curve depends upon $d\Phi/dV$; in other words the (P,V) relation is a more sensitive test for correct potential shape. Thus, for copper also, the Rydberg potential more closely approximates the interatomic interaction.

Choice of Grüneisen's Constant

The value of the Grüneisen constant γ affects the (Φ,V) curves of Benedek quite strongly. In fact, the discrepancies between Benedek's results and the theoretical results could all be removed by judicious adjustment of γ by at most 20% from the values taken here. It is difficult to say what is the correct value for γ and our values, having been obtained by a different method, differ slightly from Benedek's. The replacement of our values for γ by those of Benedek would not, however, always improve the agreement.

Girifalco and Weizer have found $\gamma \approx 0$ for Mo, W, and

Cu, and a very small value for γ for Fe. The method by which γ is determined in this work gives a result which is rather sensitive to the thermal expansion of the lattice constant, $(a_{300}-a_0)$. The truncation error in the experimental data which they have used for a_0 and a_{300} is of the same order as $(a_{300}-a_0)$ for these metals,[25] so that the expansion property was "lost" and γ turned out to be nearly zero.

[25] We may here recall the approximate rule that the total relative thermal expansion from $0°K$ to the melting point of the metal, $\Delta l/l_0 \approx 0.027$. Mo, W, Cu, and Fe are all high-melting-point elements.

Electronic Structures of Manganese-Substituted Iron-Cobalt Alloys

C. W. Chen
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

The substitution of manganese in the body-centered cubic iron-cobalt alloys has been shown to either decrease or increase the mean saturation moment of the ternary alloys. On the basis of a modified band model, this varying effect of Mn may be ascribed to the occupancy of the localized d states of the Mn atoms. An increase in the moment is observed when Mn is added to alloys with the atom ratio of $Co:Fe \geqslant 1$ in which the localized d states are just half filled according to Hund's rule. At lower ratios, however, the localized d states become first more than half empty and eventually nonexistent. The rates at which the substitution of Mn decreases the mean moment of the latter alloys change accordingly. The proposed electronic structures are consistent with observations that the increase of residual resistivities of Fe-Co alloys caused by 1 at.% Mn also varies sensitively with the $Co:Fe$ ratio of the host alloy.

A RECENT study has shown that the substitution of manganese in the equiatomic iron-cobalt alloy leads to an increase of the mean saturation moment of the ternary alloy.[1] Furthermore, this effect was found to be unique to Mn because all other transition elements reduced the mean amount. A search to find similar behavior by substitution of such elements as Cr, which resembles Mn magnetically in the metallic state, and Rh, Ir, and Pt, which exhibit similar increasing effects on the saturation moment of Fe, has proved to be futile. To attain this unique effect, Mn must fulfill two conditions: Each Mn atom must "carry" a larger moment than the average moment of the parent Fe-Co alloy and its atomic spin must be aligned in a direction parallel to that of the Fe and Co atoms.

An interesting aspect of these findings is related to the fact that the binary alloy of Fe and Co containing 35 at.% Co has hitherto displayed the highest satura-

tion magnetization among all ferromagnetic materials at room temperature. Should the substitution of Mn in alloys close to this composition continue to increase the moment, a new maximum value of saturation magnetization would be reached. It has not been possible to make a trustworthy prediction, however, because of numerous conflicting factors. At first glance, such an effect seemed quite feasible since the magnetic properties of Mn-substituted FeCo alloys were found to be strikingly similar to those of the dilute Ni alloys, despite the difference in their crystal structures. Accordingly, Fe-Co alloys with an atom ratio of $Co:Fe > 35:65$, which lie on the right side of the peak of the familiar Pauling-Slater curves[2] might provide an electronic structure of the right type for an increase in the moment to occur when Mn is incorporated. On the other hand, a deduction of this sort could be invalidated

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[1] C. W. Chen, Phil. Mag. (to be published).

[2] R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1951), 1st ed., p. 441.
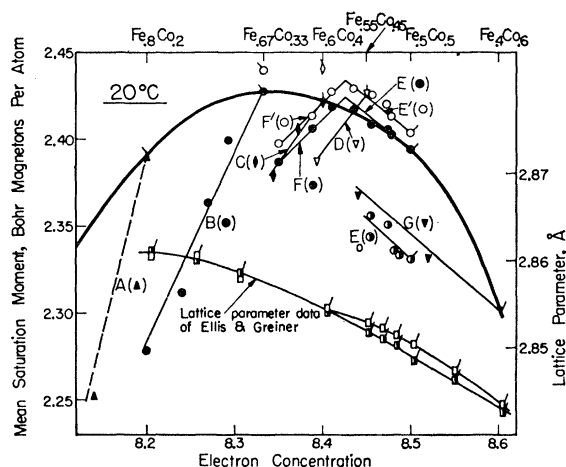
FIG. 1. Variation of the mean saturation moment of the Mn-substituted Fe-Co alloys with the average number of the outer electrons per atom. Data for the parent binary alloys are shown by symbols with short bars. Reproduced in the lower curves are the lattice parameter data for Fe-Co alloys reported by W. C. Ellis and E. S. Greiner [Trans. Am. Soc. Metals 29, 415 (1941)].

should the electronic structure of the Fe-Co alloys vary with the Co:Fe ratio in an unfavorable sense. Moreover, Mn has been shown to decrease the saturation moment of Fe at a rate corresponding to simple dilution.[3] Therefore, the magnetic effect of Mn is reversed somewhere between Fe and FeCo.

The present paper deals with an experimental investigation of the effect of Mn substitution on the saturation moments and residual resistivities of the body-centered cubic Fe-Co alloys. The results of the measurements of saturation magnetization have not only thrown light upon the various factors affecting the magnetic effect of Mn, but, coupled with residual resistivity data, have also disclosed valuable information concerning the electronic structures of the ternary alloys. However, for reasons to be cited later, no value for saturation magnetization higher than that of the 35 at.% Co binary alloy has been registered.

In the experiments, six sets of Fe-Co-Mn alloys were prepared from high-purity metals by levitation melting. The Co:Fe ratio had values ranging from 1:4 to 3:2 and each set had a fixed value. The Mn additions were limited to a few atomic percent owing to the low solid solubility. Details of chemical analyses, preliminary heat treatments, and the measurements of saturation magnetization and electrical resistance may be referred to in earlier papers.[1,4]

Prior to the saturation measurements, all samples were first furnace cooled from 800°C at a predetermined rate. This procedure permits the Fe and Co atoms to attain partial order (the degree of long-range order $S=0.6$ to 0.7 according to neutron diffraction data for

[3] E. C. Stoner, *Reports on Progress in Physics* (The Physical Society, London, 1946), Vol. 11, p. 48.
[4] C. W. Chen and G. W. Wiener, Suppl. J. Appl. Phys. 30, 199 (1959).

the binary alloy FeCo). The mean saturation moments per atom in this ordered state are shown in Fig. 1 by the solid symbols in the main curve for the binary alloys and along the branch lines for the ternary alloys. In this figure, the electron concentration $\bar{N}$ refers to the average sum of the $3d$ and $4s$ electrons per atom in the binary or ternary alloy. It is calculated from the formula $\bar{N}=7 \cdot c_{Mn}+8 \cdot c_{Fe}+9 \cdot c_{Co}$, where c_X denotes the atomic concentration of the constituent metal X and the coefficients 7, 8, and 9 represent the numbers of the outer electron per Mn, Fe, and Co atoms, respectively. In order to ascertain the role played by atomic order, samples of the FeCo alloys were reheated to 800°C, following which they were either cooled at a deliberately slow rate to insure pronounced order ($S\sim0.9$) or quenched so as to give complete disorder. Magnetic data for the ternary alloys of FeCo in the pronouncedly ordered and disordered states are shown by open symbols along lines D, E', and F' and by half-open circles along line E_0, respectively. Also shown by open symbols in Fig. 1 are the mean moments of two binary alloys, $Fe_{0.67}Co_{0.33}$ and $Fe_{0.6}Co_{0.4}$, and the $Fe_{0.55}Co_{0.45}$ alloys along line D in a pronouncedly ordered state.

It may be shown from the magnetic results summarized in Fig. 1 that the mean saturation moments $\bar{\sigma}$ of the ternary alloys in each set vary as a linear function of the atomic concentration c of Mn; that is, $\bar{\sigma}=\bar{\sigma}_0+(d\bar{\sigma}/dc)c$, where $\bar{\sigma}_0$ is the mean moment of the parent binary alloy; and that the concentration rate of change of the mean moment $d\bar{\sigma}/dc$ varies in different ways according to the Co:Fe ratio. For instance, a simple dilution effect seems to prevail in alloys with Co:Fe $=1:4$. Evidence for this is provided by the fact that the mean moment observed in the alloy $Mn_{0.05}Co_{0.19}Fe_{0.76}$ lies closely to the dashed line A depicting the simple-dilution equation $\bar{\sigma}=\bar{\sigma}_0(1-c)$. This observation is reasonable because the effect of simple dilution of Mn established in Fe is unlikely to be abruptly changed in Fe-Co alloys of relatively low Co concentrations. An equally simple situation exists in alloys with a Co:Fe ratio of 1:1 or 3:2. Here $\bar{\sigma}$ increases according to the equation

$$\bar{\sigma}=\bar{\sigma}_0(1-c)+Bc. \qquad (1)$$

Equation (1) is obtained by resolving $d\bar{\sigma}/dc$ into two components, $-\bar{\sigma}_0$, corresponding to a simple dilution effect, and B, to the effect of the exchange spin coupling between Mn and Fe or Co atoms. Lines E_0, E, E', and G originating at the observed values of $\bar{\sigma}_0$ of the respective binary alloys have been drawn to show the variation of $\bar{\sigma}$ calculated from Eq. (1) with B having a value of $+3$ μ_B per Mn atom. In most cases, the observed values of $\bar{\sigma}$ for alloys in these two sets follow the theoretical lines within experimental error. The subsequent drop of $\bar{\sigma}$ along lines F and F' is due to the precipitation of a second phase, which is also confirmed by metallographic examination. In the remaining three sets of alloys, the $d\bar{\sigma}/dc$ values are negative, signifying a

TABLE I. Distribution of the outer electrons of Mn envisaged from the magnetic results.

Alloy group	Atom ratio of Co to Fe	$d\bar{\sigma}/dc$, μ_B/at.% Mn	B, μ_B per Mn atom	Localized d states Spin up	Spin down	Contribution to the d band*
I	0:1	$-\sigma_{\rm Fe}$	0	0	0	<7
	1:4	$-\bar{\sigma}_0$	0	0	0	<7
II	1:2	-1.44	$<\bar{\sigma}_0$	$n_1\sim4$	0	$7-n_1$
	2:3	-1.0	$<\bar{\sigma}_0$	n_2	0	$7-n_2$
	9:11	-0.95	$<\bar{\sigma}_0$	n_3	0	$7-n_3$
				$(n_1<n_2<n_3<5)$		
III	1:1	$+(0.6\text{–}0.7)$	$+3$	5	0	2
	3:2	$+0.7$	$+3$	5	0	2

* Contributions to the d band in alloys of group I are uncertain because the donation to the conduction band has not been determined.

decreasing effect of Mn on $\bar{\sigma}$; but the rates diminish gradually as the Co concentration increases.

It may be concluded from the values of $d\bar{\sigma}/dc$ and, perhaps more explicitly, from the values of the constant B shown in Table I that the Fe-Co alloys containing Mn behave in three ways. When Co:Fe$\geqslant$1:1 (group III), the substitution of Mn is beneficial (in the sense that $\bar{\sigma}$ increases in accord with Eq. (1) with $B=+3$ μ_B per Mn atom, irrespective of the Co:Fe ratio and the degree of order. In another group (I), which consists of alloys having low Co contents, $B=0$ and thus Mn additions cause a decrease in $\bar{\sigma}$ by a simple dilution effect. Alloys in group II are of intermediate compositions; and since $B<\bar{\sigma}_0$, their mean moments are adversely affected by the substitution of Mn again, but at a lower rate.

It has long been recognized that several Group V compounds of Mn such as AsMn, SbMn, and BiMn are ferromagnetic with a moment of 3.4–3.5 μ_B per Mn atom.[5] This phenomenon has been attributed to an increase of the interatomic distance between Mn atoms from the standpoint of the criterion for ferromagnetism proposed by Slater.[6] Inasmuch as the lattice parameters of the bcc Fe-Co alloys decrease steadily with rising concentration of Co, as seen in the lower part of Fig. 1, it is unlikely that the magnetic effect of Mn is dependent on such a structural factor. Neither is the volume expansion recorded during ordering sufficiently large to have much influence. The insignificance of atomic order is also reflected in the rise of $\bar{\sigma}$ of the disordered Mn-FeCo alloys shown along line E_0 in Fig. 1.

In view of the variation of $d\bar{\sigma}/dc$ in various Fe-Co alloys, it may be concluded that the magnetic effect of Mn is essentially determined by the electronic structure of the host alloy. In order to explain the magnetic data, we shall first adopt a model of the electronic structure. It is assumed that, in addition to the conduction band containing the $4s$ electrons of all atom species, the $3d$ electrons of the Fe and Co atoms form a split band in the matrix, but the band structure is characterized by localized d states bound to the Mn atoms. Obviously,

this model is a compromise between a simple band model and a localized electron model. Its validity has been discussed by Friedel, Leman, and Olszewski[7] and demonstrated in several ternary systems of FeCo in the previous work.[1] On the basis of this model, the magnetic effect of Mn depends mainly upon the occupancy of the localized d states, which, in turn, is determined by the energy distribution of the localized states with respect to the Fermi level of the band structure.

For example, alloys in group I contain relatively low concentrations of Co and may be considered to behave like Fe. The d band is, therefore, characterized by the coexistence of vacant states with opposite spins.[3] Also, it will become evident in the subsequent discussion that the two bound d levels of the Mn atoms, each with room for five electrons, have probably moved above the Fermi level to higher energies. Hence, Mn atoms are unable to hold any electrons in the d shell. A simple dilution effect arises under these circumstances because, after a small donation to the conduction band, the outer electrons of Mn are accommodated in the paired vacant states of the d band. Reduction of the mean moment other than by a simple dilution effect is prohibited so long as the paired vacant d states are still available.

The electronic structure of the Mn-FeCo alloys in group III has been previously envisaged as follows: one half of the bound d states with spin down is above the Fermi level whereas the other half with spin up lies just below.[1] Consequently, each Mn atom can retain 5 electrons in the d shell with spin up; the remaining 2 electrons are contributed to the d band, which now has vacant states with spin down only. Since Mn exerts a similar magnetic effect on the Mn-Fe$_2$Co$_3$ alloys, the electronic structure should retain these features.

Comparison of the electronic structures of groups I and III suggests that Hund's rule is not fulfilled in alloys of group II. This means that when the Co:Fe ratio falls short of unity, the lower bound d level starts to ascend across the Fermi surface, thereby keeping less than 5 electrons. As the Co:Fe ratio continues to decrease, the number of the localized d electrons will

[5] W. Hume-Rothery and B. R. Coles, Advances in Physics, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 236.
[6] J. C. Slater, Phys. Rev. 36, 62 (1930).

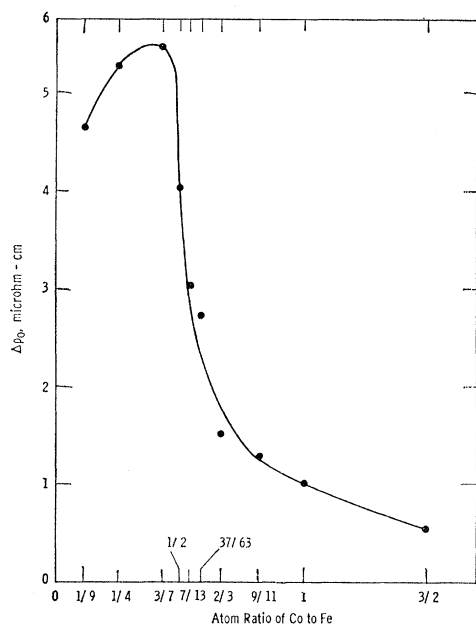[7] J. Friedel, G. Leman, and S. Olszewski, Suppl. J. Appl. Phys. 32, 325 (1961).

FIG. 2. The increase of residual resistivity of Fe-Co alloys caused by 1 at.% Mn, showing the sensitive dependence upon the atom ratio of Co to Fe.

depart still further from 5. It is shown in Table I that $n_1 < n_2 < n_3 < 5$ electrons for the three sets of alloys in group II. If Mn again makes no contribution to the s band as in the alloys of group III and n_1 is assigned with 4 electrons, Eq. (1) gives $d\bar{\sigma}/dc = -1.43\,\mu_B$ per at.% Mn, which is very close to the observed rate. Conversely, we may calculate n from the observed values of $d\bar{\sigma}/dc$, from which $n_2 = 4.21$ and $n_3 = 4.24$ electrons. Nonintegral numbers are acceptable for n in the present model as Friedel[8] has pointed out. Anderson[9] has currently arrived at a similar conclusion in a quantum theory of the localized magnetic states in nonmagnetic matrices. It is worth mentioning that, in contrast to this, a localized electron model usually requires an integral number of d electrons in association with individual atoms. Since the saturation moments observed in pure Fe, Co, and Ni are nonintegral numbers, such a requirement cannot be easily justified without invoking certain *ad hoc* assumptions.[10]

The foregoing discussion has thus given consistent explanations of the mean saturation moments of a rather complex alloy system. A real test of the proposed electronic structures, however, is provided by the in-

crease of residual resistivities of the ternary alloys. It is recalled in this connection that the increase of residual resistivity, $\Delta\rho_0$, per at.% of solute in the ternary alloys of FeCo suddenly dips to a minimum at Mn from a peak value at Cr. This abrupt drop in $\Delta\rho_0$ has been considered as an indication that while the localized d states are completely empty at the Cr atoms, half of the localized states are filled and situated just below the Fermi level at the Mn atoms. When the lower bound d level is crossing the Fermi surface, as has been proposed for alloys in group II, the density of d states should increase at the Fermi level. Consequently, $\Delta\rho_0$ is expected to rise in accordance with the band theory of electrical resistance of transition metals treated by Mott.[11] If the relative positions of the lower bound d level of the Mn atoms suggested for the various alloys in group II are correct, not only should $\Delta\rho_0$ caused by substitution of 1 at.% Mn show an increase with decreasing Co:Fe ratio, but such a $\Delta\rho_0$ curve should reach a peak at a composition corresponding to the demarcation line between groups I and II.

For an experimental verification, the resistivity measured at 4.2°K is taken to represent the residual resistivity.[1] The increase of ρ_0 due to 1 at.% Mn is plotted against the Co:Fe ratio in Fig. 2. The $\Delta\rho_0$ curve indeed exhibits a steep rise starting in the vicinity of Co:Fe=9:11 and reaching a peak at Co:Fe=3:7, the latter ratio falling between groups I and II. The resistivity results thus provide excellent support for the proposed electronic structures.

In conclusion, it may be stated that the electronic structures of the Mn-substituted Fe-Co alloys may be described conveniently in terms of a band model characterized by the existence of localized d states at the Mn atoms. The occupancy of the localized states depends largely upon the Co:Fe ratio of the host alloy. Information furnished by measurements of saturation magnetization and residual resistivity has led to consistent descriptions of the localized states in various bcc Fe-Co alloys. The maximum value of the mean saturation moment observed in $Mn_{0.06}Fe_{0.47}Co_{0.47}$ alloys is still somewhat lower than the maximum value for the binary Fe-Co alloys (2.43 vs 2.44 μ_B at 20°C), partly because the increasing effect of Mn terminates before reaching the peak of the Pauling-Slater curves and partly because the solid solubility of Mn in FeCo is low.

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