verge. From general theorems[7] about the trace functions, we know that they must oscillate rapidly as the energy traverses an allowed region with periods of the order of $1/N$, maxima greater than 2, and minima less than -2. From our calculations on specific systems, we know that the trace functions for the individual chains f^i are given by

$$f^i=2C^N\cos(N\theta+\delta)+\nu_i\,, \tag{31}$$

where

$$\lim_{N,r\to\infty}\langle\nu_i\rangle=0\,, \tag{32}$$

and C is larger than 1. There is nothing in the restriction of Eq. (32) that requires $\lim_{N,r\to\infty}\nu_i=0$ or that prevents the ν_i from making a systematic contribution to the density of states. The only conclusion that can be drawn is that the ν_i must be of the same order of magnitude and must oscillate as rapidly as the cosine term in Eq. (31). Although it is fairly simple to devise a general argument that explains why our procedure does not give exact results, it is more difficult to devise one that also explains why it gives as good an approximation as it does.

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Electronic Structure of Alloys*

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A theory of the electronic structure of alloys is presented which takes proper account of the symmetries present or absent in the alloy and does not rely on using Bloch's theorem either for the alloy or for the host metal. The band structure is worked out in an approximation which is exact for an ordered alloy and which gives a simple picture for a disordered substitutional alloy. Using this theory the band structure for the *d* electrons of the transition metal alloys is qualitatively discussed. The rigid band model is shown to fail for alloy constituents having a large valency difference and it is shown that the theory of this paper agrees with the experimental results both for magnetic moments and specific heats in such cases. A simple physical interpretation of these results is given using arguments similar to those of the conventional tight binding approximation. It is suggested that the difference between NiAl and FeAl alloys might be due to the aluminum conduction band lying above the nickel *d* band so that the latter fills, whereas the iron *d* band does not lie below the aluminum conduction band. No reference is made to theories of ferromagnetism, though it is possible that the methods used in this paper could be used to obtain a great deal more information from alloys of the transition metals than is available at the moment.

I. INTRODUCTION

THE purpose of this paper is to propose a theory of the electronic structure of alloys which is based on earlier work of Edwards and the author.[1–4] In this earlier work, the electronic structures of various disordered systems were discussed using a model of independent electrons moving in a total potential formed from individual ionic potentials which do not overlap each other. The positions of the ions are supposed to be given by some probability distribution. For example, in the case of a liquid the probability distribution can be taken as the distribution of given ionic positions as the liquid changes in time. The density of states can then be written down in terms of an average of the independent electron propagator over the distribution of systems. The averaging process can only be done approximately, but the approximation used is actually exactly true for a perfectly ordered system. The results obtained, therefore, give the correct limit in the case when the substance being considered has the form of a perfect crystal. The formalism is discussed in more detail later in this section. In the case of a perfect lattice this formalism is identical with that of Kohn and Rostoker,[5] which in the manner it will be applied in this paper avoids some of the difficulties usually associated with *d* electron band structure calculations. In such a formalism it is not necessary to distinguish whether the electrons are localized or free, though it is always helpful if they do belong to one of the limiting

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[1] S. F. Edwards, Phil. Mag. **6**, 617 (1961).

[2] S. F. Edwards, Proc. Roy. Soc. (London) **A267**, 518 (1962).

[3] J. L. Beeby and S. F. Edwards, Proc. Roy. Soc. (London) **A274**, 395 (1962).

[4] J. L. Beeby, Proc. Roy. Soc. (London) **A279**, 82 (1964). (To be referred to as I.)

[5] W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).

classes. The philosophy is to start from the t function rather than the potential. It is possible that one can estimate the former to a good degree of accuracy.

The results of applying such a technique to alloys are naturally rather complicated. The problem is clearly already more involved than a pure metal band structure calculation, which is by itself a formidable undertaking. It so happens, however, that the type of alloy in which the impurity atoms substitute for host atoms on randomly distributed lattice sites is especially simple to treat. Thus, even though the formalism (which is given in the Appendix) is valid for any type of alloy regardless of the ordering involved (i.e., solid solution, ordered, liquid, etc.), the remarks in this paper will deal only with this simple, but physically very important, case.

In order to emphasize the new features to which this theory leads, it is helpful to neglect many important physical effects. It is particularly desirable to avoid any band structure calculation, since the details involved there would completely cloud the general changes brought about by the formalism. It is fortunate that the transition metals, which are involved in most of the important alloys, possess a very useful simplifying feature. The d bands in these metals interact with their s and p band, but only in a way which does not seem to have many important consequences for the density of levels. Thus, following many band calculations, it is helpful to ignore any interactions between the d bands and the conduction bands. It is then possible to discuss the behavior of the alloy d bands in a qualitative manner without needing to do a band structure calculation and without losing all the physical content of the theory.

The problem of ferromagnetism is completely avoided in this paper. The remarks made about magnetic properties depend only on the filling or emptying of the d bands associated with the ferromagnetic elements and it does not matter how such filling leads to any given ferromagnetic effect. What one should do is to take the theories of ferromagnetism and repeat the calculations of this paper in a quantitative manner—a laborious task.

The behavior of the d bands is found to be similar to the rigid band model in many cases, except when the atomic numbers of the components of the alloys are significantly different. Thus the new model predicts correctly the filling of the d band, i.e., the reduction in the magnetic moment per atom, which occurs when chromium, vanadium, or manganese are alloyed with cobalt or nickel. The difference between the rigid band model and that of this paper is not trivial, even when they lead to the same physical result. In the alloys just mentioned, the energy levels of the d states in both host and impurity atoms each form their own bands, though the theory of this paper in no way implies that the electrons in such bands are localized about the type of atom, the energy level of which gave rise to that band. Indeed, the concept of the position of any given electron cannot be properly discussed in the theory to be presented. It does seem, however, that some progress can be made in such a discussion, and it is hoped that this calculation will be presented in a later paper.

An apparently less complicated problem is that of the addition of aluminum or copper to iron or nickel. In the case of iron the impurity conduction electrons do not appear to go into the d band, whereas in nickel they do. The important feature here is the relative positions of the host and impurity energy levels. The suggestion of this paper is that the Fermi level is lower compared to the aluminum Fermi level in nickel than in iron. The reasons why this is so are not clear, but probably depend mainly on arguments concerning screening and electrical neutrality and fall outside the scope of this paper.

A detailed discussion of the behavior of mixed s and p bands is much more difficult. The s and p bands are usually far from being tightly bound, which eliminates one possibility of providing a model of the bands. There are four energy levels involved and at least four parameters indicating the widths of the bands in the pure metals. It is not clear that such a calculation can be simplified in any case in which it is not trivial. Without any simplification the problem is rather more difficult than that of a band structure calculation following the method of Kohn and Rostoker. Only a rough analysis of this case is attempted in this paper, from which it does seem likely that a "rigid band" model such as was used by Cohen and Heine[6] will in general be reasonable because of the large bandwidths involved.

The principal feature of the theory to be presented here lies in the choice of potential to be used. One is used to describe the potential in a pure metal by supposing that a self-consistent calculation has been carried out to take into account the electron-electron interactions. The resulting potential and the independent quasiparticles moving in it are the basis of band structure calculations. It is an empirical fact that this description of the pure metal can lead to excellent agreement with experiment. Now suppose that a similar self-consistent calculation has been carried out in any given alloy. The potential at any given site will depend both on the type of atom at the site and on the atoms occupying the neighboring sites. The dependence of a given potential on the occupants of the neighboring sites is probably not large. In any case, the theory depends on there being no local deviations from the lattice structure due to either small or large impurity atoms. This absence of deviation from perfect lattice structure will be assumed throughout, as will the independence of any given potential on the types of atoms in its neighborhood. The work of Friedel[7] suggests that

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[6] M. H. Cohen and V. Heine, Advan. Phys. 7, 395 (1958).

[7] J. Friedel, Advan. Phys. 3, 446 (1954).

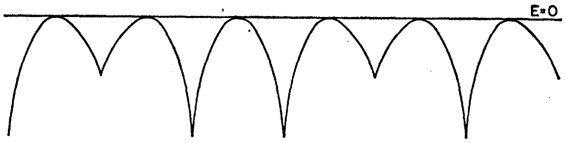

FIG. 1. Schematic representation of the alloy potential used.

this assumption is best in the transition metals. Thus, at each host atom site, there will be one potential and at each impurity atom site another. The potential thus defined for a given atom will alter from alloy to alloy and even as the solvent/solute ratio changes. Such alterations will probably be small and their effect may well be less than that due to the changes in lattice parameters on alloying. Both these effects will be ignored in the rest of this paper, despite the fact that the lattice constant is always a parameter in the formalism. When the structure of the crystal changes, however, the potential may well change significantly and this change must be borne in mind.

Thus, the picture of the alloy potential which one has after making the calculation self-consistent and neglecting some of the less important features is as shown in a schematic one-dimensional representation in Fig. 1. It is convenient, but not necessary to ignore the fact that the value of the potential midway between two atoms may depend on what types the atoms are. This value of the potential may then be chosen as the zero of energy so that the atomic potentials can be assumed (1) spherically symmetric and (2) zero outside a certain sphere, the radius of the spheres being such that the potentials do not overlap. Such potentials are commonly used in pure metal band structure calculations.[8]

The alloy potential has, therefore, been reduced to having the following four properties:

(1) The potential at each site is spherically symmetric and zero outside a certain radius.

(2) The potentials on two neighboring sites do not overlap.

(3) The potentials corresponding to sites occupied by atoms of any specific kind are identical.

(4) The potentials depend only on the structure of the crystal and not on the lattice constant or relative concentrations of the alloy constituents.

Condition (4) is a simplifying assumption which could be relaxed should it be necessary. Given a crystal potential satisfying conditions (1) to (4), it is a fairly straightforward piece of algebra to extend the theory of I to the alloy problem. This extension and a discussion of the geometric approximation used in the theory is given in the Appendix. It is not necessary to go any further into the theory in this introduction since in the case of disordered substitutional alloys, with which the bulk of the paper is concerned, there is a simple physical picture using concepts similar to those of the tight binding approximation which leads to the same result. It will be helpful if the reader has some idea of the work presented in I, but it is hoped that this paper will be, for the most part, understandable without knowledge of I. The algebra presented in the Appendix, however, depends closely on the details of I.

Before proceeding to the details of the calculation, it is perhaps worthwhile to give a simple illustration of the way in which it is suggested that the rigid band model is inadequate. One way of viewing the tight binding approximation is to consider the ions which are to form the lattice dispersed so far apart that they have no effect on each other. Consider a single bound energy level. If now the ions are moved together, the bound energy levels are all the same if one is considering a pure metal, and therefore, being degenerate, will actually split to form a band. The total density of levels in the band will stay constant, equal to the number of ions present (forgetting multiple occupancy due to spin or angular momentum degeneracy). As the ions come closer and closer together, the band broadens further and further and reduces its height.

If the same process were to be carried out in an alloy of two types of ion, then what happens depends on the relative positions of the energy levels in the different ions. Consider now one bound level in each type of ion (one is, of course, thinking of the *d* levels in transition metals). When the ions start to approach each other, but at such a density that they are still well separated, the degeneracy will split the levels into bands, one band for each of the types of ion present. These bands will be narrow and will not overlap. The electrons in either band will be localized around the type of ion from which that band has originated. What happens when the ions come closer together now depends on the bandwidths and on the splitting between the energy levels. If the bandwidths are very much greater than the splitting, then the separate bands will merge into a composite band holding one electron level for each ion present. This is just the rigid band model. If, on the other hand, the splitting is much greater than the bandwidths, the bands will to a good approximation stay separate, each holding one electron level for each ion of the appropriate type present.

These two limiting cases are illustrated in Fig. 2, in which the pictures for infinitesimal densities, extremely small densities δ, and metallic densities are compared. These pictures will be seen later to be very similar to those which arise from the theory of this paper. This is not surprising, since it will be seen in what follows that the situation considered is akin to a tightbinding situation and merely rewrites the arguments presented above, but using a firmer mathematical foundation.

The relevant parts of the previous work will now be briefly reviewed in order that some of the formulas may

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[8] F. S. Ham and B. Segall, Phys. Rev. **124**, 1786 (1961).

be used later. In I the density of states, $\rho(\mathbf{k},E)$, written in the form

$$\rho(\mathbf{k},E)=-\frac{1}{(E-k^2)^2}\frac{1}{V}\langle \mathrm{Im}\,T(\mathbf{k})\rangle\,,$$

where (1)

$$T(\mathbf{k})=\int \exp(-i\mathbf{k}[\mathbf{x}-\mathbf{x}'])T(\mathbf{x},\mathbf{x}')d\mathbf{x}d\mathbf{x}'\,,$$

and where $T(\mathbf{x},\mathbf{x}')$ is the total scattering matrix of the electron on the crystal, is expanded in terms of the total scattering matrices (or t functions) for each individul potential. Dirac brackets denote the averaging over the distribution of systems. $\rho(\mathbf{k},E)$ is defined for all $\mathbf{k}$, and is not restricted to any Brillouin zone so that one is dealing with free electrons and not with Bloch waves. The density of levels of the system is given by

$$n(E)=\int \rho(\mathbf{k},E)d\mathbf{k}\,.$$

The result given in I for the density of states is written in terms of (i) a matrix $\mathbf{G}$ which depends on the structure of the lattice and on $\mathbf{k}$ and E, but is in no way dependent on the potential and (ii) a diagonal matrix $\mathbf{t}$, the elements of which are the angular momentum components of the t function or total scattering matrix for the potential and are not dependent on the lattice. Then according to I,

$$\langle T(\mathbf{k})\rangle = N(4\pi)^2\sum_{LL'} Y_L(\mathbf{k})Y_{L'}(\mathbf{k})\{t_l(k,k)\delta_{LL'} +[\mathbf{t}(k,E^{1/2})\{\mathbf{G}+\mathbf{G}\boldsymbol{\tau}\mathbf{G}+\mathbf{G}\boldsymbol{\tau}\mathbf{G}\boldsymbol{\tau}\mathbf{G}+\cdots\} \times\mathbf{t}(E^{1/2},k)]_{LL'}\}\,, \quad (2)$$

where $\boldsymbol{\tau}=\mathbf{t}(E^{1/2},E^{1/2})$. This result includes all multiple-scattering terms and is an expansion in terms of some disorder parameter rather than any potential strength. Higher multiple-scattering terms are not always correctly dealt with in the disordered case, as will be discussed shortly. Equations (1) and (2) may be considered to describe a procedure for evaluating the density of states for a lattice of potentials in the case when the t function for the potentials is known. It is therefore instructive to observe that one can construct such a t function as follows: Consider a disordered substitutional alloy with a proportion d of solute atoms so that the solvent atoms are present in the proportion $(1-d)$. As the electron moves through the lattice (in a free-electron-like manner) it will scatter off the lattice sites. Since the potentials are not small the electron may resonate with them so that it is necessary to describe the scattering by the total scattering matrix of that site, i.e., the t function of the potential there. But when the electron arrives at any site there are probabilities $(1-d)$ and d that there will be solvent or solute atoms present on that site. The alloy, therefore, scatters the electron rather as if it were a pure metal with a potential at every site described by the t function

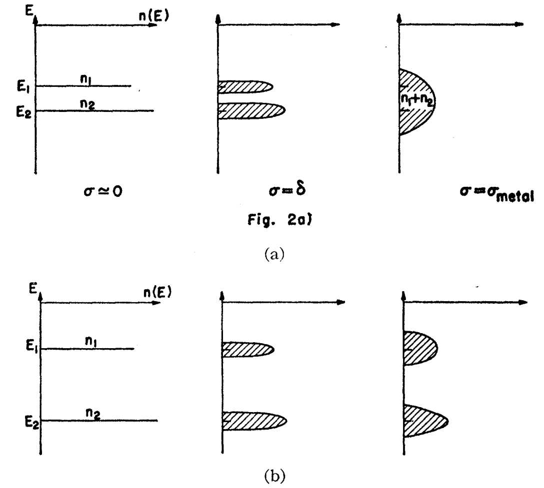

FIG. 2. The density of levels formed by n_1 ions with bound state E_1 and n_2 ions with bound state E_2 as the density, σ, increases from near zero to metallic densities. (a) bandwidth≫energy splitting, (b) bandwidth≪energy splitting.

$$t(\text{alloy})=(1-d)t(\text{solvent})+dt(\text{solute}). \quad (3)$$

This t function for the alloy need correspond to no real potential and even if it should correspond to a potential, that potential will almost certainly be pathological. Given the t function of the alloy one can then insert it into Eq. (2) and Eq. (1) to find the density of states. The more elaborate calculation presented in the Appendix yields exactly the same answer, but does so in a way which gives one greater confidence in the approximation and also enables one to discuss the diffuseness which is actually present in the density of states. This part of the problem is discussed in Sec. II. The important approximation which has been made in deriving Eq. (3) is that, although all order multiple-scattering terms have been included, those terms where, for example, the electron scatters off the potential at $\mathbf{R}_1$, then off potentials elsewhere and finally returns to scatter again off the potential at $\mathbf{R}_1$ are not correctly evaluated. Experience in the simpler cases suggests that this approximation is liable to give the detailed shape of band edges incorrectly, though not seriously so and is elsewhere a very good approximation.

The important difference between the foregoing remarks and many earlier theories is that the solvent and solute atoms are treated on an equal footing. Thus it has not been assumed that the electrons move in the Bloch states of the host metal and are scattered by the impurity atoms. What happens in a pure metal is that the concept of Bloch waves is replaced by the $\rho(\mathbf{k},E)$ of Eq. (1) defined for all $\mathbf{k}$ and this represents the splitting of Bloch waves with crystal momentum $\mathbf{k}'$ into their components with real (free electron) momentum $\mathbf{k}=(\mathbf{k}'+\mathbf{K}_i)$, where $\mathbf{K}_i$ is any vector of the reciprocal lattice. Thus the waves equivalent to Bloch waves in the alloy are built up from various parts of $\rho(\mathbf{k},E)$, which is now defined in terms of the alloy t function (3). It will indeed be seen later that the alloy bands often have little resemblance to the pure metal bands.

In Sec. II an especially simple model is discussed of lattices with vacancies, and the behavior of d bands in such lattices described. This is then extended to binary alloys in Sec. III and to a discussion of the transition metals in Sec. IV. Section V contains a brief discussion of the behavior of nontransition metal elements alloyed with transition metals.

II. LATTICES WITH VACANCIES

In order to get some feeling for the techniques to be used in discussing the density of states, it is useful to begin by analyzing an even simpler problem than that just presented in the Introduction. Suppose that the impurity being substituted in the alloy had an extremely weak potential, so weak that it could be ignored compared to the host potential. Then the alloy would be made up of only one type of potential, with vacancies appearing at random lattice sites. While this may not really seem to be a good model of any alloy it will be seen later that the mathematical problem to which it leads is part of a better model of such an alloy. Even so consider, for example, FeAl. The iron d electrons are fairly deeply bound and are mostly concentrated about the Fe ions. The aluminum ion, however, has no bound d state, so that even when the d electrons stray as far as the Al ions they will interact only slightly with the potential there and will certainly be far from any resonance. Thus, the d electrons are influenced only by the Fe ions and the Al potential may be taken as zero when calculating their properties. It will be seen later that the d electrons of FeAl behave exactly as suggested by this simple argument. This model of vacancies in a perfect lattice will be discussed in the remainder of this section.

Given that the model alloy consists of only one type of potential, the theory of I is directly applicable to it. The potential involved is that of the Fe ion and is the same as in the pure metal. The lattice structure too is the same except that the vacancies correspond to certain of the lattice points being absent. Thus, the matrix $\mathbf{G}$ in Eq. (2) is different in the alloy. $\mathbf{G}$ depends linearly on the correlation function

$$c(\mathbf{j})=\left\langle\frac{1}{\nu}\sum_{\mathbf{R}_\alpha\neq\mathbf{R}_\beta} e^{i\mathbf{j}\cdot(\mathbf{R}_\alpha-\mathbf{R}_\beta)}\right\rangle,$$

where ν is the number of Fe ions and the summations are taken over all occupied lattice sites. This correlation function can be evaluated by writing it in terms of the totality of lattice sites and of the unoccupied sites. Thus, if the lattice sites are denoted by $\mathbf{r}_\alpha$ and the vacancy positions by $\mathbf{v}_\alpha$, the correlation function becomes

$$c(\mathbf{j})=\frac{1}{\nu}\left\langle\sum_{\mathbf{r}_\alpha\neq\mathbf{r}_\beta} e^{i\mathbf{j}\cdot(\mathbf{r}_\alpha-\mathbf{r}_\beta)}-\sum_{\mathbf{r}_\alpha\neq\mathbf{v}_\beta} e^{i\mathbf{j}\cdot(\mathbf{r}_\alpha-\mathbf{v}_\beta)}\right.$$
$$\left.-\sum_{\mathbf{v}_\alpha\neq\mathbf{r}_\beta} e^{i\mathbf{j}\cdot(\mathbf{v}_\alpha-\mathbf{r}_\beta)}+\sum_{\mathbf{v}_\alpha\neq\mathbf{v}_\beta} e^{i\mathbf{j}\cdot(\mathbf{v}_\alpha-\mathbf{v}_\beta)}\right\rangle. \quad (4)$$

Given that the proportion of vacancies is d and that they are randomly distributed, there is a probability d of any given site $\mathbf{r}_\alpha$ being a vacancy $\mathbf{v}_\alpha$. Thus each sum over vacancy sites gives, upon averaging, the same sum over lattice sites reduced by a factor d. So in terms of the pure-metal correlation function

$$c^0(\mathbf{j})=\frac{1}{N}\langle\sum_{\mathbf{r}_\alpha\neq\mathbf{r}_\beta} e^{i\mathbf{j}\cdot(\mathbf{r}_\alpha-\mathbf{r}_\beta)}\rangle,$$

where N is the number of sites in the lattice, one has

$$c(\mathbf{j})=(1-d)c^0(\mathbf{j}). \quad (5)$$

Hence, finally, because of the linear dependence of $\mathbf{G}$ on c, one has

$$\mathbf{G}^a=(1-d)\mathbf{G}^p, \quad (6)$$

where superscripts a and p will be used to denote the alloy and pure metal, respectively. So the matrix $\mathbf{G}$ in Eq. (2) is different in the alloy case. The matrix $\mathbf{t}$, corresponding to the potential involved, is unaltered.

It is clear that, because of the randomness of the vacancies, the density of states will not be in the form of a relation between E and $\mathbf{k}$. Particles moving in states of a definite energy or a definite momentum will be scattered in an incoherent manner by the vacancies. Yet such concepts as the alloy Fermi surface are frequently discussed, so it is of interest to see whether it is possible to make any sort of an attack on this point. To do this it is necessary to use some more formulas from I[9] [(I4.5), (I4.6), (I4.9), (I4.10)] which give

$$\langle\operatorname{Im}T(\mathbf{k})\rangle=N(4\pi)^2\sum_{LL'}Y_L(\mathbf{k})Y_{L'}(\mathbf{k})$$
$$\times\frac{s_l(k)}{s_l(E^{1/2})}[\mathbf{M}]^{-1}{}_{LL'}\frac{s_{l'}(k)}{s_{l'}(E^{1/2})},$$

where

$$\mathbf{M}=\left(\frac{E^{1/2}}{\mathbf{s}(E^{1/2})}+\mathbf{F}_R\right)\mathbf{F}_I^{-1}\left(\frac{E^{1/2}}{\mathbf{s}(E^{1/2})}+\mathbf{F}_R\right)+\mathbf{F}_I \quad (7)$$

and

$$\begin{aligned}\mathbf{F}&=\mathbf{G}-iE^{1/2}\delta \quad && E>0\\ &=\mathbf{G} && E<0.\end{aligned}$$

$\mathbf{F}_R$ and $\mathbf{F}_I$ are the real and imaginary parts of $\mathbf{F}$ and the functions s_l are related to the t function. In the case of a perfect lattice $\mathbf{F}_I$ has the form of a set of δ functions and the density of states is then nonzero only when $\det(E^{1/2}/\mathbf{s}+\mathbf{F}_R)=0$. In all cases other than a

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[9] Equations from Ref. 4 are numbered as in that paper, but with the prefix I.

perfect lattice the distinction between positive and negative energies is a little troublesome. Consider first $E>0$. Equations (6) and (7) then give

$$\mathbf{F}^a=\mathbf{G}^a-iE^{1/2}\delta=(1-d)\mathbf{F}^p-diE^{1/2}\delta$$

and

$$[\mathbf{M}^a]^{-1}=\frac{-dE^{1/2}\delta}{[E^{1/2}/\mathbf{s}+(1-d)\mathbf{F}_R{}^p]^2+(E^{1/2}d)^2\delta}, \tag{8}$$

which means that the density of states is no longer nonzero only along a line in $E,\mathbf{k}$ but is distributed about the line

$$\det[E^{1/2}/\mathbf{s}+(1-d)\mathbf{F}_R{}^p]=0, \tag{9}$$

with a width at constant energy given approximately by

$$\Delta\mathbf{k}=E^{1/2}d/[(1-d)(\partial\mathbf{F}_R{}^p/\partial\mathbf{k})|_{\mathbf{k}_0}], \tag{10}$$

where $E,\mathbf{k}_0$ satisfy Eq. (9). This is not a very useful expression, since Eq. (8) is defined everywhere in $E,\mathbf{k}$ space and the whole result for $\rho(\mathbf{k},E)$ is extremely complicated. It is unlikely that any worthwhile comparison of this expression with experiment could be made. Following Eq. (7), the density of levels must be worked out by integrating $\mathbf{M}^a$ from Eq. (8), multiplied by a weighting factor, over all $\mathbf{k}$ space. In this integration over $\mathbf{k}$, the Lorentzian shape of Eq. (8) will not have a violently different area from the δ-function shape it would have if the width were taken to be zero. In other words, the well-defined Bloch wave has been spread by the disorder into something of the nature of a wave packet. Unless these wave packets by some chance interact strongly, they will contain the same number of electrons as the original Bloch waves. The width may therefore be ignored in calculating the density of levels, even though one cannot yet show that it is everywhere small. From Eq. (10) it is seen to be small for low concentrations of impurities.

In the case $E<0$ the matrix $\mathbf{F}$ is given by

$$\mathbf{F}^a=(1-d)\mathbf{F}^p, \tag{11}$$

so that the imaginary part, $\mathbf{F}_I$, as in the perfect lattice consists of a sum of δ functions. Thus, the density of states is nonzero only where Eq. (9) is satisfied, so that no width appears in this case. What has happened here is that a width only appears when higher order terms are taken into account in the geometric approximation. However, a general analysis of that approximation suggests that the higher order terms are usually only important near the edges of bands, which in turn suggests that the width is, in general, small except near the band edges. Evaluating Eq. (10) in the tight binding approximation [which is inconsistent since $E>0$ in Eq. (10)] one observes that $(\partial\mathbf{F}_R{}^p/\partial\mathbf{k})$ is proportional to $(\partial E/\partial\mathbf{k})$ and this too implies that the width is greatest at the band edges. Therefore, provided one only discusses the density-of-states problem, and does not discuss, e.g., transport coefficients, it seems reasonable to ignore the width on the density of states with the proviso that detailed conclusions are not drawn near band edges. Since the band structure is then given by Eq. (10) in both cases, it is most convenient to evaluate the density of states for $E<0$ and to make a formal extrapolation of the result to the region $E>0$ when this region is of interest. This procedure will be followed for the rest of the paper.

One can now return to the simple physical interpretation, given in the Introduction, of the manner in which the electron moves through the lattice. In the case of the lattice with vacancies the average t function at any given site is $(1-d)t^p$ and this may be used in Eq. (2) to give the density of states. A little care must be exercised in doing this, however, principally because the t function of Eq. (2) and the function $s(k)$ of Eq. (7) are not linearly related.

In the lattice with vacancies problem the density of states is nonzero only where Eq. (9) is satisfied. This gives a definite relation between E and $\mathbf{k}$ but it is important to note that the density of levels is no longer given by the usual integral

$$n(E)=\int\int\frac{1}{|\mathrm{grad}E|}dS, \tag{12}$$

taken over constant energy surfaces in the Brillouin zone. This is most conveniently seen in the tight binding approximation. Concentrate on that part of Eq. (9) corresponding to the angular momentum of the tightly bound state. In order to avoid complications with matrices, one may take the state to have angular momentum zero, the extension to higher angular momenta being trivial. It is then necessary to solve

$$E^{1/2}/s_0(E^{1/2})+(1-d)F_R{}^p(k,E^{1/2})=0.$$

Near the bound state energy E_0, $E^{1/2}/s_0(E^{1/2})$ has the form $(E-E_0)/(-\gamma)$ where γ is proportional to an overlap integral. The dependence of $F_R{}^p(\mathbf{k},E)$ on E is ignored in the crudest tight-binding approximation. Thus, one has

$$E=E_0-\gamma(1-d)F_R{}^p(\mathbf{k},E_0), \tag{13}$$

whereas in the pure metal, one would have had

$$E=E_0-\gamma F_R{}^p(\mathbf{k},E_0).$$

Hence the effect of the presence of the vacancies can be interpreted as a reduction in the overlap integral. In the pure metal this reduction would have the effect of narrowing the bandwidth by a factor $(1-d)$, but increasing the height of the density of levels by a factor $1/(1-d)$, the number of electrons in the band thus remaining constant. Equation (13) does indeed show that the bandwidth in the vacancy case is reduced by a factor $(1-d)$. It is important to what follows to note that the band shape does not change in its features, only in its linear dimensions. However, it will now be shown that the height of the density of levels does not increase in the alloy, so that the number of electrons in the band is reduced by a factor $(1-d)$, which is, of course, correct. The argument hinges around the function $s(k)$, which from I can be written in terms of the matrix element

$$s_l(k)\alpha\int_0^\infty j_l(kx)v(x)R_l(x)x^2dx\,.$$

Here $j_l(kx)$ is a radial Bessel function, $v(x)$ the potential, and $R_l(x)$ the radial wave function of the electron in the potential. In particular,

$$s_l(E^{1/2})=\pi^{-1}\tan\eta_l\,,$$

where η_l is the phase shift. It was remarked above that the effect of the $(1-d)$ factor was to reduce the overlap integral. This corresponds to a reduction of $s_l(E^{1/2})$ by a similar factor. The point to be made is that $s_l(k)$ will change only slightly when this happens, because the reduction in the overlap integral corresponding to the bound electron can, in general, be achieved by a very slight change in the shape of the potential, and this need hardly affect $s_l(k)$ which corresponds in a certain sense to an electron of positive energy. Thus, the last three factors in the first of Eqs. (7)

$$\frac{\mathbf{s}(k)}{\mathbf{s}(E^{1/2})}\delta\left[\frac{E^{1/2}}{\mathbf{s}(E^{1/2})}+(1-d)\mathbf{F}_R{}^p\right]\frac{\mathbf{s}(k)}{\mathbf{s}(E^{1/2})}$$

give

$$(1-d)\frac{\mathbf{s}(k)}{[(1-d)\mathbf{s}(E^{1/2})]}\delta\left[\frac{E^{1/2}}{[(1-d)\mathbf{s}(E^{1/2})]}+\mathbf{F}_R{}^p\right]\times\frac{\mathbf{s}(k)}{[(1-d)\mathbf{s}(E^{1/2})]}=(1-d)n'(E)\,. \quad (14)$$

This is $(1-d)$ multiplied by the factor which would have given the density of states in the pure metal, $n'(E)$, with a smaller overlap integral. The extra factor $(1-d)$ in Eq. (14) shows that, though the bandwidth is reduced by $(1-d)$, the density of states does not increase. In other words, the effect on the band of replacing certain of the pure metal ions with vacancies, is to decrease its width without changing its shape [as will be seen by the factor $n'(E)$], in such a way that it holds the correct number of electrons. Though the argument has been given in the tight-binding limit, it will be nearly true in other cases; the bandwidth will be reduced with only a slight change in band shape. This result will be useful in the next section where the behavior of binary alloy systems is discussed.

III. BINARY ALLOYS

Consider once more the model of an alloy discussed in the Introduction. The electron moves as if it were in a perfect metal alloy with a potential at each site possessing the t function

$$t'=(1-d)t^1+dt^2\,, \quad (15)$$

where t^1 and t^2 are the t functions for the solvent and solute potentials, respectively. Then by neglecting the diffuseness of the density of states, as discussed in the previous section, one sees that the density of states is nonzero only when

$$\det\left[\frac{E^{1/2}}{\mathbf{s}'(E^{1/2})}+\mathbf{F}_R{}^p\right]=0\,, \quad (16)$$

where $\mathbf{s}'(E^{1/2})$ is given by

$$s_l'(E^{1/2})=-E^{1/2}\,\mathrm{Re}t_l'(E^{1/2},E^{1/2})\,. \quad (17)$$

The feature of s' and t' which is important in the work to follow is that they both have singularities at the bound states of the electron in either solvent or solute potentials. This is clear from Eq. (15) since a singularity in either t^1 or t^2 implies a singularity in t'.

It is necessary to simplify Eq. (16), since its solution is still harder than an ordinary band-structure calculation. This process can be begun by noting the form of $\mathbf{F}_R$ in bcc and fcc lattices. In the case that s-, p-, and d-bound states all exist in one or another of the components of the alloy, $\mathbf{F}$ is a (9×9) matrix. The (4×4) part of $\mathbf{F}$ which corresponds to the s and p bands and the (5×5) part corresponding to the d band happen to be numerically much larger than the (4×5) and (5×4) "off-diagonal" elements. Thus it seems reasonable to neglect the latter and hence to split the problem into two parts, corresponding to the s- and p-bands problem, and the d-band problem. This is a common approximation in the transition metals: the interaction between s and d electrons is rarely considered. So far as this paper is concerned, the aim is to expose the important features of the model and not to attempt a rigorous calculation. As mentioned in the Introduction, this approximation should not be too serious.

The d bands alone can be discussed fairly well. Since they are close to being tightly bound, the behavior of $s'(E^{1/2})$ can be approximated quite closely. It is useful to assume the d bands to be so tightly bound that they all have the same shape, this shape being mainly determined by the lattice structure. Consider first the solution of the relevant part of Eq. (16)

$$\det\left[\frac{E^{1/2}}{\mathbf{s}_2'(E^{1/2})}+\mathbf{F}_R{}^p\right]=0\,. \quad (18)$$

In the pure metal $E^{1/2}/s_2'(E^{1/2})$ has the general form $(E-E_1)/(-\gamma_1)$ near the bound d state at E_1, giving an equation which may be written formally as

$$E=E_1+\gamma_1\mathbf{F}_R{}^p\,.$$

This is really a matrix equation but will for the moment be treated as a scalar equation. $\mathbf{F}$ is bounded as a function of **k**, showing that E lies within certain limits. The remainder of the terms in Eq. (7) for $\rho(\mathbf{k},E)$ will give the shape of the band. γ determines the width of the band. Now add an impurity to this metal, the impurity having a bound d state at E_2 with overlap integral γ_2. For the alloy

$$\frac{E^{1/2}}{s_2'(E^{1/2})}=\frac{-1}{(1-d)[\gamma_1/(E-E_1)]+d[\gamma_2/(E-E_2)]}=\frac{-(E-E_1)(E-E_2)}{\gamma'[E-E(d)]},$$

where

$$E(d)=\frac{(1-d)\gamma_1E_2+d\gamma_2E_1}{\gamma'}$$

lies between E_1 and E_2, and

$$\gamma'=(1-d)\gamma_1+d\gamma_2.$$

Figure 3 shows sketches for the behavior of $E^{1/2}/s'(E^{1/2})$ both for the perfect crystals of metal potentials 1 and 2, and for their alloy. It is clear that the behavior is considerably more complicated in the alloy case than in the pure substances. There is a singularity at the energy $E(d)$ where, because the function $\mathbf{F}$ is bounded, the density of states is zero. (Since this constitutes a band edge the geometric approximation is suspect in this region and one should perhaps understand by zero the phrase "much smaller than expected.") Away from $E(d)$, the alloy $E^{1/2}/s'(E^{1/2})$ becomes asymptotic to $1/\gamma'\{E-[E_1+E_2-E(d)]\}$.

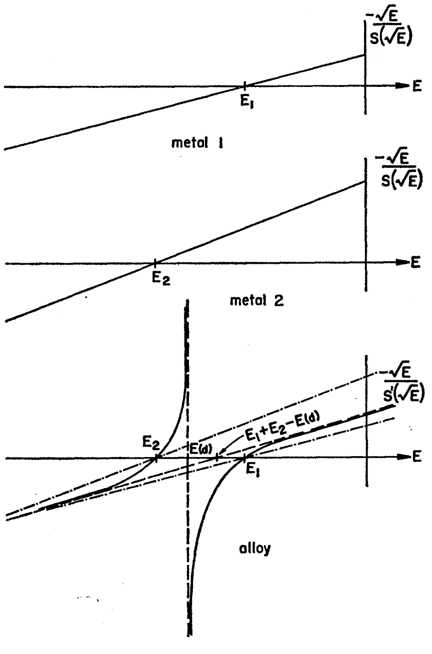

FIG. 3. Curves showing the behavior of $E^{1/2}/s'(E^{1/2})$ for both pure metals and for the alloy.

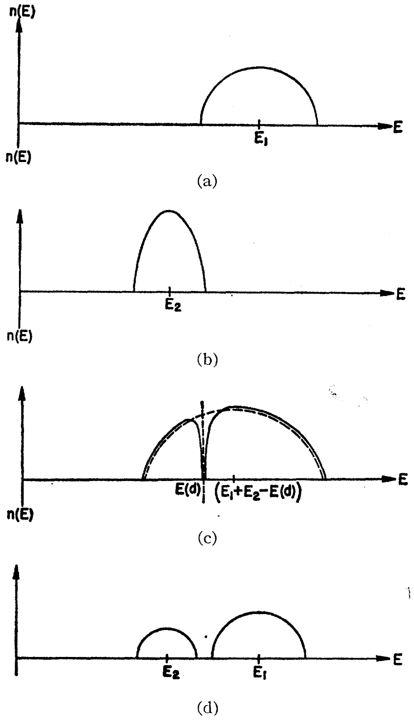

FIG. 4. An idealized representation of the density of states in the cases of two pure metals, (a) and (b), and for their alloys (c) when the bandwidth≫energy splitting, and (d) when the bandwidth≪energy splitting.

The calculation has yet to be reduced to manageable proportions. Consider, therefore, the following model. The band structure is determined as the solution of the equation

$$E^{1/2}/\mathbf{s}'(E^{1/2})=-\mathbf{F}$$

and the density of states increases as the absolute size of $\mathbf{F}$ decreases. Thus, for crystals of potentials 1 and 2 the densities of states are as given in Figs. 4(a) and 4(b). The widths of the bands are given by $2\gamma_i|\mathbf{F}_{\max}|$ and the heights are inversely proportional to the widths. For the alloy this model possesses two parameters, γ' and $|E_1-E_2|$. The width $2\gamma'|\mathbf{F}_{\max}|$ is a weighted mean of the widths of the constituents, and this must be compared with the energy difference $|E_1-E_2|$. The two limiting cases are very different:

(a) Width$\gg|E_1-E_2|$

Here $E^{1/2}/s'(E^{1/2})$ is asymptotic to

$$(1/\gamma')\{E-[E_1+E_2-E(d)]\}$$

and is only very different from that line in the neighborhood of $E(d)$. Thus, in this case, the band is as drawn in Fig. 4(c), having width $2\gamma'|\mathbf{F}_{\max}|$ and being centered on the energy $E_1+E_2-E(d)$. There is a sudden decrease to zero at the energy $E(d)$ which lies about halfway up the band for a symmetrical band. This de-

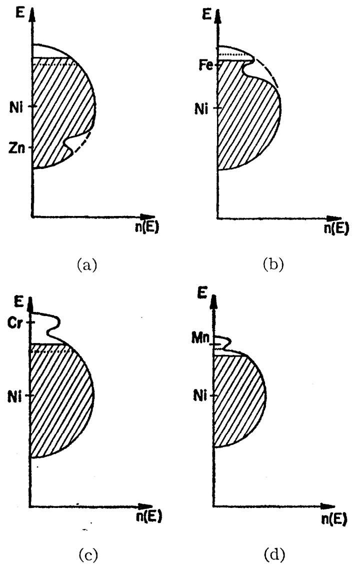

FIG. 5. The suggested behavior of the density of states in the nickel alloys (a) NiZn, (b) NiFe, (c) NiCr, (d) NiMn. The dotted line represents the position of the Fermi surface prior to alloying.

crease is a consequence of the approximation, in general one would expect noticeable decrease in $n(E)$, but not right down to zero.

(b) Width$\ll|E_1-E_2|$

In this case one is only interested in the behavior of $E^{1/2}/s'(E^{1/2})$ when it is very small. This happens near E_1 and E_2, where $-E^{1/2}/s'(E^{1/2})=(E-E_1)/(1-d)\gamma_1$ and $(E-E_2)/d\gamma_2$, respectively. This leads to the situation as presented in Fig. 4(d). These two cases are clearly closely connected with the simple tight-binding discussion of the alloy problem given in the Introduction. What the theory presented above has enabled one to do is to discuss the approximations involved in the case of an alloy. It would further enable one to put the whole calculation on a quantitative basis were the ion potentials sufficiently well known.

Before considering the cases intermediate between (a) and (b), one should consider the behavior of the real shape of the bands rather than the model bands just discussed. The important feature described in the last section for the single band in the presence of vacancies was that, though changing its width, it did not change its shape or height. By this means the band managed to contain the correct number of electron states. It is not unreasonable to assume that the same effect occurs here. Thus, it is presumed that $s'(k)$ is not changed on alloying, while $s'(E^{1/2})$ is changed, so that the bands given in Fig. 4(d) and by the dashed line in Fig. 4(c) will have the characteristic shape of the tightly bound d bands. In each case the band heights actually adjust themselves so that the bands contain the appropriate numbers of electrons, i.e., 5 in Fig. 4(c); $5(1-d)$ in the E_1 band and $5d$ in the E_2 band of Fig. 4(d).

In intermediate cases the bands of Fig. 4(c) go into those of Fig. 4(d) by moving apart and changing their relative sizes from holding an equal number of electron states to holding numbers proportional to the number of atoms possessing the energy level in question. These conclusions are, for the most part, in contradiction to the rigid band model, which corresponds to the dashed line in Fig. 4(c). Thus it will be seen in the next section how the breakdown of the rigid band model in alloys between transition metals of much different valences can be explained simply by the model presented in this section.

The real band-structure problem is not quite so simple as has just been suggested, because the shape of the band is not symmetrical about the energy level E_i, due to Brillouin-zone effects. Thus, the gap at $E(d)$ will not appear in the middle of the band (in term of numbers of electron states) even when the energy levels are close together. It is perhaps better to say that the gap appears at $E(d)$ which for small concentrations of impurities is close to the impurity bound-state energy.

When the bands are not tightly bound there will be other complicating features, which really need much more detailed calculation before they can be described.

Finally, in this section, it is necessary to make a few remarks about the spatial localization of the electrons. Even though an electron lies in a band which is formed around the energy level associated with a given type of atom, it is not true that the electron is actually localized around atoms of that type. The electrons will all spend some time on one type of atom and some on another. What one can say, however, from the tight binding type of approach to the two-band picture, is that the electron will spend most of its time near to one particular type of atom, unless its energy happens to lie roughly in the middle of the two levels. Thus it is important that talking of a "Ni band" or a "V band" does not imply any localization of electrons in space, but only the position in energy of the band in question.

The results derived above will now be applied to the problems of actual transition-metal alloys.

IV. THE TRANSITION-METAL ALLOYS

The discussion of the previous section has provided a qualitative picture of the way in which the d bands of alloys behave when both constituents of the alloy have bound d states. The most important physical situations in which this occurs are in the alloys of the transition metals. All that remains is to determine the positions of the d electron bound states in these metals, after which one is able to describe the predictions of the model for such alloys. The model will be seen to give significantly different results from those of the rigid band model in just those cases in which the latter fails: where the valency difference between the alloy constituents is large.

In the free atoms the binding energy of any given level increases as the atomic number increases. Thus, going from vanadium to nickel in the transition metals, the *s* state goes from ~7.5 to ~9 eV while the *d* state goes from ~16 to perhaps 25 eV. (These figures are roughly estimated from the ionization potentials.) This suggests that in the crystals of these metals the *d* levels will move lower with increasing atomic number. The decrease per unit change in atomic number will probably be less than in the free atoms, partly because the *d* levels are raised relative to the *s* levels by the manner in which the crystal potential of our model is formed. But it seems reasonable to choose a value of between 1 and $1\frac{1}{4}$ eV lowering of the *d* level for unit increase in atomic number.

The *d* band itself in the transition metals has a width of the order of 4–8 eV depending on the source used, so that if it is assumed that the band is roughly symmetrical about the energy level it is possible to analyze the behavior of the various alloys in detail as follows:

(a) Nickel Based Alloys

(*1*) *Copper and zinc.* Here the splitting between the host and impurity energy levels is small compared with the bandwidth so that the situation of Fig. 4(c) applies. The band will be of the same shape as the nickel band except for the gap between the energy levels [see Fig. 5(a)]. The band will fill just as in the rigid band picture and the magnetic moment will decrease according to the electron/atom ratio. There is no change from the rigid band model. (See also next section.)

(*2*) *Cobalt and iron.* Again the energy level splitting is small so that the band shape is roughly unchanged. The gap will now lie above the nickel energy level [Fig. 5(b)], but the band will be filled to a point above the gap where the situation is just like that of the rigid band model. The magnetic moment will increase as the electron/atom ratio decreases, according to the usual two-band picture of ferromagnetism. Note, however, that for large iron concentrations a behavior similar to that of manganese is found, which is a deviation from the solution proposed here.

(*3*) *Chromium and vanadium.* These elements have valences considerably different from that of nickel and the rigid band model does not explain the behavior of their magnetic moments. According to the model of this paper, since the energy splitting is large, the situation of Fig. 4(d) will apply, the band becoming two bands, one about each energy level. On this picture the lower band will contain ~10 states per nickel atom, so that, since the electrons will fill the lowest available states, the band around the nickel energy level will be filled by the impurity *d* electrons, as shown in Fig. 5(c), so that these elements behave in a similar manner to copper and zinc. This filling of the band accounts for the decrease in magnetic moment observed experimentally, in contradiction to the rigid band model where the band empties . (See Fig. 6, in which the heavy line shows the behavior predicted by the rigid band model.)

(*4*) *Manganese.* One might expect the behavior of manganese in nickel to be anomalous even given the crudity of the model used here, since the manganese energy level, and hence the gap in the density of levels, is near to the nickel Fermi level [see Fig. 5(d)]. Without a more detailed calculation involving some theory of ferromagnetism, it is impossible to suggest exactly what the model predicts. One of many explanations is perhaps worth mentioning. The nickel band is assumed to just overlap the manganese energy level, so that at first an almost common band is formed with the result that the moment increases as increased proportions of manganese reduce the electron/atom ratio. As the nickel bandwidth decreases it will pull away from the manganese energy level to such an extent that the model of Fig. 4(d) is appropriate, so that the manganese *d* electrons will fill the nickel band, reducing the magnetic moment as in NiCr (see Fig. 6). The behavior of nickel-manganese alloys is indeed anomalous, some magnetic ordering changes being involved. These ordering changes may not be entirely unrelated to the discussions of this paper, since each of the *d* subbands will separately behave as in Figs. 4 and 5. The bandwidths will vary between the subbands and so vary the energy splittings. One must clearly have a much more detailed understanding of the band structure in the pure metals before being able to make definitive statements about the magnetic-ordering question.

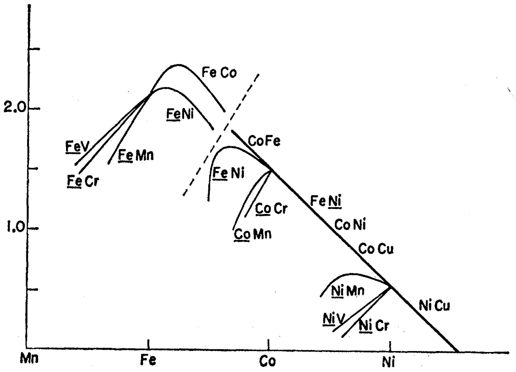

FIG. 6. The number of unpaired spins per atom plotted against electron/atom position in the periodic table. fcc crystals are to the right of the dashed line, and bcc crystals to the left. See, e.g., the review by J. Crangle [*Electronic Structure and Alloy Chemistry of the Transition Elements*, edited by Paul A. Beck (Interscience Publishers, Inc., New York, 1963)].

(b) Cobalt Based Alloys

(*1*) *Iron, nickel, and copper.* As in the nickel alloys, provided the energy splitting is sufficiently small, the rigid band model gives a correct explanation of the band shape, the gap in the band predicted by the model discussed above being well clear of the Fermi level.

(*2*) *Chromium and manganese.* The picture here is the same as for NiV and NiCr, the *d* band forming around the impurity *d* level loses its electrons to the band around the cobalt *d* level, which thus fills up.

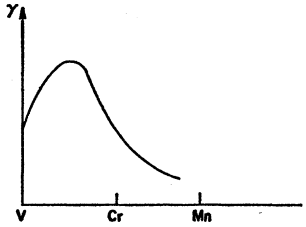

FIG. 7. Suggested specific heat of VNi plotted against electron/atom ratio.

(c) Iron Based Alloys

(*1*) *Manganese, cobalt, vanadium, and chromium.* Here again the rigid band picture prevails, so that only the electron/atom ratio is important.

(*2*) *Nickel.* The behavior of FeNi is not really well described by this model, since the band gap should be well clear of the level to which the band is filled. One would expect the rigid band model to work correctly. An effect similar to that involved in NiMn might be the cause of this behavior.

It will be seen, therefore, that this model explains in a qualitative manner nearly all the magnetic moment results for the transition-metal alloys. In order to get the model in its proper perspective, it is useful to see to what extent such a model could arise from other viewpoints. The approach to alloys which is usually adopted is one in which the effect of an impurity potential on the band structure of the host crystal is analyzed. Such calculations involve screening and other effects by means of which good agreement with experiment can often be obtained. A result very similar to the one given above has been given in such terms by Friedel.[7,10] What happens in Friedel's picture is that in, e.g., CoCr, the Cr *d* shell becomes a resonant level above the Fermi energy and at least one of its magnetic subbands will become empty, the electrons going mainly into the *d* band with the opposite spin direction. The remaining electrons in the Cr *d* band must then be considerably extended in space to account for the neutron diffraction data,[11] which shows that the reduction in magnetic moment occurs around the Co atoms and not by an increase in the moment of the Cr atoms in the opposite direction. Such a viewpoint is not too far different from that discussed in this paper.

If the model suggested above is correct for the transition metals, then the specific heat for metals of large valency difference should be different from that predicted by the rigid band model, especially near the lowest electron/atom values. As the low-atomic-number energy band empties, one should observe a peak in the specific heat such as drawn in Fig. 7 for VNi.[11a]

Thus, the picture given in this paper, crude as it is, can explain fairly well the behavior of the *d* electrons in the transition-metal alloys. With further refinement, and probably with some more detailed understanding of the pure-metal band structure, it seems likely that these alloys could contribute much to one's understanding of the problem of magnetism.

Before leaving this topic it is of interest to compare the theory presented so far with an approach used by Hubbard[12] to a different problem. The problem considered by Hubbard is that of the effect of correlations on narrow energy bands. He takes first only *s* bands and extends the theory in a second paper[13] to include *d* bands. The particular correlation effect which Hubbard considers is the effective repulsion felt by electrons of opposite spin because of exchange integral effects. Thus an electron of given spin sees a different potential depending on whether the ion in question is or is not already occupied by an electron of opposite spin. Hence the problem of determining the band structure for electrons of spin-up (say) is like an alloy problem, and will be given by curves like Figs. 4(c) or 4(d) depending on the parameters involved. The band structure for spin-down electrons can then be determined in terms of the spin-up electrons and the whole treated self-consistently. Such a treatment is outside the scope of this paper, but it is worthy of note that the curves of Figs. 3 and 4 are almost identical with those derived by Hubbard.

V. ALLOYS OF THE TRANSITION METALS WITH OTHER ELEMENTS

Following the remarks of the Introduction, and the proof given in the Appendix, the behavior of an alloy is described by the *t* function

$$t' = (1-d)t^1 + dt^2, \tag{19}$$

compounded from the *t* functions of the alloy constituents. In the last section the *d* part only was considered for the transition metals. Consider now the alloy FeAl discussed already in Sec. II. The *t* function for the Al ion will contain only a very small *d* part, since the lowest *d* state in aluminum is a resonant state far above zero energy. Thus for the *d* levels one has $t' \simeq (1-d)t^2$, precisely as was discussed in Sec. II. Thus, in the case of alloys between transition metals and lighter elements, one expects the *d* band to behave as discussed in that section, the bandwidth reducing, but the shape remaining constant.

The behavior of the *s* and *p* bands has thus far been neglected. The *t* functions for both *s*- and *p*-angular momenta will have pairs of singularities corresponding to those of the constituent *t* functions. The bands will be mixed just as in the ordinary metal case, so the behavior of the alloy *s*, *p* bands is likely to be extremely complicated. The only possibility of a simplifying feature in this case is the large width usually associated with these bands. If this dominates the splitting be-

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[10] J. Friedel, Nuovo Cimento Suppl. 7, 287 (1958).

[11] C. G. Shull, Congres Solvay, Bruxelles, 1954 (unpublished).

[11a] *Note added in proof.* Experimental results on VNi alloys do not show this structure (T. M. Srinivasan, unpublished).

[12] J. Hubbard, Proc. Roy. Soc. (London) **A276**, 238 (1963).

[13] J. Hubbard, Proc. Roy. Soc. (London) **A277**, 237 (1964).

tween energy levels, then one might expect a rigid band type of theory to work except for isolated alloys where the Fermi surface lies close to one of the gaps. The prescription suggested by this theory is as follows. The t functions for the s and p bands in the alloy have to be formed separately from those of the pure metals. One must then consider the mixing of the bands corresponding to these averaged t functions. It will be noticed that the work of Cohen and Heine,[6] which gives such good agreement with many experimental results, could be considered to use just such a prescription. The policy in this paper is to neglect the s-p band problem altogether and to derive only those results which do not need a discussion of this point. Thus in the alloys among the transition metals, discussed in the preceding section, it was implicitly assumed that the alloying did not change significantly the general shape of the s-p band and in particular the number of s states available below the top of the d band.

Such an assumption concerning the s and p bands can also be made in the case when the alloy constituents are not both transition metals. In this case, however, one must be careful to fix the position of the modified bands with respect to the d band. Define the "solvent Fermi level" by putting into the modified s and p bands the number of electrons appropriate to the solvent atom. When solute atoms are added to the solvent crystal, the levels will adjust themselves to minimize the energy. If the bands arising from these levels are filled with the number of electrons appropriate to the solute, one will find a "solute Fermi level." If this level lies above that of the solvent, then electrons will spill over into the solvent bands. Thus, in the NiV alloys discussed earlier, the vanadium "Fermi level" is considered to lie above that of nickel.

The suggestion of this paper concerning the difference between FeAl and NiAl alloys can then be stated in the form of a comparison of the Fermi levels involved. What seems to happen is that the aluminum Fermi level adjusts itself in iron, and in other host metals to be nearly the same as the solvent Fermi level. This would mean no spill over of electrons into the iron d band, which contains, therefore, the same number of electrons/atom with the result that the magnetic moment per iron atom does not change.[14] This last conclusion depends upon the result of Sec. II which showed that only the bandwidth and not the band shape changes with increased impurity concentration. Also the low-temperature specific heat does not change in agreement with experiment. That this does not work for nickel[15] would seem to be due to the aluminum Fermi level lying above that of nickel, so that the nickel d band is filled, the magnetic moment being reduced. It would certainly seem that it is the behavior of NiAl which is anomalous rather than FeAl. One possible reason for the solvent and solute Fermi levels being equal could be simply that the aluminum prefers to be electrically neutral, so that the appropriate number of electrons arrange themselves to stay near to the Al ions.

The conclusions just drawn may well not work for the lighter transition elements, since the d bands there are not too tightly bound and the results of Sec. II will not apply. Thus, the behavior of TiVAl ternary alloys is not in contradiction to the above remarks.

VI. CONCLUSIONS

It has been shown how the rigid band model for the d electrons of transition metals may be improved to account for the experiments on the magnetic moments of alloys involving transition-metal elements having a large valency difference. The theory proposed has been discussed only in a qualitative fashion, but seems to fit the results quite well. A simple physical picture of how the rigid band model breaks down has been given by analogy with a pure-metal tight-binding calculation.

All this is not very startling, and could even be described as an empirical correlation of the experimental results. This is, however, not quite fair, since the theory itself is based on approximations which are probably valid in the cases discussed and which could be worked out quantitatively if such an elaborate calculation were justifiable.

The principal virtue of the whole scheme is that it does open the possibility that the transition-metal-alloy experimental results may be of great value in understanding the phenomena in the pure transition metals. This has already occurred in the dilute alloys of the transiton metals in other substances, which have introduced several new features into the problem of ferromagnetism.

ACKNOWLEDGMENTS

The author is grateful to Professor Sir Nevill Mott and to Professor S. F. Edwards, who between them were responsible for the inception of this work. He is also grateful to Professor J. Bardeen, Professor P. A. Beck, and Dr. J. Hubbard both for some useful suggestions and criticisms, and for many stimulating discussions concerning the material presented in this paper.

APPENDIX

(a) The Geometric Approximation with Two Types of Potential

The symbolic series (I2.2) for the T function may be written in the same form

$$T=\sum_{\alpha} t_\alpha+\sum_{\alpha\neq\beta} t_\alpha G_0 t_\beta+\sum_{\alpha\neq\beta,\beta\neq\gamma} t_\alpha G_0 t_\beta G_0 t_\gamma+\cdots,$$

where more than one type of potential is present, but now t_α is the t function, centered on the position R_α, corresponding to the type of potential present on the

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[14] A. Arrott and H. Sato, Phys. Rev. **114**, 1420 (1959).

[15] R. M. Bogarth, *Ferromagnetism* (D. Van Nostrand and Company, Inc., New York, 1951).

site R_α. To make this point explicit and to assist in the summation of the series it is necessary to split T into four parts, given by

$$T^{11}=\sum_{\alpha} t_\alpha{}^1+\sum_{\alpha\neq\beta} t_\alpha{}^1 G_0 t_\beta{}^1+\sum_{\alpha\neq\beta,\beta\neq\gamma} t_\alpha{}^1 G_0 t_\beta G_0 t_\gamma{}^1+\cdots, \tag{A1}$$

$$T^{12}=\sum_{\alpha\neq\beta} t_\alpha{}^1 G_0 t_\beta{}^2+\sum_{\alpha\neq\beta,\beta\neq\gamma} t_\alpha{}^1 G_0 t_\beta G_0 t_\gamma{}^2+\cdots, \tag{A2}$$

with similar definitions for T^{21} and T^{22}. Here $t_\alpha{}^i$ is given by the t function corresponding to the potential v_i, when the atom at α is of type i, and is otherwise zero. T^{ij} corresponds to that part of the total T function in which the electron scatters firstly off an atom of type i and lastly off one of type j. Each internal summation in the third and higher order terms will also split into separate summations over the atoms of types 1 and 2. (These and the following remarks may be extended in a trivial manner to alloys with more than two types of atoms present.)

Now proceed exactly as in I. Each t function is analyzed into its angular-momentum components and the angular integrations, involving G_0, carried out [cf. (I2.7)]. The summation corresponding to (I2.8) is now complicated by the presence of the two different potentials. The approximation to be used is, however, still the same; each $S^{\alpha\beta(ij)}$ is replaced by its average value. The bracketed superscripts here indicate that the S in question lies between t functions corresponding to potentials of types i and j. Thus, each $S^{\alpha\beta(ij)}$ will be replaced by

$$S^{(ij)}=\frac{1}{N_i}\sum_{\alpha\neq\beta} S^{\alpha\beta(ij)}, \tag{A3}$$

where N_i is the number of atoms of type i. As in I, this approximation leads to the correct answer in the case of a perfect lattice (i.e., an ordered alloy) and is rather hard to discuss in any other case. It should be a good approximation in the case of a substitutional alloy with a small proportion of impurities. In the case of alloys in which the two components appear in proportions of the same order, the approximation should again be fairly good provided that the electronic mean free path is much longer than some local "range of ordering." As suggested in the text, the approximation is likely to predict least accurately the details of the density of states near band edges.

Each $S^{(ij)}$ is now treated as in (I2.10) to (I2.14) and the radial integrations performed [cf. (I2.15)]. There are now two sets of radial integrals for t^1 and t^2. Finally (A1) and (A2) take the forms:

$$\begin{aligned}T^{11}(\mathbf{k})=(4\pi)\sum_{LL'} N_1 Y_L(\mathbf{k})Y_{L'}(\mathbf{k})\{&t_l{}^1(k,k)\\&+[\mathbf{t}^1(k,E^{1/2})\{\mathbf{G}^{11}+\sum_{i=1,2}\mathbf{G}^{1i}\boldsymbol{\tau}^i\mathbf{G}^{i1}\\&+\sum_{i,j=1,2}\mathbf{G}^{1i}\boldsymbol{\tau}^i\mathbf{G}^{ij}\boldsymbol{\tau}^j\mathbf{G}^{j1}+\cdots\}\mathbf{t}^1(E^{1/2},k)]_{LL'}\},\end{aligned}$$

$$\begin{aligned}T^{12}(\mathbf{k})=(4\pi)^2\sum_{LL'} N_1 Y_L(\mathbf{k})Y_{L'}(\mathbf{k})[&\mathbf{t}^1(k,E^{1/2})\\&\times\{\mathbf{G}^{12}+\sum_{i=1,2}\mathbf{G}^{1i}\boldsymbol{\tau}^i\mathbf{G}^{i2}+\cdots\}\mathbf{t}^2(E^{1/2},k)]_{LL'},\end{aligned}$$

where $\boldsymbol{\tau}^i=\mathbf{t}^i(E^{1/2},E^{1/2})$, with similar expressions for $T^{21}(\mathbf{k})$ and $T^{22}(\mathbf{k})$. Care must be taken in summing these series, for the $\mathbf{G}^{ij}$ are already matrices (with respect to angular momentum) without regard for the superscripts i, j. The sums are in terms of two denominators $\mathbf{M}_1$ and $\mathbf{M}_2$

$$\begin{aligned}\mathbf{M}_1&=(1-\mathbf{G}^{22}\boldsymbol{\tau}^2)(\mathbf{G}^{12}\boldsymbol{\tau}^2)^{-1}(1-\mathbf{G}^{11}\boldsymbol{\tau}^1)-\mathbf{G}^{21}\boldsymbol{\tau}^1,\\ \mathbf{M}_2&=(1-\mathbf{G}^{11}\boldsymbol{\tau}^1)(\mathbf{G}^{21}\boldsymbol{\tau}^1)^{-1}(1-\mathbf{G}^{22}\boldsymbol{\tau}^2)-\mathbf{G}^{12}\boldsymbol{\tau}^2,\end{aligned} \tag{A4}$$

and are explicitly

$$\begin{aligned}T^{11}(\mathbf{k})=(4\pi)^2\sum_{LL'} N_1 Y_L(\mathbf{k})Y_{L'}(\mathbf{k})\{&t_l{}^1(k,k)\delta_{LL'}\\&+[\mathbf{t}^1(k,E^{1/2})\mathbf{M}_1{}^{-1}\{\mathbf{G}^{21}+(1-\mathbf{G}^{22}\boldsymbol{\tau}^2)(\mathbf{G}^{12}\boldsymbol{\tau}^2)^{-1}\mathbf{G}^{11}\}\\&\times\mathbf{t}^1(E^{1/2},k)]_{LL'}\},\end{aligned} \tag{A5}$$

$$\begin{aligned}T^{12}(\mathbf{k})=(4\pi)^2\sum_{LL'} N_1 Y_L(\mathbf{k})Y_{L'}(\mathbf{k})\{&\mathbf{t}^1(k,E^{1/2})\mathbf{M}_1{}^{-1}\\&\times[\mathbf{G}^{22}+(1-\mathbf{G}^{22}\boldsymbol{\tau}^2)(\mathbf{G}^{12}\boldsymbol{\tau}^2)^{-1}\mathbf{G}^{12}]\mathbf{t}^2(E^{1/2},k)\}_{LL'}.\end{aligned} \tag{A6}$$

$T^{22}(\mathbf{k})$ and $T^{21}(\mathbf{k})$ are found by interchanging superscripts 1 and 2 throughout Eqs. (A5) and (A6).

These expressions for $T(\mathbf{k})$ are clearly too complicated to be of any real general use, even though in any specific problem once the potentials and their distribution are known, the calculation of $\rho(\mathbf{k},E)$ is not a great deal harder than a similar calculation involving only a single type of potential. The dominant features can be obtained from the zeros of the denominators, i.e., when $|\mathbf{M}_1|=0$, $|\mathbf{M}_2|=0$. (The zeros of $|\mathbf{M}_1|$ and $|\mathbf{M}_2|$ are actually identical.) For substitutional alloys the equations are a little simpler, and in the particular case of disordered substitutional alloys, to be discussed in part (b) of this Appendix, can be reduced to a useful form which has the straightforward physical interpretation discussed in the text. There is a good chance that in the ordered case too a useful expression could be derived. This has not so far been attempted.

(b) The Substitutional Alloy

If it is supposed that the atoms forming the alloy are distributed on a perfect lattice, in such a way that the solute atoms are randomly distributed on the lattice sites, then the above formulas can be reduced to more convenient proportions. Following (I5.2), $S^{(ij)}$ can be written in terms of the correlation functions

$$c^{(ij)}(\mathbf{l})=\left\langle\frac{1}{N_i}\sum_{\alpha\neq\beta} e^{i\mathbf{l}\cdot(\mathbf{R}_\alpha{}^i-\mathbf{R}_\beta{}^j)}\right\rangle.$$

The superscript to $\mathbf{R}$ indicates the type of potential which must be present at the site $\mathbf{R}$ in order that the term be included in the sum. In the case being considered here, all the $c^{(ij)}$ are the same to within factors involving the proportion of the solute present, d. Such a correlation function was evaluated explicitly in the text [see Eqs. (4) and (5)], and the details will not be given here. In terms of the perfect-lattice correlation function $c^0(\mathbf{l})$ the results are

$$\begin{aligned} c^{(11)}(\mathbf{l}) &= c^{(21)}(\mathbf{l}) = (1-d)c^0(\mathbf{l}), \\ c^{(22)}(\mathbf{l}) &= c^{(12)}(\mathbf{l}) = dc^0(\mathbf{l}). \end{aligned} \tag{A7}$$

As was discussed in the text, following Eq. (7), it is now necessary to decide whether to discuss the case $E>0$ or the case $E<0$. The former case leads to the density of states having a width, which is physically correct, whilst the latter leads to the simpler expressions for the density of states. It will again be assumed here that the error involved in neglecting the diffuseness in the density of states is small and that it can be ignored without serious error.

Thus for $E<0$, the function $\mathbf{G}^0$ of (I2.14) for the perfect host lattice is the only way in which the lattice structure enters the problem, the $\mathbf{G}^{ij}$ being given from (A7) by

$$\mathbf{G}^{22} = \mathbf{G}^{12} = d\mathbf{G}, \quad \mathbf{G}^{11} = \mathbf{G}^{21} = (1-d)\mathbf{G}.$$

The matrices $\mathbf{M}_1$ and $\mathbf{M}_2$ simplify a great deal now, becoming

$$\begin{aligned} \mathbf{M}_1 &= [(1-d)\mathbf{G}\boldsymbol{\tau}^2]^{-1}[1-d\mathbf{G}\boldsymbol{\tau}^2-(1-d)\mathbf{G}\boldsymbol{\tau}^1], \\ \mathbf{M}_2 &= [d\mathbf{G}\boldsymbol{\tau}^1]^{-1}[1-d\mathbf{G}\boldsymbol{\tau}^2-(1-d)\mathbf{G}\boldsymbol{\tau}^1], \end{aligned}$$

so that, finally, the important factor in the expression for $\rho(\mathbf{k},E)$ is given by

$$\begin{aligned} \operatorname{Im}\langle T(\mathbf{k})\rangle = \operatorname{Im}\langle \sum_{ij=1,2} T^{(ij)}(\mathbf{k})\rangle = N(4\pi)^2 \sum_{LL'} Y_L(\mathbf{k})Y_{L'}(\mathbf{k})\{[d\mathbf{t}^2(k,E^{1/2})+(1-d)\mathbf{t}^1(k,E^{1/2})] \\ \times \operatorname{Im}[\{1-[d\boldsymbol{\tau}^2+(1-d)\boldsymbol{\tau}^1]\mathbf{G}\}^{-1}\mathbf{G}][d\mathbf{t}^2(E^{1/2},k)+(1-d)\mathbf{t}^1(E^{1/2},k)]\}_{LL'}, \end{aligned} \tag{A8}$$

where the reality of $\mathbf{t}^i(p,q)$ for $E<0$ has been used. Now, by comparing with (I2.16) in the same region of energy, one is able to see that Eq. (A8) is the density of states for a perfect lattice having a pseudo t function given by

$$\mathbf{t}' = d\mathbf{t}^2 + (1-d)\mathbf{t}^1, \tag{A9}$$

and this is exactly the result predicted by the simple physical arguments of the Introduction.

In this approach one sees more clearly the approximations which have contributed to the derivation of Eq. (A9). They are:

(1) The geometric approximation, which implies that certain terms have been wrongly evaluated. These terms are those in which the electron scatters off one potential (all multiple scattering terms are included by the use of the t function), moves away to scatter elsewhere, then returns to scatter off the original potential. It has been suggested, without any real proof, that this approximation only leads to significant error when the energy being considered lies in a band gap or near to a band edge.

(2) The neglect of diffuseness in the density of states. This is very similar to the suggestion that there exists a reasonably well-defined Fermi surface in alloys. This was discussed to some extent in the text where once more the error seemed likely to be largest near the band edges. However, this width in the density of states is heavily involved in transport properties and must be carefully considered when calculations of transport coefficients are being attempted.