic moment is mostly determined by the d electrons. Then, we turn our attention to the DOS of d bands. From figure 1, we can see that the DOS of Co and Mn have similar shapes near the Fermi level in alloys containing the group IIIb elements (Alloy (IIIb)) and those containing the group IVb elements (Alloy(IVb)). In both alloys, the minority spin electrons have the Fermi level at the broad valley of the DOS. The majority spin electrons unoccupy the hump near the Fermi level for X = Al or Ga, while they occupy for X = Si, Ge or Sn. Whether the majority spin electrons of magnetic atoms occupy or unoccupy the hump of the DOS produces the difference in the magnetic moment, that is, the moments on Co and Mn sites are larger for Alloy(IVb) than for Alloy(IIIb), as the experimental results show.

The Mn hyperfine field in Co_2MnX is, as already mentioned in section 2, mainly determined by the large magnetic moment of Mn itself, since the effect of the neighbouring Co atoms is small because of the small magnetic moments. The H_{core} value on Mn sites is linearly related to their own moment but H_{val} is almost the same for all of the alloys. On the other hand, the Co sites have Mn atoms, which have large magnetic moments, as their nearest neighbours, and therefore the Co hyperfine field is not determined only by the small moment of Co itself. We expect that the sign of H_{val} on Co sites is positive if H_{val} is determined only by the magnetic moment of Co and that the sign is negative if H_{val} is determined by the magnetic moment of the nearest neighbour Mn rather than the magnetic moment of Co itself. The sign of H_{val} on Co sites is determined by the competition between these contributions. Table 2 shows that the sign of H_{val} on Co sites in Co_2MnX (X = Si, Ge) is positive, while the sign in Co_2MnX (X = Al, Ga) is negative. Therefore, it may be said that the effect of nearest neighbour magnetic atoms is stronger in Alloy(IIIb) than in Alloy(IVb). (In the case of Sn, the sign is negative but the absolute value is small.)

In the above paragraph, we considered the influence of neighbouring magnetic atoms on H_{val} in terms of the sign of H_{val}. The sign of H_{val} is, as already mentioned in section 2, identical to the sign of n_s (the difference of s electrons between majority and minority spins) and H_{val} is linearly related to n_s. Thus, we turn our attention to the DOS of s electrons in figure 2. First, we consider the DOS of s electrons on Co sites. For Alloy(IIIb), the Fermi level is located at the valley in both majority and minority spins. On the other hand, for Alloy(IVb) the Fermi level is located at the valley in minority spin but it is located in a small, broad peak of the DOS for the majority spin. Owing to this different occupancy of s electrons, n_s is negative for Alloy(IIIb) and positive for Alloy(IVb) except for Sn as seen in table 2. Secondly, concerning Mn atoms the Fermi level is located

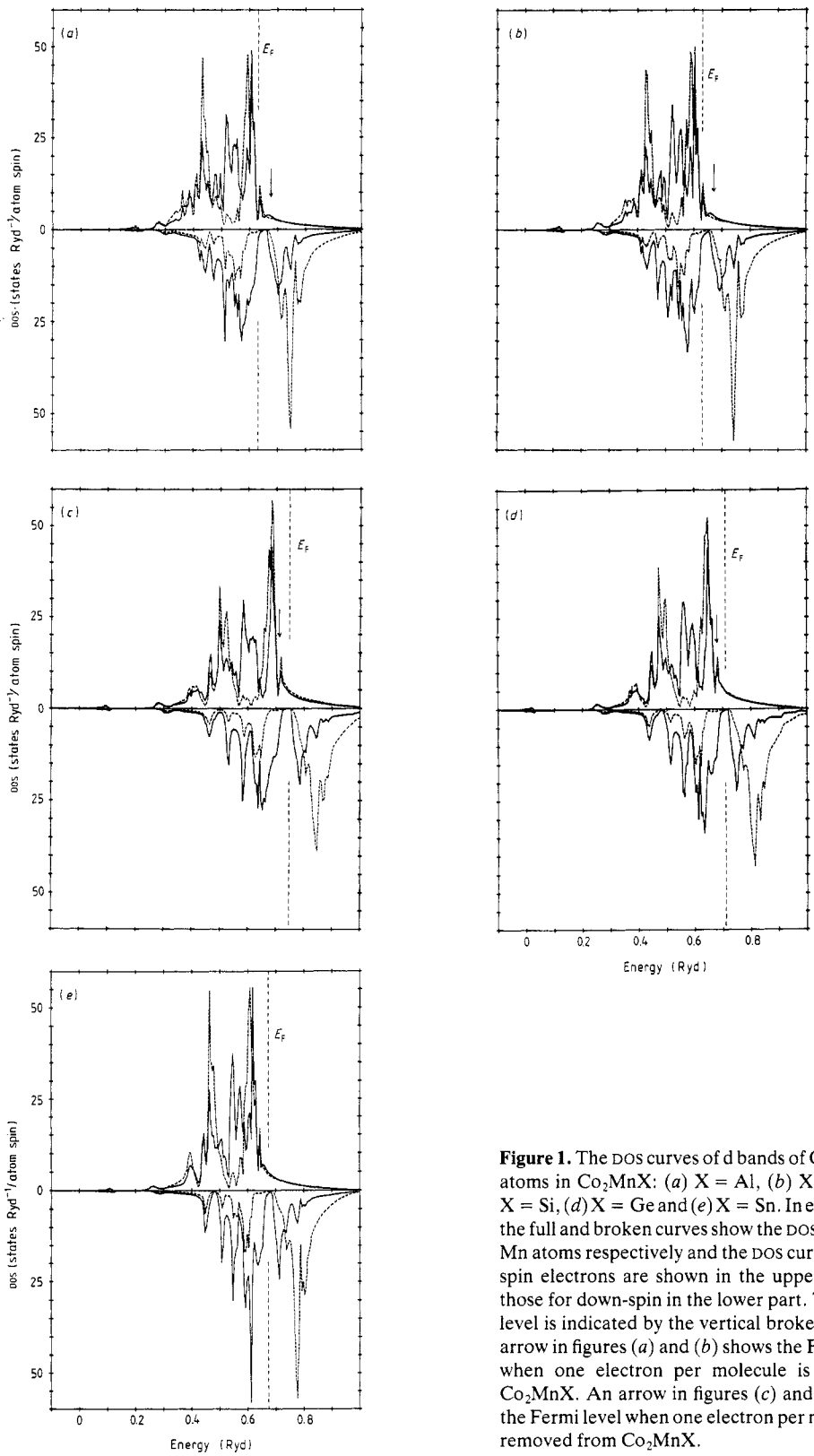

Figure 1. The DOS curves of d bands of Co and Mn atoms in Co_2MnX: (*a*) X = Al, (*b*) X = Ga, (*c*) X = Si, (*d*) X = Ge and (*e*) X = Sn. In each figure, the full and broken curves show the DOS of Co and Mn atoms respectively and the DOS curves for up-spin electrons are shown in the upper part and those for down-spin in the lower part. The Fermi level is indicated by the vertical broken line. An arrow in figures (*a*) and (*b*) shows the Fermi level when one electron per molecule is added to Co_2MnX. An arrow in figures (*c*) and (*d*) shows the Fermi level when one electron per molecule is removed from Co_2MnX.

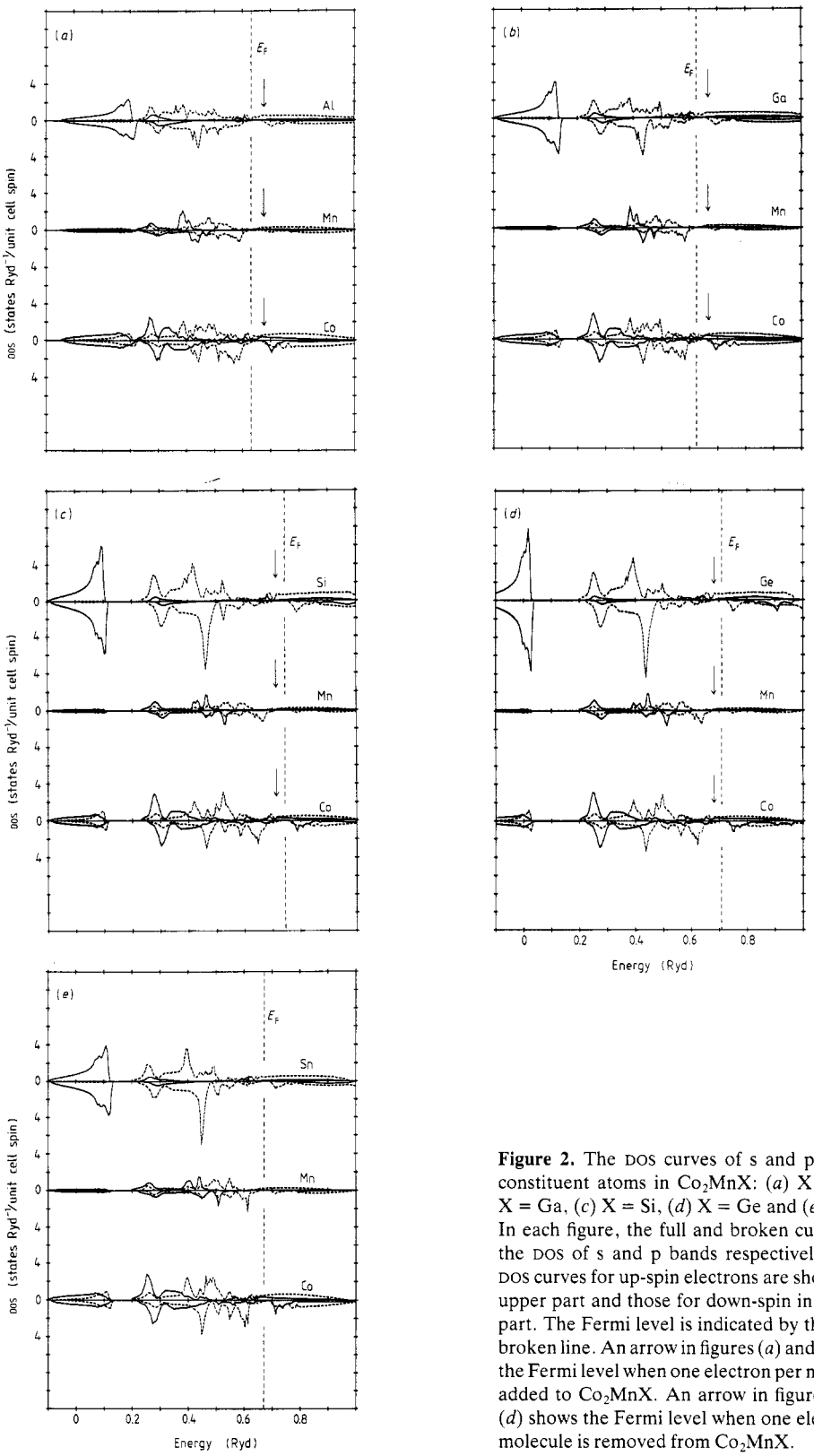

Figure 2. The DOS curves of s and p bands of constituent atoms in Co_2MnX: (*a*) X = Al, (*b*) X = Ga, (*c*) X = Si, (*d*) X = Ge and (*e*) X = Sn. In each figure, the full and broken curves show the DOS of s and p bands respectively and the DOS curves for up-spin electrons are shown in the upper part and those for down-spin in the lower part. The Fermi level is indicated by the vertical broken line. An arrow in figures (*a*) and (*b*) shows the Fermi level when one electron per molecule is added to Co_2MnX. An arrow in figures (*c*) and (*d*) shows the Fermi level when one electron per molecule is removed from Co_2MnX.

in the flat, no-peak region of the DOS in both types of alloys. This leads to the fact that n_s has almost the same value for all alloys in contrast to d electrons.

As explained above, the occupancy of electrons of magnetic Co and Mn atoms is different in two types of alloys, even though the DOS's shapes near the Fermi level for the alloys are similar to each other. The different occupancy is due to the difference of the valence-electron number between non-magnetic IIIb and IVb elements. This can be understood, for example, by comparing the DOS of Co_2MnAl and Co_2MnSi. Adding one electron to Co_2MnAl, the number of electrons per molecule becomes equal to that of Co_2MnSi and the Fermi level shifts to the position shown by an arrow in figures 1(*a*) and 2(*a*). This relative position in the DOS is quite similar to the relative position of the Fermi level for Co_2MnSi shown by a broken line in figures 1(*c*) and 2(*c*). On the other hand, removing one electron from Co_2MnSi, the Fermi level shifts to the position shown by an arrow in figures 1(*c*) and 2(*c*) and locates at a similar position to the Fermi level of Co_2MnAl shown by a broken line in figures 1(*a*) and 2(*a*). The same situation is seen between Co_2MnGa and Co_2MnGe. Thus, the difference in magnetic properties between Alloy(IIIb) and Alloy(IVb), which results from the different occupancy of electrons, arises from the difference of only one electron in a non-magnetic X atom in Co_2MnX. In conclusion, in Heusler alloys Co_2MnX (X = Al, Ga, Si, Ge and Sn), the valence-electron number of a given atom X is one of the important factors when considering the magnetic properties.

Acknowledgments

We would like to thank Professor M Kawakami of Kagoshima University for providing us with information. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan. The numerical calculations were performed on the HITAC M-280 at the computer centre of the University of Tokyo and the FACOM M-382 at the computer centre of Kyushu University.

References

Ishida S, Asano S and Ishida J 1984 *J. Phys. Soc. Japan* **53** 2718
Ishida S, Otsuka Y, Kubo Y and Ishida J 1983 *J. Phys. F: Met. Phys.* **13** 1173
Janak J K, Moruzzi V L and Williams A R 1975 *Phys. Rev.* B **12** 1257
Kawakami M 1989 *Hyperfine Interactions* **51** 993
Kawakami M, Kasamatsu Y and Ido H 1987 *J. Magn. Magn. Mat.* **70** 265
Kohn W and Rostoker N 1954 *Phys. Rev.* **94** 1111
LeDang K, Veillet P and Campbell I A 1978 *J. Phys. F: Met. Phys.* **8** 1811
Rath J and Freeman A J 1975 *Phys. Rev.* B **11** 2109
Watson R E and Freeman A J 1961 *Phys. Rev.* **123** 2027
Webster P J 1971 *J. Phys. Chem. Solids* **32** 1221
Yoshimura K, Miyazaki A, Vijayaraghavan R and Nakamura Y 1985 **53** 189