

Finally, we should like to point out the versatility of the scheme suggested in Sec. IIIA for making measurements of ultrasonic attenuation. This method, which utilizes a commercial sampling oscilloscope together with an X-Y recorder, enables one to record the data directly onto a sheet of graph paper. As Fig. 3 illustrates, one can record the pulse echo train directly by using the internal sweep of the oscilloscope. To measure the variation of attenuation coefficient with some independent variable, one may select any echo in the echo train and measure its change in amplitude as the independent variable is changed in magnitude. This

technique is illustrated in Figs. 5-10 and 13, in which the variation of pulse amplitude with applied magnetic field under various circumstances has been recorded.

ACKNOWLEDGMENTS

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Electronic Specific Heat and Saturation Magnetization of Cr-Fe and Fe-Co Alloys*

L. BERGER

Carnegie Institute of Technology, Pittsburgh, Pennsylvania

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The collective model of ferromagnetism is applied to various models for the upper third of the $3d$ band profile of bcc alloys of transition metals. In the first band profile, we consider a rectangular sub-band with rounded lower and upper edges, assuming an intra-atomic exchange integral just large enough to produce ferromagnetism. The low-temperature specific-heat coefficient γ is found to have a sharp peak at the electron concentration where ferromagnetism starts (almost empty sub-band) and a deep minimum at the concentration with largest saturation magnetization (half-filled sub-band). This agrees qualitatively with the measurements by Cheng, Wei, and Beck in Cr-Fe and Fe-Co alloys. The agreement becomes quantitative if a second similar model of the band profile is used where the density of states inside the sub-band is not constant, but drops linearly with increasing energy. The calculated zero-temperature saturation magnetizations agree well with the Slater-Pauling curve for these alloys. In a third model, the sharp peak of γ is not a simple consequence of the action of the collective model, but reflects the existence of a real peak in the assumed band profile. Then this peak of γ is predicted to happen at an electron concentration slightly larger than the one at which ferromagnetism starts; this seems to be found experimentally in the Cr-Fe series. The calculated saturation magnetizations again agree with the Slater-Pauling curve.

INTRODUCTION

A GREAT wealth of experimental data on the electronic specific heat of body-centered cubic alloys of the first transition series is now available, due to the work of Cheng, Wei, and Beck¹ and of other authors.²⁻⁶ This gives direct information about the profile of the $3d$ band, at least in the case of alloys where no ferromagnetic spin polarization is present.

The purpose of the present work is to investigate theoretically the effect of a ferromagnetic spin polarization on the low-temperature electronic specific heat of

bcc alloys in the framework of the collective approach to ferromagnetism, assuming various models of the band profile. Using the same models, the zero-temperature saturation magnetizations for these series of alloys have also been computed, to be compared with the well-known experimental Slater-Pauling curve.⁷⁻¹³ The present work should also provide a general picture of the electronic structure of the ferromagnetic bcc iron alloys.

It is by comparing the predictions of the collective model with the magnetization data that Slater⁷ and Pauling⁸ were able to conclude that a region of low density of states should exist in the profile near the Fermi level of chromium. Unfortunately, the value of the magnetization is rather insensitive to the details of

* Work supported in part by the U. S. Office of Naval Research and the National Science Foundation.

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³ E. A. Starke, C. H. Cheng, and P. A. Beck, *Phys. Rev.* **126**, 1746 (1962).

⁴ K. Schröder, *Phys. Rev.* **117**, 1500 (1960).

⁵ K. Schröder and C. H. Cheng, *J. Appl. Phys.* **31**, 2154 (1960).

⁶ K. Schröder, *J. Appl. Phys.* **32**, 880 (1961).

⁷ J. C. Slater, *Phys. Rev.* **49**, 537, 931 (1936).

⁸ L. Pauling, *Phys. Rev.* **54**, 899 (1938).

⁹ W. Shockley, *Bell System Tech. J.* **18**, 645 (1939).

¹⁰ P. Weiss and R. Forrer, *Ann. Phys.* **12**, 279 (1929).

¹¹ M. Fallot, *Ann. Phys.* **6**, 305 (1936).

¹² A. Arrott and H. Sato, *Bull. Am. Phys. Soc.* **3**, 42 (1958).

¹³ M. V. Nevitt and A. T. Aldred, *J. Appl. Phys.* **34**, 463 (1963).

the band profile. By combining the specific-heat information and the magnetization information, we will see that a more detailed picture of the profile may be obtained.

As the collective model of ferromagnetism, in its original form, is not adequate at finite temperatures, the calculations are done only in the limit of vanishing temperature.

THE COLLECTIVE MODEL OF FERROMAGNETISM

The collective model of ferromagnetism has been discussed by Stoner and by Wohlfarth.¹⁴ A notation similar to that of Wohlfarth¹⁴ will be used here. Electrons of a given spin orientation have a density of states $\nu(\epsilon)$, where ϵ is the one-electron energy. The function $\nu(\epsilon)$ is the same for both spin orientations, and is independent of band filling (rigid band approximation). The Fermi level for electrons of spin down is called ϵ_{01} , and that for electrons of spin up is ϵ_{02} . An exchange energy $-J$ is assumed between any two electrons of the same spin orientation; instead of J used by Lidiard,¹⁵ Wohlfarth¹⁴ introduces the parameter θ' defined by $\theta' = NJ/2k$, where k is the Boltzmann constant and N the number of electrons per atom in the band. The energy of the electron system at zero temperature is

$$\begin{aligned} E &= \int_0^{\epsilon_{01}} \epsilon \nu(\epsilon) d\epsilon + \int_0^{\epsilon_{02}} \epsilon \nu(\epsilon) d\epsilon - \frac{J}{2} N_1^2 - \frac{J}{2} N_2^2 \\ &= \int_0^{\epsilon_{01}} \epsilon \nu(\epsilon) d\epsilon + \int_0^{\epsilon_{02}} \epsilon \nu(\epsilon) d\epsilon - \frac{J}{2} N^2 + J N_1 N_2, \end{aligned} \quad (1)$$

where N_1 and N_2 are respectively the number of electrons with spin down, and with spin up

$$N_1 = \int_0^{\epsilon_{01}} \nu(\epsilon) d\epsilon + 2.65; \quad N_2 = \int_0^{\epsilon_{02}} \nu(\epsilon) d\epsilon + 2.65; \quad (2)$$

$$N = N_1 + N_2.$$

In Eq. (2), the origin of the energy scale has been chosen in such a way as to correspond to the Fermi level of a nonferromagnetic alloy having $N = 5.3$ electrons per atom.

The condition for an extremal value of the total energy E under the constraint of constant number of electrons N may be written

$$\epsilon_{02} - \epsilon_{01} = J \int_{\epsilon_{01}}^{\epsilon_{02}} \nu(\epsilon) d\epsilon. \quad (3)$$

Equation (3) is the basic equation of the collective model of ferromagnetism in the case of zero tempera-

ture. For a given value of N , it always has the paramagnetic solution $\epsilon_{01} = \epsilon_{02}$. If $\nu(\epsilon)$ exceeds the value $\nu_c = 1/J$ at the paramagnetic Fermi level, the paramagnetic solution is unstable, and some ferromagnetic solution will set in, with $\epsilon_{01} < \epsilon_{02}$. This ν_c will be called the "critical" density of states. If $\nu(\epsilon) < \nu_c$, the paramagnetic solution is stable; however, a ferromagnetic solution may sometimes still exist even under these conditions, as will be mentioned in a later section.

When ϵ_{01} and ϵ_{02} have been found for a given value of N , by solving Eq. (3), the values of N_1 and N_2 may be calculated by Eq. (2).

The coefficient γ of the low-temperature electronic molar specific heat may be calculated too^{16,14}

$$\gamma = \frac{1}{3} \pi^2 k^2 N_0 (\nu(\epsilon_{01}) + \nu(\epsilon_{02})), \quad (4)$$

where N_0 is Avogadro's number. This equation is valid only when T is much smaller than the Curie temperature.

The zero-temperature saturation magnetization μ , expressed in Bohr magnetons per atom, is given by

$$\mu = \frac{1}{2} g (N_2(\epsilon_{02}) - N_1(\epsilon_{01})), \quad (5)$$

where N_1 and N_2 have been defined by Eq. (2), and where g is the g factor as measured by ferromagnetic resonance.¹⁷

The existence¹⁸ of spin waves in ferromagnetic materials and the persistence¹⁹ of permanent magnetic moments above the Curie point of iron and nickel imply that the collective model of ferromagnetism in its original form¹⁴ does not completely describe the thermal excitations of a ferromagnet. Therefore, the present paper will be limited to the case of vanishing temperature. However, this does not imply that *all* results of the theory become wrong at finite temperature. In fact, we will see later that the zero-temperature theory does not really require spin alignment in order to apply, but only a spontaneous spin polarization. Some of its results for γ might be valid even above the Curie point of a ferromagnet, provided disordered moments are still present.

It is also known that the collective model and the rigid band approximation are concerned only with the electron distribution on the energy scale. They say nothing about the charge density or spin density in space. Therefore, only certain properties can be predicted, like the specific heat or the bulk magnetization.

Provided these natural limitations of the collective picture are taken into account, it should apply as well to iron alloys as to nickel alloys, at vanishing temperature. More sophisticated many-body methods²⁰ are necessary at finite temperature.

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¹⁷ A. J. P. Meyer and G. Asch, J. Appl. Phys. **32**, 330S (1961).

¹⁸ P. E. Tannenwald and R. Weber, Phys. Rev. **121**, 715 (1961).

¹⁹ J. A. Hofmann, A. Paskin, K. J. Tauer, and R. J. Weiss, Phys. Chem. Solids **1**, 45 (1956).

²⁰ D. C. Mattis, Phys. Rev. **132**, 2521 (1963).

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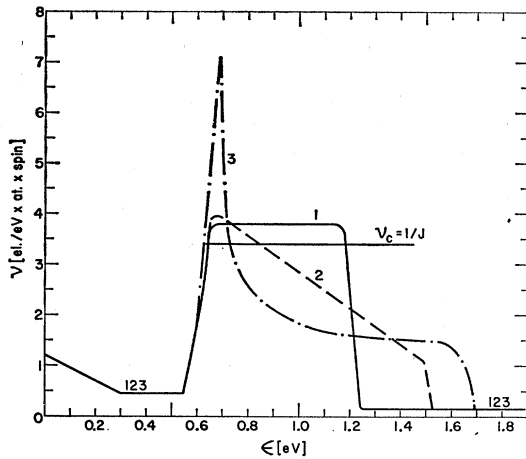


FIG. 1. The three band profiles for the upper third of the $3d$ band of bcc alloys of the first transition series. The curves are numbered according to the band profile they describe. The horizontal straight line indicates the value of the "critical" density of states ν_c above which ferromagnetism sets in, assuming $J=0.294$ eV \times atoms per electron in the case of the first band profile.

THREE BAND MODELS AND CALCULATION DETAILS

A rectangular sub-band with rounded edges is considered first (solid curve of Fig. 1). This very simple model will be called the first band profile. The sub-band is assumed to describe roughly the upper third of the $3d$ band of bcc alloys, above a region of low density of states located around the Fermi level of chromium. The origin of the energy scale corresponds to the Fermi level of an alloy having $N=5.3$ electrons per atom.

In the region below the lower edge of the rectangular sub-band where ferromagnetism is absent, measurements of electronic specific heat¹ (on V-Cr alloys and dilute alloys of iron in chromium) give directly the values of $\nu(\epsilon)$. This experimental information has been used to draw the solid curve of Fig. 1 for $\epsilon < 0.6$ eV. Similarly, the constant value of $\nu(\epsilon)$ drawn above the top of the $3d$ band ($\epsilon > 1.25$ eV) has been chosen in such a way as to reproduce correctly the measured electronic specific heat of (fcc) copper.²¹

Chromium and its dilute alloys with iron are known to have some kind of an antiferromagnetic spin polarization below room temperature.²² Because of this complication, one might think that the specific-heat measurements do not give directly the band profile in these alloys. However, measurements of specific heat in bcc alloys of the second or the third transition series,²³ which are not antiferromagnetic, give a very similar band profile in this range; in particular, there is a low density of states at the Fermi level when $N=6$ electrons

per atom. The presence of antiferromagnetism in alloys will be completely ignored in the present work.

The shape of the rectangular sub-band itself (Fig. 1) has been chosen arbitrarily. However, it will be shown to lead, when combined with Eq. (3) of the collective model, to a correct prediction of the main features of the electronic specific heat results as measured¹ in series of ferromagnetic Cr-Fe and Fe-Co alloys, and to give values of the saturation magnetization in agreement with the measured Slater-Pauling curve for these alloys. A constant value $J=0.294$ eV \times atoms per electron is assumed for the exchange constant. This value is such that the critical density of states, indicated by a horizontal straight line in Fig. 1, will be slightly smaller than the maximum value of ν reached in the sub-band.

A different band model has also been used (see the dashed curve in Fig. 1), in order to improve the agreement with experimental γ data. As before, the edges of the sub-band are slightly rounded. However, the density of states, instead of remaining constant inside the sub-band, now decreases linearly with increasing energy. This will be called the second band profile.

It becomes then necessary to assume that the exchange constant J increases gradually with electron concentration. The following relation is assumed:

$$J(N) = \frac{1}{2.35 - 0.77(N-8)}. \quad (6)$$

This specific expression is such that the density of states (of one spin direction) $\nu(\epsilon)$ at the Fermi level remains always slightly larger than the critical value $\nu_c = 1/J(N)$ while the sub-band is being filled. Otherwise, ferromagnetism would soon stop.

A third model, which exhibits a sharp peak of the density of states, is defined by the curve having both dashes and dots in Fig. 1. The exchange constant is assumed to be given here by

$$J(N) = \frac{1}{2.2 - 0.5(N-8)}. \quad (7)$$

In the case of each of the three band profiles, Eq. (3) has been solved for a few hundreds of values of the electron concentrations N , using the electronic computer, Bendix G-20, at the Carnegie Institute of Technology. The method is the following.

Information about the band profile is fed into the computer under the form of a table of values of $\nu(\epsilon)$, where ϵ varies from 0.00 to 2.00 eV by increments of 0.01 eV. Corresponding tables of $N_1(\epsilon_{01})$ and $N_2(\epsilon_{02})$ are computed, using Eq. (2) and integrating by the method of trapezoids. All possible pairs $(\epsilon_{01}, \epsilon_{02})$ with $0 \leq \epsilon_{01} \leq \epsilon_{02} \leq 2.00$ eV are then generated one after the other, by increments of 0.01 eV. Every time the left side $\epsilon_{02} - \epsilon_{01}$ and the right side $J(N_2(\epsilon_{02}) - N_1(\epsilon_{01}))$ of Eq. (3) are computed and compared; if they are found

²¹ J. G. Daunt, see: C. J. Gorter, *Progress in Low Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1957), Vol. 1, p. 202.

²² N. S. Rajan, R. M. Waterstrat, and P. A. Beck, *J. Appl. Phys.* **31**, 731 (1960).

²³ F. J. Morin and J. P. Maita, *Phys. Rev.* **129**, 1115 (1963).

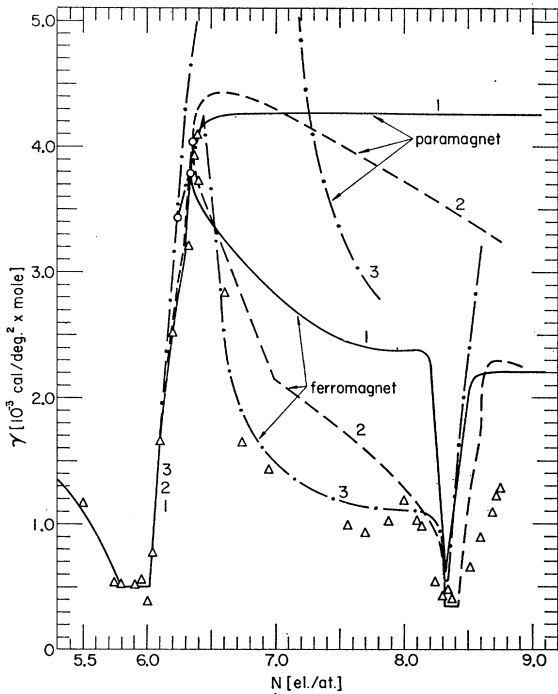


FIG. 2. Electronic specific heat coefficient γ versus electron concentration N , for each of the three band profiles. The triangles represent the corresponding experimental data for V-Cr, Cr-Fe, and Fe-Co alloys. The circles indicate where ferromagnetism is predicted to start for each of the band profiles.

to be approximately equal, the values of ϵ_{01} , ϵ_{02} , $N_1(\epsilon_{01})$, $N_2(\epsilon_{02})$ are printed. The corresponding values of N , of γ , and of μ are calculated, using Eqs. (2), (4), and (5), and also printed. We assume $g = 2.094$, which is the experimental value for pure iron.¹⁷

PREDICTION OF γ AND μ AND COMPARISON WITH EXPERIMENT

The γ results, as calculated with the collective model of ferromagnetism in the case of each of the three band profiles, are shown in Fig. 2 as a function of the electron concentration N . The point where ferromagnetism is predicted to start is indicated by a circle. The curves marked "paramagnet" refer to the case $J = 0$, where the alloy would always remain a Pauli paramagnet.

The most striking feature of the γ curves for a ferromagnet, obtained with the first and with the second band profiles, is the presence of a sharp peak at the exact electron concentration at which ferromagnetism starts. It is easy to understand the physical reason for the existence of this peak. When the $3d$ band starts being filled, the alloy is a Pauli paramagnet at first. The two Fermi levels are identical and contribute equal amounts to the density of states. According to Eq. (4), the curve for γ will be simply an image of the band profile, and will rise rapidly when the rectangular sub-band starts filling up at $N = 6.2$ electrons per atom corresponding to the left

side of the peak. However, as soon as the critical density of states necessary for ferromagnetism is reached, the Fermi level ϵ_{01} of the spin down electrons moves rapidly back below the lower edge of the sub-band, thereby reducing drastically its contribution to the density of states of the ferromagnet. The value of γ drops therefore rapidly to a fraction of its maximum value, according to Eq. (4), and this corresponds to the right side of the peak. The calculated location of the Fermi levels has been plotted as a function of N in Fig. 3, for each of the three band profiles.

By many calculations performed with different values of J , it has been found that the γ peak is especially prominent if $\nu_c = 1/J$ is only slightly smaller than the maximum density of states reached in the sub-band. Secondly, the peak is sharp only if the lower edge of the sub-band is not too rounded and if the slope at the edge is large enough. However, if the edge is rounded only very little, and if the slope at the edge is too high, the peak may be so sharp and so narrow as to escape detection. It vanishes completely in the case of an exactly rectangular band. This can be understood easily: In order for the peak to exist, there must be at least a small interval of ϵ , located at the edge of a sub-band, where ν is rising rapidly but has not yet reached the critical value.

A similar peak of γ is predicted at an electron concentration corresponding to almost complete filling of the sub-band and to the end of the ferromagnetic range. It plays however no role in practice, as no bcc alloy exists in the first transition series with $N > 8.8$ electrons per atom.

To sum up what has been said above, the sharp peak of γ predicted at $N = 6.4$ electrons per atom by the first or the second band model is of an electronic nature, but gives only a very distorted image of the true band pro-

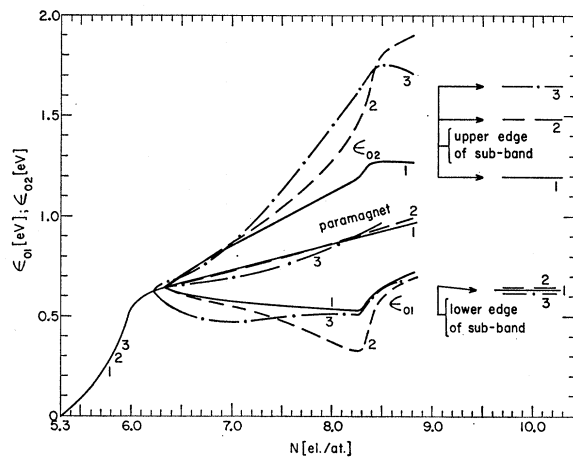


FIG. 3. Fermi level ϵ_{01} of spin-down electrons, and Fermi level ϵ_{02} of spin-up electrons, for each of the three band profiles. The Fermi level $\epsilon_{01} = \epsilon_{02}$ of a Pauli paramagnet is also represented. The location of the sub-band edges is indicated by horizontal lines on the energy scale.

file in these alloys. The profile has no sharp singularities. The existence of the γ peak is rather a consequence of the onset of ferromagnetic spin polarization in a sub-band with somewhat rounded edges. This peak would be much less prominent, or even completely absent, in bands of other shapes.

In the case of the third band profile, a γ peak is also obtained. However, it is located at a value of N slightly higher than the one at which ferromagnetism starts (see Fig. 2). Moreover, it is merely a consequence of the existence of a singularity of the band profile itself.

Another feature of the theoretical curves of Fig. 2 for a ferromagnet is a minimum for $N=8.3$ electrons per atom. The physical reason for this minimum is the following: At this electron concentration, the Fermi level ϵ_{01} is below the lower edge of the sub-band, while the Fermi level ϵ_{02} is above the upper edge (Fig. 3). Therefore, the contributions of both Fermi levels to the density of states are very small. This applies to all three band profiles.

The low-temperature electronic specific heat of bcc V-Cr, Cr-Fe, and Fe-Co alloys has been measured by Cheng, Wei, and Beck.¹ The experimental values of γ are shown as triangles on Fig. 2. A sharp peak is present in the experimental γ curve at $N=6.4$. This value is close to that at which ferromagnetism starts. Schroder^{2,4} has measured the specific heat of some Cr-Fe alloys at elevated temperatures (up to 620°K) in order to investigate further the nature of this peak. It seems probable that the peak is really electronic in nature, and is not due to the magnetic anomaly of the specific heat occurring in the neighborhood of the Curie point of a ferromagnet. The Curie point, though falling very rapidly, is in fact still around 50°–80°K in this range,¹³ that is, much higher than the temperature at which the low-temperature measurements have been made. As the curves of C_V/T versus T^2 are reasonably linear at low temperature, it does not seem that superparamagnetic clusters^{5,6} should play a major role in the peak either.

As can be seen in Fig. 2, some degree of agreement has been reached between the experimental results for γ and the predictions of the collective picture as applied to our models of the band. The agreement may be said to be quantitative in the case of the second or third band profile.

The interpretation of the specific-heat data derived from the first or the second band profile is totally different from that suggested by Cheng, Wei, and Beck¹ themselves, who assume that the data give a direct idea of the true $3d$ band profile; similarly, Goodenough²⁴ interprets the peak of γ as representing the true band profile for electrons of e_g symmetry type.

The theoretical results for the saturation magnetization μ will be discussed now (see Fig. 4). The curves are made up of two parts. In the first part, μ increases by approximately one Bohr magneton for every electron

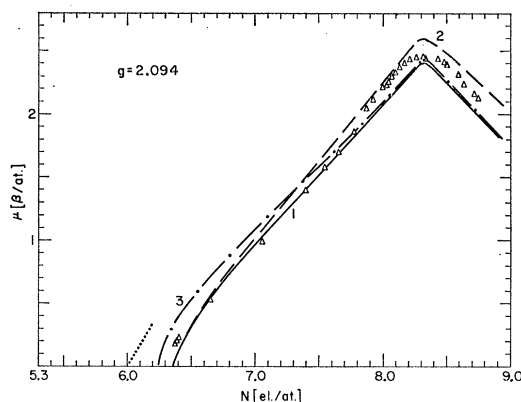


FIG. 4. Zero-temperature saturation magnetization μ versus electron concentration N for each of the three band profiles. The triangles represent the corresponding experimental data for Cr-Fe and Fe-Co alloys. The dotted line represents the saturation magnetization of localized states split off the lower edge of the sub-band, as deduced from susceptibility measurements on paramagnetic Cr-Fe alloys.

added to the alloy. The physical reason is that the Fermi level ϵ_{01} of spin-down electrons remains stationary below the lower edge of the sub-band, while ϵ_{02} rises through the sub-band (Fig. 3). In the second part of the curve, corresponding to a more than half-filled sub-band, μ decreases approximately by one Bohr magneton for every electron added to the alloy. Here ϵ_{02} remains stationary above the upper edge, while ϵ_{01} rises through the sub-band. The two linear parts of the curve are connected by a rounded region. One notices also, at the left end of the μ curve, a rounded part starting with a vertical (or almost vertical) tangent.

The low-temperature saturation magnetization of bcc Cr-Fe alloys has been measured by Fallot,¹¹ and by Nevitt and Aldred.¹³ That of bcc Fe-Co alloys has been measured by Weiss and Forrer.¹⁰ These data, converted to Bohr magnetons per atom, are plotted as triangles in Fig. 4. They constitute a part of the so-called Slater-Pauling curve.⁷⁻⁹ We see again rather good agreement between theory and experiment. There is little difference here between the results from the various band profiles.

The calculated numbers N_1 and N_2 of electrons of each spin are plotted in Fig. 5 as a function of N .

CHOICE BETWEEN THE VARIOUS BAND PROFILES

Of the three band profiles which have been investigated, the first one does not deserve more attention as it is only in qualitative agreement with the experimental data. The results obtained with the second and with the third band profile will now be discussed in more detail, in an effort to decide which one of these two is to be preferred.

According to the present calculations, the Fermi level of spin-down electrons in iron ($N=8$) is located below the lower edge of the rectangular sub-band. As a result, the density of states at the Fermi level

²⁴ J. B. Goodenough, Phys. Rev. **120**, 67 (1960).

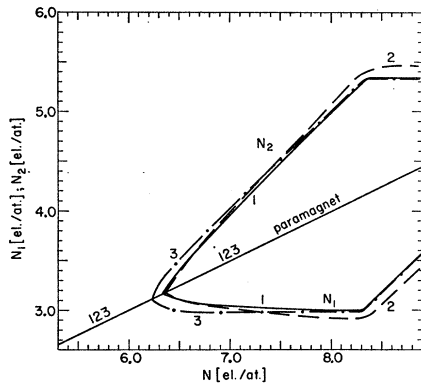


FIG. 5. Number N_1 of spin-down electrons, and number N_2 of spin-up electrons, for each of the three band profiles. The number $N_1 = N_2$ for a Pauli paramagnet is also represented.

is contributed mostly by spin-up electrons, in qualitative agreement with contact potential measurements by Walmsley.²⁵ The second band profile gives $p=0.60$, and the third one $p=0.53$, where $p=\nu(\epsilon_{02})-\nu(\epsilon_{01})/\nu(\epsilon_{02})+\nu(\epsilon_{01})$. Walmsley²⁵ finds experimentally $p=1$, so that the agreement is not quantitative. This may come from the fact that the present theory does not differentiate between the Fermi levels of $3d$ and $4s$ electrons.

The band profiles may be compared with the electronic specific-heat data²³ for bcc alloys of the second or third transition series, which are not ferromagnets but rather Pauli paramagnets. These data should give a direct idea of the correct band profile. No sharp peak is present at $N=6.4$ in Mo-Re and Mo-Tc alloys. Instead, there is a rounded lower edge very similar to the one assumed for our second band profile (Fig. 1). Similarly, measurements of the superconducting transition temperature in these alloys should give some idea of the band profile. There is, again, only a rounded edge and a flat maximum, but no sharp peak, in bcc Mo-Re and W-Re alloys²⁶ at $N=6.4$. The same flat maximum has been found²⁷ in Cr-Re alloys. In all of these alloy series, the bcc range extends only up to approximately $N=6.5$, so that most of the sub-band remains out of sight.

Wood²⁸ has recently done an augmented-plane-wave (APW) band calculation for bcc paramagnetic iron. The Wood profile has been calculated in more detail through an analytical interpolation procedure by Cornwell and Wohlfarth²⁹; it has some similarities with the present band profiles, in particular, the existence of a region of low density of states near the Fermi level of chromium, but there are also large differences. For example, the width of the part of the $3d$ band located

above the Fermi level of chromium is at least 2 eV in the case of the Wood profile, and only 1 eV for our second or third profile. Wood's maximum density of states is correspondingly smaller than the present ones, so much that it cannot account for the γ values observed in Cr-Fe alloys. Moreover, the lower edge of Wood's sub-band exhibits a more complicated structure than the experimental γ data seem to indicate.

Cheng, Wei, and Beck¹ have given a model of the band profile derived from their own specific-heat measurements in V-Cr, Cr-Fe, and Fe-Co alloys. It is very similar to the third band profile. However, as their analysis of the data does not take explicitly into account the exchange splittings and their variation with band filling, the minimum of γ present for $N=8.3$ appears in their model to be caused by a corresponding minimum of $\nu(\epsilon)$, while it is, in the present models, a direct consequence of ferromagnetism.

As was said before, a sharp γ peak has been observed^{2,4} even above the Curie points of Cr-Fe alloys. This seems at first to exclude the second band profile as a possible one, since with this profile the γ peak would be due to the existence of ferromagnetism. However, a little reflection shows that a spontaneous spin polarization is required to produce the peak, but not necessarily a spin alignment. Permanent magnetic moments exist¹⁹ in iron above the Curie point, but are disordered. This situation can be described by band theory, as Herring and Kittel^{30,31} have shown, if a direction of quantization of the spin is chosen which is different in each lattice cell, and which is parallel to the local direction of the atomic magnetic moment (direction of the intra-atomic exchange field). The wave function of a "spin-up" Bloch wave is chosen in such a way that the spin is everywhere parallel to the local quantization direction. The "spin-down" Bloch waves are defined in a corresponding manner. These Bloch waves are approximate eigenfunctions of the Hamiltonian, provided the precession period of a spin in the local intra-atomic exchange field is smaller than the time of flight of an electron over a length equal to the range of the short-range order of the atomic moments. In the representation of these Bloch waves, the description of the ferromagnet is not very different above and below the Curie point. In particular, the density of states at the Fermi level would not change appreciably. The Fermi level of spin-up electrons would be different from that of spin-down electrons even above the Curie point. One does not know how good this approximation is in the case of ferromagnetic Cr-Fe alloys, but it suggests that the same mechanism by which the collective model of ferromagnetism and the second band profile lead to the existence of a γ peak at low temperature will give the peak even above the Curie point, if disordered permanent magnetic moments are present.

²⁵ R. H. Walmsley, Phys. Rev. Letters **8**, 242 (1962).

²⁶ J. K. Hulm and R. D. Blaugher, Phys. Rev. **123**, 1569 (1961).

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²⁸ J. H. Wood, Phys. Rev. **126**, 517 (1962).

²⁹ E. P. Wohlfarth and J. F. Cornwell, Phys. Rev. Letters **7**, 342 (1961); see also: J. Phys. Soc. Japan **17**, Suppl. B-1, 32 (1962).

³⁰ C. Herring and C. Kittel, Phys. Rev. **81**, 869 (1951).

³¹ C. Herring, Phys. Rev. **87**, 60 (1952); **85**, 1003 (1952).

As can be seen by comparing Figs. 2 and 4, the peak of the experimental γ curve is located at a slightly higher electron concentration than the one at which the experimental magnetization curve starts. On the contrary, this shift seems absent in the theoretical curves derived from the second band profile. However, the shift might have been present in these curves too, if the band profile had been modified very slightly in such a way as to have the concavity turned upwards in a small region near $\epsilon=0.65$ eV. The basic idea is that ferromagnetism may start before the critical density of states is reached, provided the concavity is turned upwards. This point is not discussed any further here, as the numerical calculations have not been done with enough resolution on the electron concentration scale to permit a detailed analysis of the phenomenon. The shift may also be due to another cause, which is discussed below.

High-temperature measurements^{32,33} of magnetic susceptibility in dilute alloys of iron in chromium seem to indicate the existence of disordered permanent magnetic moments amounting to more than two Bohr magnetons on each iron atom. These alloys are Curie paramagnets at high temperature, and antiferromagnets below room temperature. Similar paramagnetic moments exist³⁴ on iron atoms dissolved in molybdenum, homolog of chromium in the second transition series. The saturation magnetization which would be observed in dilute Cr-Fe alloys if these permanent moments could be entirely aligned by a powerful applied field is shown by a dotted straight line on Fig. 4. This spin polarization is probably of a different nature than the one which exists in ferromagnetic Cr-Fe alloys at higher iron concentration and which gives rise to the Slater-Pauling curve. It cannot be described within the rigid band approximation. It affects the localized states split off the bottom of the rectangular sub-band by the potential of the iron impurities,³⁴ and not the sub-band itself. Because of a lack of experimental data, it is not yet clear how the dotted magnetization curve of the dilute paramagnetic alloys is to be connected continuously to the experimental curve of the ferromagnetic alloys (Fig. 4). This introduces additional uncertainty into the shape of the left end of the Slater-Pauling curve. According to theory,³⁴ these localized states should vanish when the density of states becomes large, that is, when $N > 6.5$. It is quite possible that the presence of these magnetic localized states is the reason why ferromagnetism starts slightly before the sharp γ peak, in the Cr-Fe series. However, as the peak exists in measurements done much below the Curie point, it cannot be due to the thermal disordering of these states.

When the third band profile is used, a shift is obtained

³² R. Lingelbach, *Z. Physik. Chem. (Frankfurt)* **14**, 1 (1958).

³³ M. M. Newman and K. W. H. Stevens, *Proc. Phys. Soc. (London)* **74**, 290 (1959).

³⁴ A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, *Phys. Rev.* **125**, 541 (1962).

automatically in the theoretical results for γ and μ . The sign of the shift is the same as in the case of the experimental data.

As a conclusion, a part of the available evidence favors the second band profile, and another part the third band profile, and it does not seem possible at the present time to choose between them. This is the reason why both have been investigated in detail. Some other evidence about this question will be discussed in the next section. It is derived from the consideration of the V-Fe alloys and of the Ti-Co-Fe alloys.

It seems probable that these band profiles are the only ones compatible with the specific heat and magnetization data, in the sense that the real band profile for these alloys should be close to either the second or the third band profile, or lie somewhere in between.

PROPERTIES OF OTHER ALLOYS AND LIMITATIONS OF THE PRESENT THEORY

It is known^{35,36} that the rigid band approximation on which the collective model of ferromagnetism rests is valid when the valences of the two components of the alloy differ by only one or two. Therefore, it can be used on Cr-Fe and Fe-Co alloys. It might apply also to a lesser extent to the V-Fe alloys, for which magnetization¹³ and specific-heat data¹ exist. It is not expected, *a priori*, to work well on the Ti-Co-Fe alloys, for which experimental data exist too,³ as the valence difference is too high.

Another factor is the value of J . The intra-atomic exchange integral is not expected to obey a rigid band model, but rather, to depend on an average of the local properties of atoms of the alloy. In particular, it is somewhat doubtful that J would be large enough to cause ferromagnetism in Cr-Mn alloys. Then, according to theory, the γ coefficient should follow the curve labeled "paramagnet" in Fig. 2, rather than the curve labeled "ferromagnet." The experimental values¹ of γ in the bcc Cr-Mn series seem effectively to rise considerably around $N=6.2$, in agreement with theory. However, the range of these bcc alloys stops near $N=6.5$, so that much uncertainty remains.

The present theory should apply to the bcc Fe-Ni alloys. However, no experimental data on γ are available.

In the case of the V-Fe alloys, a sharp γ peak is observed at $N=5.9$ instead of 6.4. In the alloy corresponding to the peak (31% Fe), the curve¹ of C_v/T versus T^2 is sufficiently straight to suggest that the peak might really be electronic in nature. It is remarkable that ferromagnetism also starts at $N=5.9$ in that series.¹³ This tends to show that the existence of the peak is connected to the ferromagnetism, and favors the second model.

³⁵ J. Friedel, *Advan. Phys.* **3**, 446 (1954).

³⁶ J. C. Slater, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 19, p. 81.

A large peak of γ exists at $N=6.4$ in ordered Ti-Fe-Co alloys.³ Even though the rigid band approximation is not expected to apply very well to these alloys, the peak is probably due to the same cause as in the case of the Cr-Fe alloys. Nevitt has not found³⁷ any measurable magnetization in ordered TiCo($N=6.5$) at 7°K. Neutron diffraction³⁸ failed to show any ordered moments in TiCo at 4°K. These facts seem to show that the γ peak is not associated with the beginning of a ferromagnetic region. Therefore the second of the band profiles seems at first to be ruled out. However, it cannot be excluded that the alloys might have very low Curie points. It is repeated here that the second band profile does not really require ferromagnetic alignment above $N=6.4$ in order to give the γ peak, but only the existence of permanent atomic magnetic moments due to the polarization of the $3d$ band. Moreover, according to the theoretical curve based on the second profile (Fig. 4), the average atomic magnetic moments would not be larger than 0.3 Bohr magneton per atom in this region, so that they might be difficult to detect by neutron diffraction even if they were ordered.

A limitation of the present theory is the fact that, as said earlier, the antiferromagnetism of the nonferromagnetic Cr-Fe alloys is completely neglected. This antiferromagnetism consists probably of a "spin-density wave" or of a spiral structure, of the type suggested by Overhauser and Arrott.³⁹ Such a magnetic structure cannot be described by a simple shift of the two Fermi levels. The exchange potential set up by the spin density

itself mixes strongly together various Bloch waves of energy close to the Fermi level.

A cusp is present in the experimental γ curve at pure iron (Fig. 2). Similar cusps exist in the case of other pure metals.⁴⁰ They cannot be explained by the rigid band model,⁴¹ and no further attention is paid to them in the present work.

CONCLUSIONS

It has been found that two different models of the band profile can account in a satisfactory way for the electronic specific heat and magnetization data in Cr-Fe and Fe-Co alloys in the limiting of vanishing temperature. In particular, both of them predict correctly the presence of a sharp peak of the electronic specific heat at an electron concentration close to that where ferromagnetism starts. In the case of one of these models, the sharp peak is not caused by any singularity of the profile, but rather, by the motions of the Fermi levels for electrons of both spins. These motions have been investigated with the help of the collective model of ferromagnetism. It is not possible at the present time to decide which of these models is the correct one.

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³⁷ M. V. Nevitt, *J. Appl. Phys.* **31**, 155 (1960).

³⁸ R. J. Chandross and D. P. Shoemaker, *J. Phys. Soc. Japan* **17**, Suppl. B-3, 16 (1962).

³⁹ A. W. Overhauser and A. Arrott, *Phys. Rev. Letters* **4**, 226 (1960).

⁴⁰ R. Ehrat and D. Rivier, *Helv. Phys. Acta* **33**, 954 (1960).

⁴¹ H. Jones, *Phys. Rev.* **134**, A958 (1964).