

Electronic Structure of CsCl-Type Transition Metal Alloys

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Transition metal alloys have a tendency to make a stable ordered lattice of the CsCl-type, when the average number of conduction electrons (including d -electrons) is the same as that of Cr. The electronic structures of VMn, TiFe and ScCo are investigated by the self-consistent KKR method, to clarify the stability of these alloys. It is found that the density-of-states of these alloys has a deep valley in the middle region, by which bonding and antibonding orbitals are well separated, and the Fermi energy lies in the valley. The electronic structure of ordered alloy ScCu is also investigated. Here the narrow d -bands of Cu are situated well below the d -bands of Sc, and s -, p -electrons are polarized by about 0.6/atom at the Cu-cell. Thus, the ionic bond seems to be important to make a stable ordered lattice of ScCu.

§ 1. Introduction

This is the third paper dealing with the electronic structure of transition metal alloys. In the first paper,¹⁾ the electronic structure of the ordered alloy FeCo was investigated. The ordered alloy FeCo is ferromagnetic and has the CsCl-type structure. In the second paper,²⁾ the electronic structure of the ordered ferromagnetic alloy Ni₃Mn and the ordered antiferromagnetic alloy NiMn were considered. The former has the fcc structure as a whole and the latter has the tetragonal layer structure. In the present paper, the electronic structure of four transition metal alloys of the CsCl-type will be investigated. They are VMn, TiFe, ScCo and ScCu. They are paramagnetic substances. Incidentally, the present work is stimulated by the interesting article by Nevitt³⁾ entitled "Alloy Chemistry of Transition Elements".

Figure 1 of the present paper is the reproduction of Fig. 12 in that article. As seen from Fig. 1, alloys of AB type, where A and B are one of the 3d-transition metal atoms and the average number of the electrons of A and B is equal to that of Cr, are apt to make an ordered lattice of the CsCl-type structure. They are VMn, TiFe and ScCo. When Ti is replaced by V, or Sc is replaced by Ti, the crystals VFe and TiCo make an ordered lattice of the CsCl-type structure. As

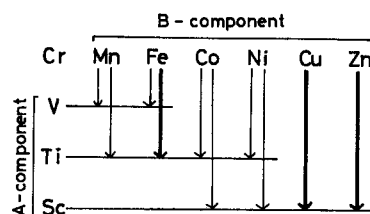


Fig. 1. A diagram of transition metal alloys of CsCl structure. The two elements connected by an arrow make an alloy of CsCl structure. The two elements connected by a heavy arrow make a very stable lattice.

seen from Fig. 1, however, they are less stable as compared with TiFe. Further, ScCu and ScZn make the ordered lattice of the CsCl-type structure, although their average number of electrons per atom is somewhat deviated from that of Cr.

A few years ago we calculated the electronic structure of Cr⁴⁾ in a perfect antiferromagnetic state having the CsCl-type spin structure. The most important character of the band structure of Cr is the existence of the energy gap. Although the width of the gap is narrow, it spreads in the region of the nearly equal energy in the k -space and the large part of the Fermi surface of Cr in the paramagnetic state are separated by the energy gap and disappear in the magnetic state. As is well known, this energy gap performs an important role for stabilization of the antiferromagnetic state in Cr. Indeed, there is a remarkable relation between the energy value of the paramagnetic state and that in the corresponding antiferromagnetic state. That is, if $E_p(n, k) > E_F$, then $E_A(n, k) > E_p(n, k)$, but if $E_p(n, k) < E_F$, then $E_A(n, k) < E_p(n, k)$, where E_F is the Fermi energy of Cr and $E_p(n, k)$ and $E_A(n, k)$ are the corresponding $E(k)$ values in paramagnetic and antiferromagnetic state of Cr, respectively. This means that the band structure of bcc transition metals is almost separated into two parts just near the Fermi surface, and the lower part makes bonding states and the higher part makes antibonding states by the CsCl-type perturbation. The energy gap in Cr is a typical example of such situation.

It is important to note that the number of the states for the conduction electrons (including $3d$ electrons) below the energy gap is evaluated as 6.1/atom.⁵⁾ As is well known, the perfect antiferromagnetic state is not realized in pure Cr, but it is realized at Cr-Mn alloys with a small amount of Mn atoms. According to the band theory, the spin structure of transition metals or of their alloys depends critically upon the band structure and the number of electrons occupying the bands. In general, the theoretical prediction seems to be in accord with observation.

In antiferromagnetic Cr the difference in the lattice potential is produced by the spin structure through the effective exchange interaction. In the ordered lattice of the AB-type, difference in the potential comes from the difference in the atomic potential of A- and B- atoms, when the state is paramagnetic. If an alloy is magnetic, the potential difference due to the spin structure is superposed on the difference due to the atomic potential. The typical example of magnetic alloys in CsCl structure is FeCo. The structure of the minority spin bands of FeCo is quite similar to that of Cr.¹⁾ Therefore, if the Fermi energy is assumed to lie in the energy gap, the number of conduction electrons occupying the minority spin states is estimated as 6.1/pair and spin. Then, the magnetic moment of ferromagnetic FeCo is easily evaluated as $4.8\mu_B$, which is in an excellent agreement with experiment. (See Fig. 2.) The fact that the energy gap divides the energy bands almost into two parts and the number of states below the energy gap is close to 6/pair and spin is the most important character of the electronic

structure of the transition metal alloys of the CsCl-type structure. Therefore, if the number of conduction electrons/pair and spin is close to 6 in a certain AB-type alloy, then the ordered state of the CsCl structure is expected to be realized owing to the gain in the band energy. Then the state should be paramagnetic. The main purpose of the present paper is to ascertain the characteristic features mentioned above by a direct calculation for VMn, TiFe and ScCo.

As for the ordered state of ScCu and ScZn, Nevitt has pointed out the importance of the ionic bond between two kinds of atoms. In the present paper, the ionic character of the transition metal alloys of the CsCl-type structure will be investigated by the direct calculation. In § 2 the method of calculation will be mentioned quite briefly. In § 3 the results of calculation will be shown by figures and tables. In § 4 the physical picture of the transition metal ordered alloys will be mentioned on the basis of the results obtained by the calculation.

§ 2. Method of calculation

The band structure is calculated by KKR with muffin-tin approximation. The method of calculation was given in a previous paper.⁶⁾ The self-consistent Hartree-Fock-Slater potential is constructed for the paramagnetic state. In order to have a reliable result of the charge polarization in binary alloys, the self-consistent procedure is of vital importance. The long range Coulomb interaction between atomic cells must be considered. The value of the parameter in the Slater exchange potential⁶⁾ is taken as 0.8 throughout the work. As it is convenient to use the same value of the constant potential outside of each muffin-tin sphere, so the different value is used for the radius of two muffin-tin spheres. The density-of-states is determined by Matheiss' interpolation method⁷⁾ from the knowledge of energy values at 35 points in 1/48 of the first Brillouin zone.

§ 3. Results of calculation

(a) VMn, TiFe and ScCo

The $E(k)$ curves of VMn along some high-symmetric axes are shown in

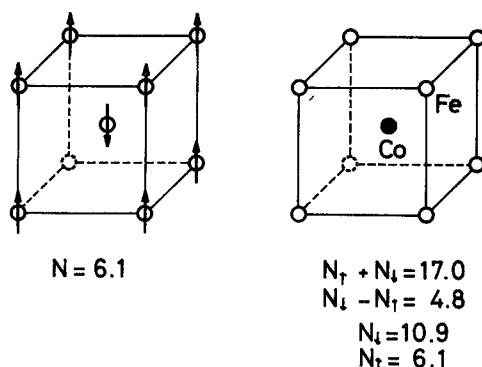


Fig. 2. Spin structure of a perfect antiferromagnetic bcc lattice and the atomic arrangement of ferromagnetic FeCo. The number of conduction electrons (including d -electrons) in the up-spin bands and in the down-spin bands are shown below the figure.

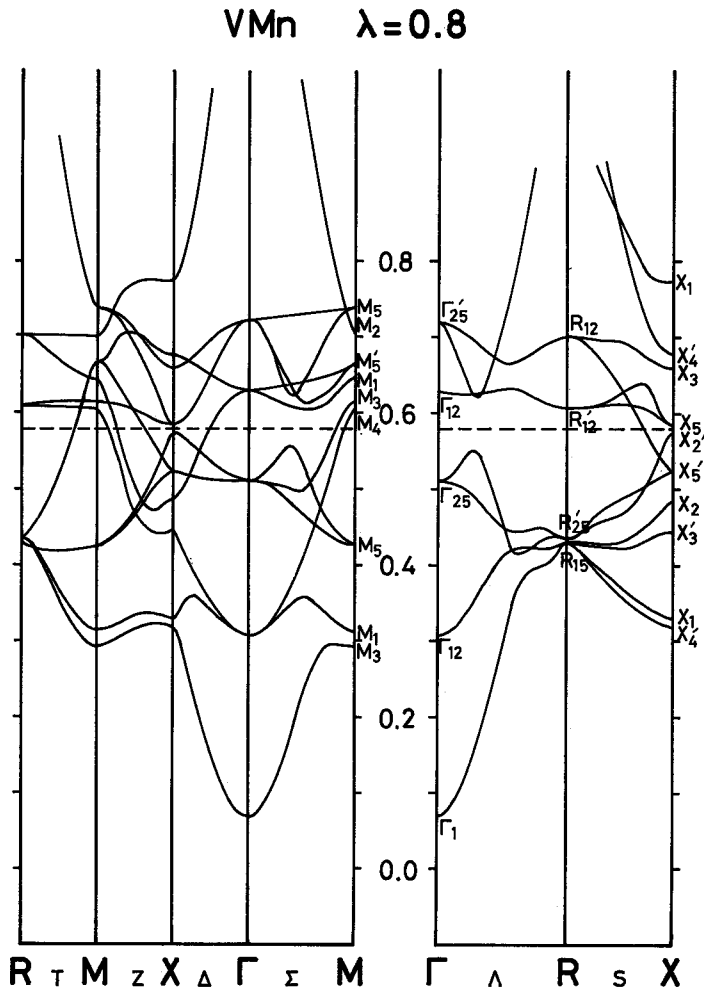


Fig. 3. $E(k)$ curves of VMn. The energy unit is rydberg.

Fig. 3. They look quite similar to those of Cr in the antiferromagnetic state and of FeCo in the minority spin state. This is an example of the well-known fact that the general character of the band structure or of the density-of-states of transition metals is almost determined by the symmetry of the lattice potential. The energy gap is concentrated in the middle part of the energy curves. The density-of-states in Fig. 4 shows more clearly a deep dip in the middle of the curve and Fermi energy lies in this low-density region as anticipated from the general consideration mentioned before.

The $E(k)$ curves of TiFe along some high-symmetry axes are shown in Fig. 5. The total density-of-states is shown in Fig. 10 and the Fe- and Ti-partial densities-of-states are shown in Fig. 6. They show clearly that the lower part

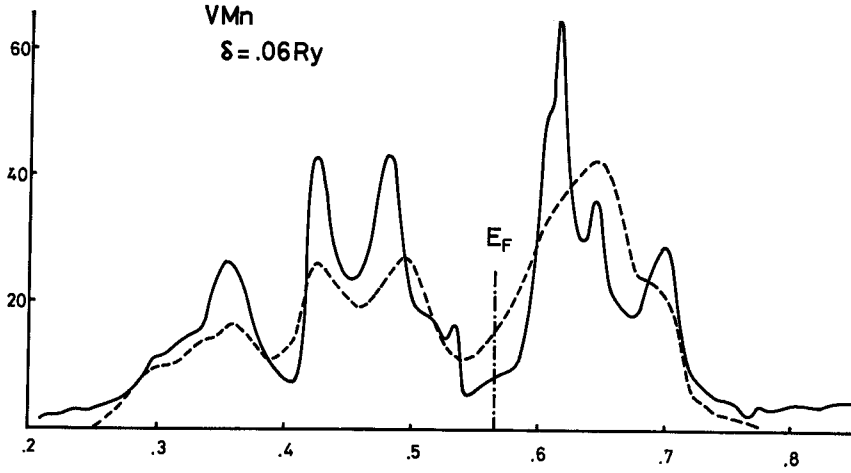


Fig. 4. Density-of-states of VMn in the ordered state. The position of the Fermi energy is indicated by a vertical line. The energy unit is rydberg. The density-of-states of the disordered state is shown in a dotted curve. It is calculated by the coherent potential approximation.

TiFe $\lambda = 0.8$

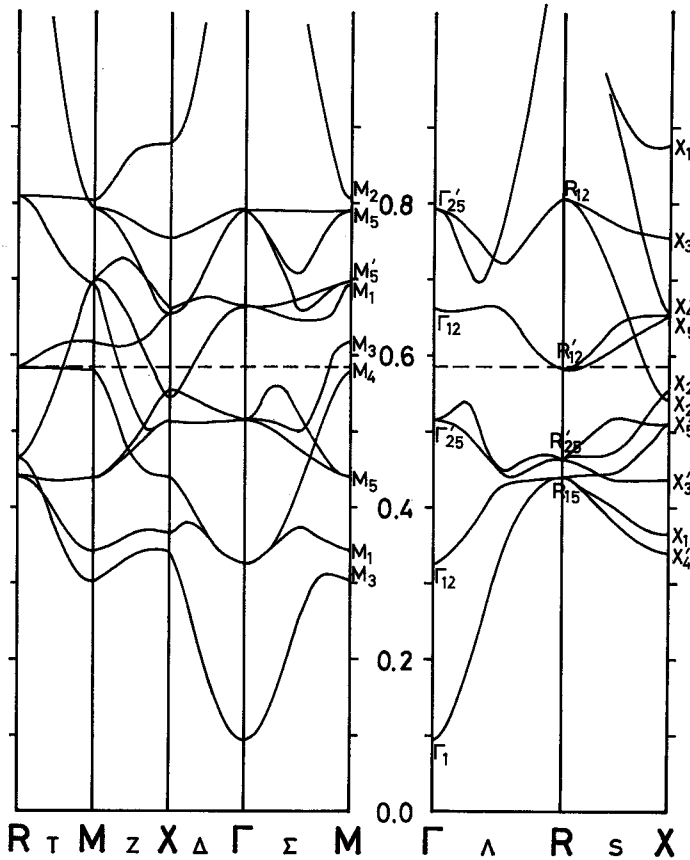


Fig. 5. $E(k)$ curves of TiFe.

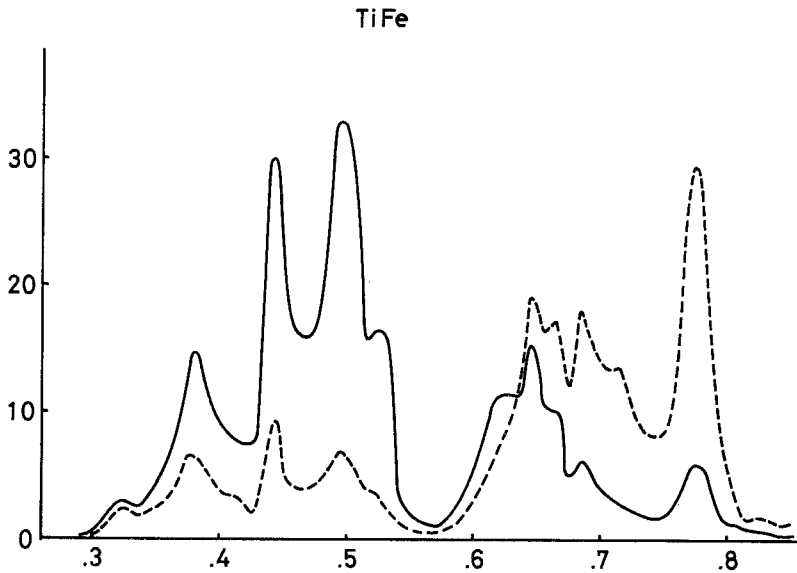


Fig. 6. A partial density-of-states of TiFe. The full curve shows that of Fe and the dotted curve shows that of Ti.

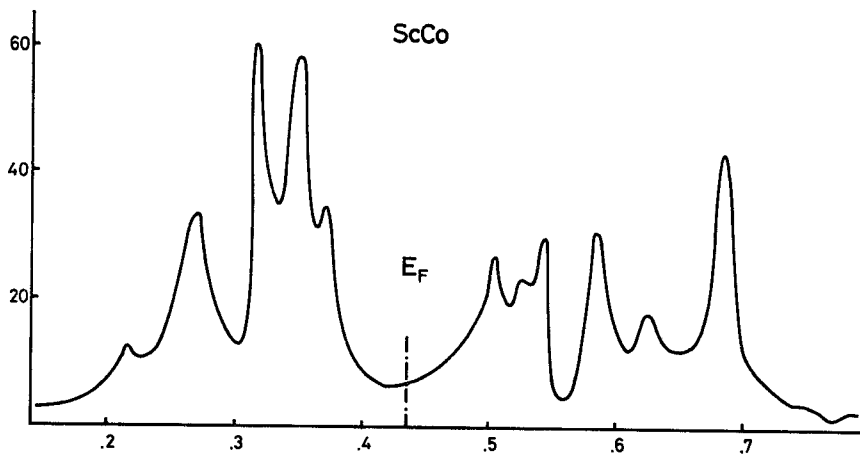


Fig. 7. Density-of-states of ScCo.

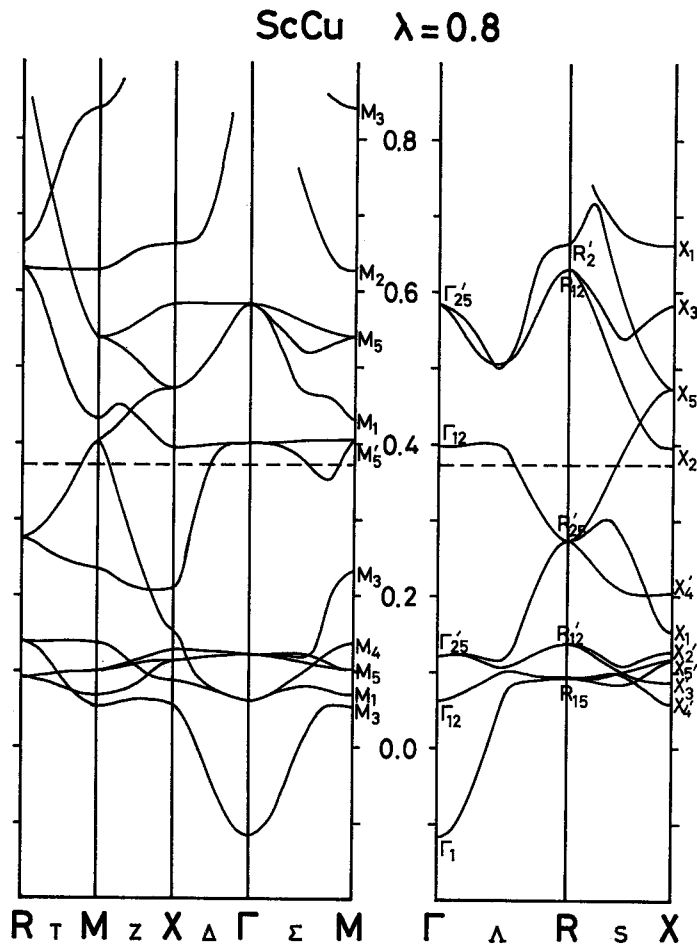
of the energy bands is mainly Fe-like and the upper part is mainly Ti-like. Each component has a deep valley in the middle region. It may be noticeable that the Fermi energy of TiFe lies slightly above the minimum of the density-of-states. The most stable configuration for the CsCl-type structure seems to contain a little more Ti-component rather than fifty and fifty. The minimum value of the density-of-states corresponds to $0.8 \text{ mJ/mole deg}^2$ of the electronic specific heat coefficient. The value at the Fermi surface corresponds to about $1.0 \text{ mJ/mole deg}^2$. The density-of-states of ScCo is shown in Fig. 7. It also looks quite

Table I. The energy values $E(k)$ at four points of high symmetry. The unit is rydberg.

	VMn	TiFe	ScCo	ScCu
Γ_1	0.069	0.094	-0.015	-0.118
Γ_{12}	0.307	0.325	0.234	0.062
$\Gamma_{25'}$	0.512	0.515	0.367	0.122
Γ_{12}	0.630	0.664	0.551	0.399
$\Gamma_{25'}$	0.721	0.793	0.719	0.584
X_4'	0.320	0.339	0.211	0.056
X_1	0.329	0.363	0.254	0.154
X_3'	0.445	0.440	0.306	0.088
X_5'	0.524	0.514	0.360	0.115
X_2	0.486	0.544	0.484	0.395
X_2'	0.574	0.554	0.386	0.129
X_5	0.581	0.652	0.583	0.473
X_4'	0.676	0.653	0.456	0.207
X_3	0.658	0.753	0.702	0.582
X_1	0.774	0.877	0.802	0.663
M_3	0.293	0.303	0.198	0.054
M_1	0.774	0.877	0.802	0.663
M_5	0.425	0.439	0.319	0.101
M_4	0.605	0.580	0.405	0.139
M_3	0.615	0.617	0.454	0.234
M_5'	0.666	0.697	0.537	0.404
M_1	0.647	0.694	0.586	0.429
M_5	0.738	0.791	0.690	0.539
M_2	0.699	0.803	0.754	0.627
R_{15}	0.430	0.441	0.312	0.092
$R_{25'}$	0.434	0.466	0.369	0.275
$R_{12'}$	0.608	0.582	0.406	0.140
R_{12}	0.703	0.808	0.759	0.852
R_2'	—	—	0.943	0.665

similar to that of VMn and of TiFe, but the width of the low density region is wider at ScCo, because the difference in the potential of the atoms increases in ScCo. The additional information about the band structure would be obtained from Table I.

Next, let us talk about the nature of the wave functions. Since the potential is different in the two kinds of muffin-tin spheres, the states below the Fermi energy have a larger amplitude on the average at the cells of lower potential, and the states above the Fermi energy have a larger amplitude on the average at the cells of higher potential. As mentioned previously, the condition of charge neutrality is not conserved in these alloys and the lattice has some ionic character. In order to see the degree of the charge polarization, we show in Table II the

Fig. 8. $E(k)$ curves of ScCu.

s -, p - and d -components of the charge in each kind of the muffin-tin spheres and the total charge outside of the muffin-tin spheres. If the condition of charge neutrality were conserved, the nearly equal amount of s -, p -components is expected, and the difference in d -components is expected to be approximately 2, 4 and 6 at VMn, TiFe and ScCo, respectively. As seen from this table, however, the polarization of charge increases rapidly from VMn to ScCo. It is noticeable that the charge polarization comes mainly from the d -electrons.

(b) ScCu

The energy bands of ScCu along some high-symmetrical axes are shown in Fig. 8. The energy bands narrowly concentrated around the energy levels of 0.1 Ry are of copper-like, and the energy levels coming from Sc are situated at higher-energy region and they form much wider bands. The density-of-states in

Table II. The charge distribution of conduction electrons (including *d*-electrons) in four alloys VMn, TiFe, ScCo and ScCu. The notation r_i indicates the radius of the inscribed sphere, the notations *s*, *p* and *d* denote the respective component of the charge in the inscribed sphere, and finally the notation out denotes the amount of charge outside the inscribed spheres. They are normalized to be the total number of the conduction electrons. The charge polarization is defined as a half of the difference in the charge in two inscribed spheres, although the volumes of two inscribed spheres are not equal in the present case.

	r_i	<i>s</i>	<i>p</i>	<i>d</i>	out
VMn (V)	2.456	0.34	0.37	3.14	2.00
(Mn)	2.415	0.41	0.40	5.35	
TiFe (Ti)	2.475	0.32	0.34	2.10	1.90
(Fe)	2.395	0.43	0.41	6.50	
ScCo (Sc)	2.634	0.31	0.30	1.13	1.70
(Co)	2.513	0.50	0.39	7.67	
ScCu (Sc)	2.762	0.32	0.29	1.24	1.50
(Cu)	2.567	0.70	0.47	9.48	

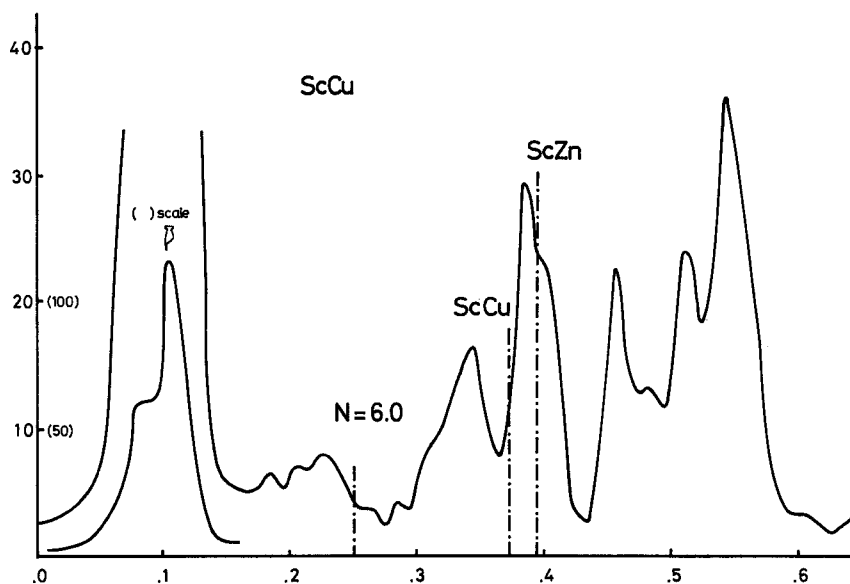


Fig. 9. Density-of-states of ScCu. The position of the Fermi energy is indicated by a vertical line named by ScCu. Under the rigid-band approximation the Fermi energy of ScZn is expected to be at the position indicated by a vertical line named by ScZn.

Fig. 9 shows more clearly the character of the energy bands of ScCu. It looks quite different from the density-of-states of VMn, TiFe and ScCo. The information about the charge distribution is given in Table II. The copper sphere is

now negatively charged by about 0.4 and the Sc sphere is positively charged by the same amount (see Table II). The charge polarization comes mainly from the s -, p -components, because the copper cell cannot be much negatively polarized by the d -electrons.

§ 4. Discussion

In transition metal alloys the crystal potential in a cell depends upon the constituent atom occupying the cell and sometimes it may happen that the potential is considerably different. Then the energy levels mainly belonging to the atom of the higher potential go up and are detached from the remaining levels. In the following we shall call the detached states "antibonding orbitals" and the remaining states "bonding orbitals". When the energy separation of these states is appreciable, the density-of-states coming from d -bands becomes quite small in the region between the bonding and antibonding levels, although the density-of-states of s - and p -bands is nearly constant in the wide energy range. As a result, there appears a deep valley in the total density-of-states. If the Fermi level lies in this low-density region, that is, either almost all bonding orbitals are occupied and antibonding orbitals are completely empty, or bonding orbitals are completely occupied and almost all antibonding orbitals are empty, then the ordered state seems to be quite favorable because of the gain in the band energy. The CsCl structure has the proper advantage of the energy separation mentioned before. This situation was already emphasized in the study of antiferromagnetism of Cr, and of ferromagnetism of FeCo. As seen from Figs. 4, 6 and 7, it is demonstrated here for VMn, TiFe and ScCo.

One must note that the separation of the two kinds of orbitals may happen both in ordered states and in disordered states. One expects that the separation is more complete in the ordered state than in the disordered state, because the effect of the potential difference is cooperative in the ordered state. Thus, it may be quite interesting to calculate the density-of-states of VMn and TiFe in the disordered state by the coherent potential approximation^{8),9)} and compare them with those of the ordered state already shown in Figs. 4 and 6. (Such calculation and comparison were made for Ni-Cu¹⁰⁾ and for Ni-Mn alloys.²⁾) The method of calculation by CPA is essentially the same as of Kirkpatrick et al. The density-of-states of the unperturbed state is determined from the HFS self-consistent-band calculation of bcc Mn with $\alpha=0.8$. The difference of the d -level between the two constituent atoms is given by the difference of the d -resonance levels of each atomic site in the HFS band calculation of ordered alloys mentioned previously. They are of 0.062 Ry for VMn and 0.158 Ry for TiFe. The density-of-states of the disordered alloy VMn is shown in Fig. 4 together with that of the ordered state. That of the disordered alloy TiFe is shown in Fig. 10. They are of d -states, because the present CPA calculation gives only the states of the

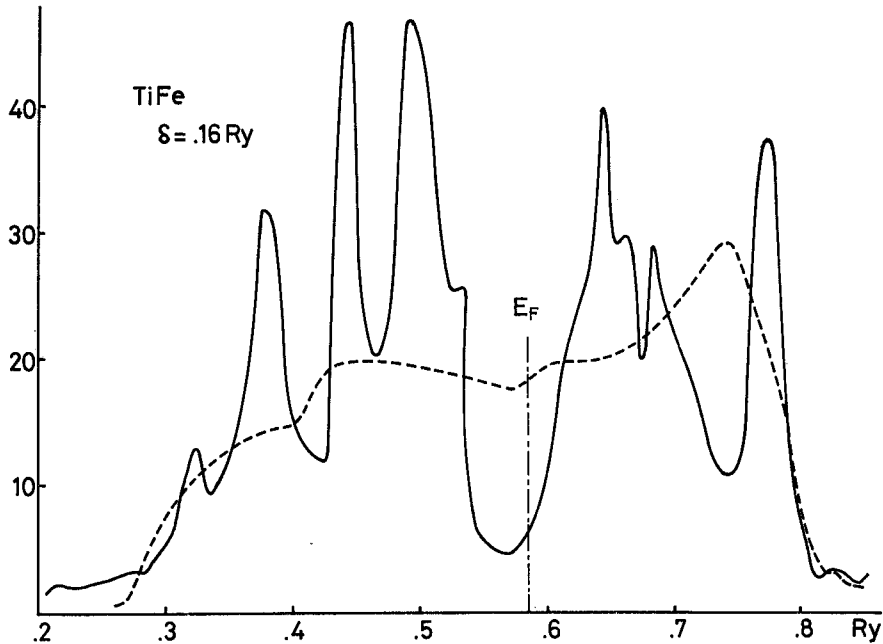


Fig. 10. Density-of-states of TiFe in the ordered state and that in the disordered state. The former is shown in a full curve and the latter is shown in a dotted curve.

d-character. As seen from figures the total width of the density-of-states in the disordered state is approximately equal to that in the ordered state. The results are quite interesting in that the density-of-states of VMn in the disordered state looks quite similar to that in the ordered state, but that of TiFe looks quite different from that of the ordered state. The reason may be the following. In VMn the potential difference of the both constituent atoms is so small that the density-of-states of the disordered alloy still keeps the character of the pure bcc transition metals even in the disordered state. Therefore, a deep valley in the middle region is of the character of the pure bcc lattice. One may say that the rigid band model is applicable to this case. In TiFe the potential difference becomes larger, so that the partial density-of-states of Ti shifts upwards relative to that of Fe to fill up the energy gap. (In the ordered state the symmetry of the CsCl-type lattice works to make a valley in the middle region, but it is not expected in the disordered lattice.) As seen from Fig. 1 the ordered state of TiFe is highly stable, but that of VMn is not. The difference seems to come from the character of the density-of-states of the two alloys in the disordered state.

The present argument has some similarity with the famous Hume-Rothery rule of the alloy, but there is some difference between them. As is well known, the Hume-Rothery rule argues that the Brillouin-zone structure of the alloy is

such a shape and size that it just touches a free-electron Fermi surface. Here the Brillouin zone is the most important factor, because the conduction electrons are seen from the free electron picture. In the transition metal alloys, however, the zone structure is not of the first importance, but the occupation number of the electrons in the separated bonding and antibonding orbitals is of primary importance.

Next, let us consider the ordered alloy VFe and TiCo, in which the number of conduction electrons is 13. In these cases the situation becomes complex, because there are two possibilities in the electronic configuration. The one is the paramagnetic configuration, in which about 0.5 electrons/pair and spin occupy the energy region above the minimum in the density-of-states in each spin state. The other is the ferromagnetic state, in which approximately one electron/pair and spin occupies the majority spin states above the minimum in the density-of-states, but there are no electrons above the energy gap in the minority spin bands. It is a rather difficult problem for the band theory to decide which state is realized in the specific substance. One may say, however, that the magnetic moment should be less than one μ_B . Further, if one may rely on an analogy with the cases of Cr and FeCo mentioned previously, one expects that the minority spin bands are filled up with 6.1 electrons/pair and the value of the magnetic moment is $0.8\mu_B$. This value seems to be close to the experimental value at VFe. According to experiment, TiCo is paramagnetic. One expects that the coefficient of the electronic specific heat of TiCo is much larger than that of TiFe, because the Fermi energy of TiCo is now in the hill of the density-of-states above the valley. This situation is qualitatively confirmed by experiment.

According to experiment the ordered alloys ScCu and ScZn are highly stable. As shown in Table II, the difference in the number of *s*-, *p*-electrons in the inscribed spheres is of 0.56, while the corresponding quantity is of 0.10, 0.18 and 0.27 in VMn, TiFe and ScCo, respectively. Thus, the Madelung energy seems to be especially important for cohesion of ScCu. One must note that the results mentioned above are derived from the muffin-tin approximation. The nonmuffin-tin approximation should be adopted in order to have an accurate quantitative result.

In the article of Nevitt³⁾ mentioned before there are many tables showing the alloy systems of various phases. The CsCl-type phase is the simplest one. Many of them have a rather complicated lattice structure, so that it is not easy to determine their band structure with sufficient accuracy. The case worked out in the present paper is a noticeable exception. Although it is too speculative to judge from the results of the CsCl-type structure, it seems to be probable that the band structure, or the density-of-states of the specific type phase, has some character to be effective to stabilize itself (that is, each phase has its own key word). In general, the idea of bonding and antibonding orbitals is a very useful conception to understand the stability of the alloy system. The charge polariza-

tion or the Madelung energy seems to be another important factor, but it is not very sensitive to the lattice symmetry. The separation of the bonding and antibonding orbitals, or the distribution of energy gap, may take place in some special ways in each phase. The effectiveness of the energy gap depends critically upon the number of conduction electrons.

Needless to say, it is a laborious task to calculate the band structure of some complex phases mentioned before with sufficient accuracy, but the computational difficulty will be surmounted by a progress in technic in future. One may argue that the cohesive energy must be evaluated in order to say a decisive word to alloy problems. It is true that that is a final goal, but it is a very difficult many-body problem. Rather, the key word must be discovered first, and it seems to be within the power of the band theory.

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