states with an upper edge 5 ev below the vacuum level. Energy distribution data are consistent with this picture. Krumhansl has arrived at a more complete energy structure by combining this result with the optical data obtained at Cornell.[13]

Photoelectric data for $h\nu<5$ ev are treated only briefly. They are not believed to represent intrinsic emission from BaO. Yields in this region are variable and are ascribed to imperfections, some of which may be metastable; a more complete interpretation has not been attempted. Such yields are complicated further by Franck-Condon effects, by rapid changes in optical properties, and by an effect like the exciton-enhanced photoelectric emission observed in alkali halides.

We are indebted to Harvey Brooks, J. A. Burton, Malcolm Hebb, Conyers Herring, and A. W. Hull for stimulating conversations.

[13] J. Krumhansl, Phys. Rev. **82**, 575 (1951) (T). Calculations by D. A. Wright, Proc. Phys. Soc. (London) **60**, 13 (1948), place the edge and center of the occupied band 2.6 and 6.6 ev, respectively, below the vacuum level. This location of the band center is consistent with our result; the empirical value of the band width used by Wright in locating the edge was probably too large.

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Statistical Theory of Properties of Solid Solutions

R. SMOLUCHOWSKI
Carnegie Institute of Technology, Pittsburgh, Pennsylvania
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Properties of binary solid solutions are considered from the point of view of the fluctuation of local composition in the crystalline lattice. These variations influence the properties of the alloys by varying the corresponding local concentration of electrons. A simple general statistical method is given for calculating properties of random and ordered solid solutions. The theory is applied to saturation magnetization, temperature coefficient of electrical resistivity, thermoelectric power, and to other properties in various alloys. A satisfactory agreement with experiment is obtained.

1. INTRODUCTION

THE studies of properties and of behavior of solid solutions are very important for understanding of metals. The change of composition makes possible, in favorable cases, the distinction between the influence of various factors and the estimate of the validity of the inevitable theoretical approximations. Many of the properties are closely related to the behavior of "free" electrons and in particular to their concentration. Typical examples here are saturation magnetization, magnetic susceptibility, electronic specific heat, Hall effect, electrical resistance, optical properties, etc. In the conventional theoretical approach to these phenomena, in accord with the band theory point of view, the metal is treated as a whole and the particular property is related to the average electronic concentration.

This strict band approach is justified when the electrons in question are very nearly free and their wavelength large compared to the atomic size. For more tightly bound electrons, as for instance in transition metals, the local electronic configuration of an atom and of its nearest surroundings should be taken into account. Such theories, if exact, are very complicated and therefore a simpler, approximate procedure is desired. The present paper describes such a method which incorporates the main features of the band theory and of the "local" point of view.

Since the average electronic concentration does not depend upon the state of order in a crystal lattice, it is clear that a statistical treatment of local electronic configuration is particularly important in a consideration of the influence of order[1] on the properties and phenomena mentioned above. A first attempt in this direction was made[2] in a theory of the influence of order on magnetostriction of iron-cobalt alloys. It appeared later that the procedure there employed, although satisfactory for the specific purpose, led to a wrong dependence of the saturation magnetization on composition. The new method here presented is a simple general tool, it explains various experimental facts (including the relation between order and magnetostriction), and it applies to many alloy systems.

2. THE STATISTICAL METHOD

The basic procedure in the theory is to calculate first the fluctuations of the local electronic configuration, then to estimate their individual contributions to the particular property and finally to sum the contributions of the various fluctuations. The first question is thus the choice of the proper size n of the group of atoms within which the electronic fluctuation has a significant meaning for the particular property. A natural assumption is to consider as a basic unit an atom and its nearest neighborhood. In a close-packed lattice, either

[1] R. Smoluchowski, Intern. Conf. on Magnetism, Grenoble, 1950; J. phys. radium **12**, 389 (1951); Phys. Rev. **78**, 638 (1950).
[2] R. Smoluchowski and J. E. Goldman, Phys. Rev. **75**, 140 (1949).

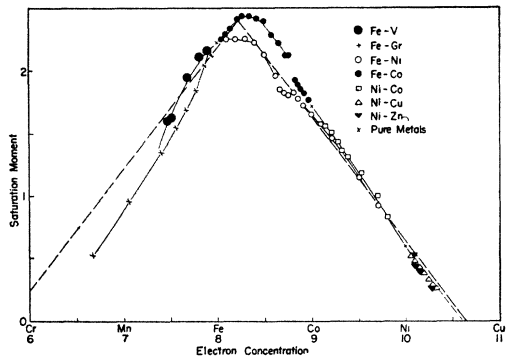

FIG. 1. Saturation magnetization in alloys.

cubic or hexagonal, an atom has twelve nearest neighbors and so, together with the central atom, there are thirteen atoms in the basic group. In a body-centered lattice, the six second nearest neighbors are only about 15 percent further out than the eight nearest and so a group of fifteen atoms, an atom and its fourteen neighbors, seems to be a proper choice (the third nearest neighbors are already over 40 percent further away). For a perfectly random binary alloy of A and B, in which the concentration of atoms A is p and the concentration of atoms B is $q=1-p$, one calculates the probability of having r atoms B among the n atoms in the group from the usual formula,

$$P_{n,r}=\binom{n}{r}p^{n-r}q^{r}. \tag{1}$$

Knowing the number of free electrons in both kinds of atoms, one obtains the probability of the occurrence of a particular local electronic concentration. The next step, the calculation of the contributions of the various local fluctuations to the particular property depends much upon the state of the theory of the property, upon whether the contributions are additive or not, and will in general differ from case to case.

3. SATURATION MAGNETIZATION

Saturation magnetization of alloys is usually correlated with electron concentration in an essentially

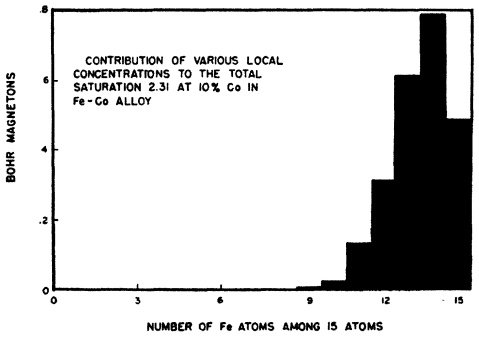

FIG. 2. Contribution of various fluctuations to the saturation moment of a random Fe-Co alloy.

semi-empirical manner, using the assumption that the $3d$-band is divided into two parts of appropriately chosen size. This theory leads, in the well-known manner, to a saturation moment which decreases linearly, at a rate of one Bohr magneton per electron, from its maximum value of about 2.56 at 8.35 electrons per atom as indicated in Fig. 1. A criticism of this point of view and an alternate explanation of the behavior was proposed elsewhere.[1] We assume that an ideally linear behavior of the saturation magnetization on both sides of the maximum is understood.

a. Iron-Cobalt Alloys

We shall apply now the method outlined above to the body-centered iron-cobalt alloys. For several reasons, this is a particularly simple and interesting case: the maximum saturation occurs at a 35 percent Co composition, the body-centered phase of that system extends up to 70 percent Co, and the lattice constant, the α-γ transformation temperature, the melting point, etc.,

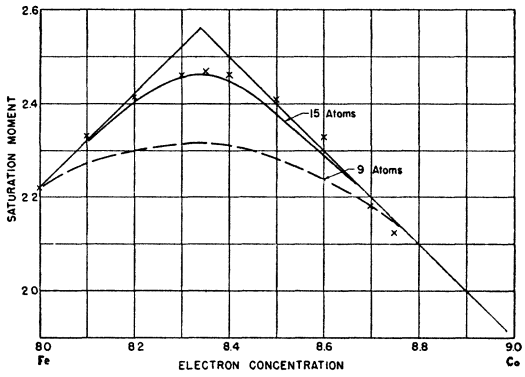

FIG. 3. Local and statistically averaged saturation moments for Fe-Co alloys.

vary only a little in that whole range. This is in contrast with the iron-nickel system considered later.

The saturation moment of pure iron is 2.22, that of body-centered cobalt is not known and so we have to obtain it by extrapolating the data for cobalt-rich alloys in the body-centered phase. The result is 1.90 as compared with 1.71 for hexagonal cobalt. On the basis of these values, the saturation magnetization reaches the maximum value of 2.56 at an electron concentration 8.34.

The linear relationship shown in Fig. 1 makes it possible to assign to each fluctuation of electron concentration a contribution to the saturation moment. These contributions, multiplied by the proper probability factors (1) for the occurrence of various ratios of atoms Fe and Co in the group of 15 atoms, are shown in Fig. 2 for an alloy containing 10 percent Co. The total moment in that case is 2.31. The results for the whole range of composition, together with the experimental points are shown in Fig. 3. The agreement is within $1\frac{1}{2}$ percent which is satisfactory in view of the approximate

character of the theory. It may be noted here that had we assumed that the basic group in a body-centered lattice consists only of the eight nearest neighbors and the central atom, then the theoretical curve would fall much too low as shown in Fig. 3.

As indicated in the foregoing, the statistical treatment of local concentrations is particularly suitable for considering the influence of order since the degree of order does not influence the average electron concentration. The calculation of the saturation moment in a perfectly ordered 50:50 iron-cobalt alloy, on the basis of our theory, is as follows. In the ordered alloy there are only two alternatives in composition of the 15-atom group, either seven iron atoms and eight cobalt atoms or vice versa. The two electron concentrations are 8.467 and 8.533 giving for the saturation moments 2.43 and 2.37 with the average value 2.40. The theory indicates thus an increase of the saturation moment of about one percent on ordering. Experiment gives an increase of about four percent, which is not too satisfactory an agreement, although the sign and the order of magnitude are correct.

An interesting check of this theory can be obtained from neutron diffraction experiments. The presence of the small difference of only three percent between the moments 2.43 and 2.37 should be easily distinguished from the presence of the large difference of about 25 percent between the normal saturation moments of pure iron and pure cobalt as required by the usual theory. Preliminary, though not conclusive, results[3] seem to be in agreement with the existence of a small rather than large difference between the magnetic moments associated with the Fe and Co sites.

b. Iron-Nickel Alloys

A similar calculation has been made for the body-centered iron-nickel alloys using a 15-atom group. The difficulty in this case is due to the short range of composition within which the alloys are body-centered cubic and the highly irregular behavior of the lattice constant, which is presumably related to the complicated conditions in the two-phase region. The results are in fair agreement with experiment as shown in Fig. 4. In view of the uncertainty of extrapolation of the body-centered data to pure nickel, the usual value 0.6 was assumed for the saturation moment of nickel.

An interesting case in this alloy system is the face-centered cubic $FeNi_3$ composition in which an ordered lattice has a six percent higher saturation moment than the random lattice. It is natural to suppose that, since the face-centered iron is nonmagnetic, the iron atoms which are nearest neighbors in a random $FeNi_3$ lattice will not contribute to the saturation moment. This conclusion follows also from consideration of the known relationship between magnetic interaction, interatomic distance, and the size of the *d*-shell. The calculation of the saturation moment for the random $FeNi_3$ proceeds thus in the usual manner using a 13-atom group, but the contribution from each fluctuation is decreased in proportion to the iron-iron pairs. The result is 1.02 Bohr magnetons. In the ordered lattice we have again only two types of groups, a Ni atom surrounded by 8 Ni and 4 Fe atoms and a Fe atom surrounded by 12 Ni atoms. The average saturation moment corresponding to the two types of neighborhoods taken in proper ratio is 1.10. This corresponds to an increase of the saturation moment by eight percent in a rather good agreement with the experimental value of six percent. The absolute value of both calculated saturation moments is somewhat too low.

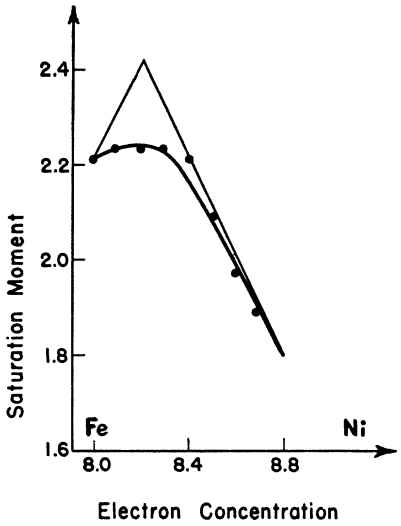

FIG. 4. Local and statistically averaged saturation moments for Fe-Ni alloys.

The procedure followed for the $FeNi_3$ alloy is applicable to other alloys[1] and can be briefly summarized as follows: In calculating contributions of the various concentration fluctuations account has to be taken of the variability of the magnetic interaction with distance between atoms as given, for instance, by the Néel curve.[1] Particular pairs of atoms in a fluctuation may lead to vanishing (or even negative) moments.

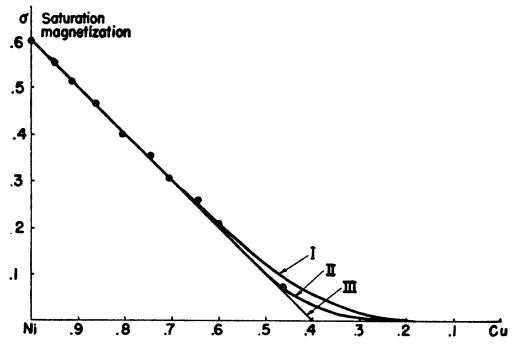

FIG. 5. Local and statistically averaged saturation moments for Cu-Ni alloys.

[3] C. G. Shull, private communication.

The sum of the thus adjusted contributions is the calculated total saturation moment.

c. Copper-Nickel Alloys

The copper-nickel system shows a very regular variation of the saturation moment with composition: starting with 0.6 at pure nickel, the moment decreases linearly with increasing copper content and extrapolates to zero at 60 percent copper in agreement with the gradual filling up of the d-band of nickel. It is thus important to see whether the statistical theory accounts satisfactorily for this behavior. The procedure is identical with that described previously: fluctuations of 13 atoms containing 6 or more nickel atoms contribute magnetic moments equal to the number of holes in the respective d-bands. The question whether all such fluctuations actually contribute irrespectively of the atomic arrangement will be taken up later. By multiplying the moments by the corresponding probability and summing the results, one obtains the curve I shown in Fig. 5. It appears that up to about 40 percent copper the behavior is linear and in agreement with experiment. At 54 percent copper, however, there is a definite discrepancy. This seems to be connected with the implicitly made assumption that as long as a fluctuation has less than 60 percent copper, it will contribute to the magnetic moment. We know that only three-dimensional arrays of atoms can be ferromagnetic and thus not all configurations of nickel atoms in a fluctuation will contribute to magnetism, although the fluctuation may have less than 60 percent copper. It seems natural to expect a configuration to be ferromagnetic if the nickel atoms form a cluster which extends across the 13-atomic group. A convenient way to express this condition is to require that in at least two neighboring close-packed directions, i.e., [110], all the neighbors of the central atom be nickel atoms. This condition is satisfied for all fluctuations having 8 and more nickel atoms. The probability that the condition is satisfied in other fluctuations is easily computed and for fluctuations containing seven and six nickel atoms it is 0.43 and 0.23 respectively. Thus the contributions of these fluctuations to the total magnetic moment have to be correspondingly reduced. Curve II in Fig. 5 shows the result. The agreement with the lowest experimentally certain point[4] is good.

It would be of great interest to go to slightly higher copper content and check the theoretically predicted deviation from linearity. An indirect confirmation of this nonlinearity is perhaps the large field dependence of magnetic susceptibility at 14 and 20°K in alloys containing 30 and more percent nickel as found by Kaufmann and Starr.[5]

[4] N. F. Mott and H. Jones, *Theory of Properties of Metals and Alloys* (Oxford University Press, London, 1936).
[5] A. R. Kaufmann and C. Starr, Phys. Rev. **63**, 445 (1943).

4. TEMPERATURE COEFFICIENT OF RESISTANCE

Transition metals show an abnormally high electrical resistance and, as shown by Mott,[6] the effect is satisfactorily explained by scattering of the conducting s-electrons into the unfilled states in the d-band. If the d-band is almost full, as it is in nickel, palladium, etc., the density of states $n(E)$ varies as

$$(E_0-E)^{\frac{1}{2}} \tag{2}$$

where E_0 corresponds to the top of the d-band. In that case, the probability of $s\rightarrow d$ scattering decreases with increasing temperature because of the temperature spread (of the order kT) of the Fermi distribution and the resulting change in the density of d-states into which the conducting s-electrons, at each E, can be scattered. Mott has calculated ϕ, the ratio of the relaxation time of conduction electrons with and without temperature spread of the Fermi distribution for various T/T_0 where T_0 is defined by $kT_0=E_0-E'$ and E' is the energy at Fermi surface. Multiplying the resistance calculated on the basis of the usual Gruneisen function by ϕ good agreement is obtained for palladium with $T_0=3450$. The change of $n(E)$ is greatest near the top of the band, and thus the effect of temperature on $s\rightarrow d$ scattering should be most pronounced for small T_0, and may lead to a vanishing or even negative temperature coefficient. The temperature-dependent resistance of nontransition, "normal," metals at not too low temperature, is proportional to T. For transition metals, it is thus proportional to $T\phi$ and

$$(d\rho/dT)(T/\rho)=1+(T/\phi)(d\phi/dT) \tag{3}$$

where ϕ depends upon T/T_0 and $d\phi/dT<0$. This temperature effect is, of course, independent of any ferromagnetic effects which also affect the $s\rightarrow d$ scattering and which are not being considered here.

The importance of $s\rightarrow d$ scattering indicates that in an alloy in proximity of a composition which corresponds to the boundary between an open and a filled d-band, the fluctuations of electron concentration should play an important role in determining the temperature coefficient of resistance. This is particularly well illustrated by the variation of the temperature coefficient of resistance in copper-nickel and silver-palladium alloys. In all such binary alloys, between Ni, Pd, Pt and Cu, Ag, Au, it is usually assumed that the 0.6 empty states in the unfilled d-band of the transition metal are gradually filled up by the excess of the s-electrons in the noble metal over the 0.6 electron in the s-band of the transition metal. The filling up would be completed at 60 percent of the noble metal. It would appear thus that the temperature dependence of resistance should be normal up to 40 percent of transition metal and from then on it may be abnormally low or abnormally high depending upon the importance

[6] N. F. Mott, Proc. Roy. Soc. (London) **153**, 699 (1936); **156**, 368 (1936); Proc. Phys. Soc. (London) **47**, 571 (1935).

of $s \rightarrow d$ scattering, ferromagnetic effects, etc. This conclusion is clearly not in agreement with experiment which shows that an anomalous influence of temperature is observed for as low contents of transition metals as 20 percent. It will be shown that the statistical theory of the local concentration fluctuations explains quantitatively the experimental facts.

a. Copper-Nickel Alloys

In a previous section, it was shown that the statistical method is in agreement with experimental data on the saturation moment in copper-nickel alloys. As is well known, the evidence indicates, with considerable certainty, that in these alloys, containing less than 40 percent copper, the $3d$-band is full. At higher nickel content, the $3d$-band is progressively less filled and finally the material becomes magnetic (at 400°K near 77 percent nickel). Figure 6 shows that the quantity $(d\rho/dT)(T/\rho)$ is not only low near 40 percent nickel, but it is abnormally low down to a nickel content of only 15 percent where, according to the band theory, there should be no $s \rightarrow d$ scattering. (As "normal" behavior a constant $(d\rho/dT)(T/\rho)$ is considered; this is not unreasonable in view of the difference of only 10 percent between the Debye characteristic temperatures of copper and nickel.)

In order to interpret this irregular behavior as due to the presence of local concentration fluctuations, we consider groups of 13 atoms, each having i transition atoms, a characteristic electron concentration c_i, resistivity ρ_i, probability of occurrence p_i, and a T_0 which we shall denote T_i. For each fluctuation an equation of type (3) is satisfied with the appropriate ρ_i and $\phi_i = \phi(T/T_i)$. Resistivities, in general, are of course not additive and so, in order to calculate the total $(d\bar{\rho}/dT)(T/\bar{\rho})$ resulting from the randomly distributed fluctuations in a given volume of metals, we use the formula,

$$\bar{\rho} = \prod_{i=0}^{13} \rho_i^{p_i}, \tag{4}$$

which gives

$$\frac{d\bar{\rho}}{dT}\frac{T}{\bar{\rho}} = 1 + \sum_{i=0}^{13} \frac{T}{T_i}\frac{p_i}{\phi_i}\frac{d\phi_i}{d(T/T_i)}. \tag{5}$$

This expression is further simplified by observing that Mott's numerically calculated ϕ can be approximated by $\exp[a(T/T_i)^2]$ with $a = 2.4$. We have then

$$\frac{d\bar{\rho}}{dT}\frac{T}{\bar{\rho}} = 1 - 2a\sum_{i=0}^{13} p_i\left(\frac{T}{T_i}\right)^2. \tag{6}$$

The critical concentration of 40 percent nickel corresponds to 7.8 Cu and 5.2 Ni atoms in the basic group. Thus for all fluctuations containing more than 8 Cu atoms $\phi = 1$ or $a = 0$. For other fluctuations, one obtains $T_i = T_0(n_i/0.6)^{\frac{1}{2}}$ from the known concentration n_i of empty d states in a particular fluctuation and the known $T_0 = 2200$ for nickel. The probabilities p_i are again calculated from the binominal coefficients applicable to perfectly random solid solutions. T_8 was put equal to T_7, since in these fluctuations the d-band is either just filled or almost full and the small uncertainty in the value 0.6 for the critical concentration of copper would make a clearcut distinction rather artificial. This point will be discussed again later.

The theoretical curve is compared with experimental points and with the best average experimental curve in Fig. 6. The data were taken from the work of Svensson[7] for $T = 400$°K. The comparison is made only for alloys containing less than 70 percent nickel, because at higher nickel content the alloys become ferromagnetic and there different effects play a role. The agreement is striking particularly in the position of the two concentrations at which the temperature coefficient of resistance vanishes. One of them, near 50:50, is the well-known constantan alloy. The good agreement in the

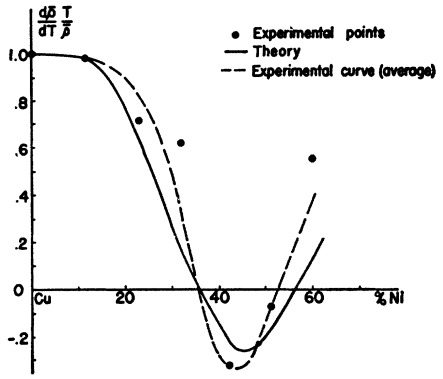

FIG. 6. Temperature variation of electrical resistance of Cu-Ni alloys.

absolute value of the minimum is rather fortuitous since, as mentioned before, and as follows from Eq. (4), most of the negative contributions are due to these fluctuations for which T_i is small and the latter is extremely sensitive to the critical concentration c_c at which the d-band is considered full. This sensitivity may be the reason why the unusually low temperature coefficients are relatively rare and are so much affected by minor soluble impurities. On the other hand, if the statistical treatment here used is correct, then the temperature coefficient of resistance can serve as a sensitive indicator of the exact value of the critical concentration. On the whole, one can say that, as a result of the presence of only discrete values of electron concentrations c_i encountered in the fluctuations, only these alloy systems will show a very small or even negative $d\bar{\rho}/dT$ in which the critical concentration c_c is close to one of the c_i's. The corresponding T/T_i is then very high. Thus a small change in c_c effects strongly

[7] B. Svensson, Ann. Physik (5) **25**, 263 (1936).

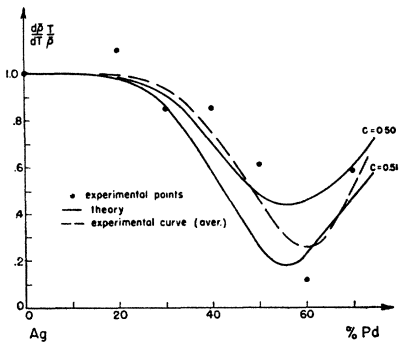

FIG. 7. Temperature variation of electrical resistance of Ag-Pd alloys.

the absolute value of $d\bar{\rho}/dT$ near the minimum, while the position of the minimum itself is always in proximity of c_c. In connection with the above, it should be kept in mind that in the calculation it was assumed that Mott's function ϕ, and its exponential approximation, is directly applicable to the copper-nickel alloys. This may not be actually the case in a more detailed treatment, although the uncertainty affects ϕ primarily for high T/T_i values which, as discussed above, are not too critical for the theory.

b. Silver-Palladium Alloys

These alloys present a case very similar to the copper-nickel alloys considered above. However, due to the lack of ferromagnetism there is no sensitive clue as to the exact composition at which the d-band is filled. Measurements of magnetic susceptibility, thermoelectric power, etc., permit the conclusion[4] that the d-band becomes filled up near 50 percent silver rather than at 60 percent as in the copper-nickel alloys. In his discussion of resistivity of palladium, Mott concluded that $T_0=3450°K$. Repeating the previous calculation with palladium concentrations, $c_c=0.50$ and $c_c=0.51$, one obtains the two curves shown in Fig. 7. The agreement is satisfactory. The curves illustrate also the previously discussed sensitivity of the absolute value of the minimum to a small variation in the critical concentration. The concentration $c_c=0.51$ seems to fit better.

On the basis of the above results, the conclusion might be drawn that palladium metal has about 0.5 electron in the s-band and 0.5 hole in the d-band. However, the relationship between the number of holes in the d-band of a pure metal and the concentration of an added element at which the band is full is perhaps not so simple as it is usually supposed. In other words, the difference between c_c for nickel-copper and for palladium-silver alloys may not be due simply to a difference in the number of holes c_h in the d-bands of the pure transition metals. The usual assumption in relating c_c to c_h is that at low concentration of the monovalent metal the number of electrons in the s-band is the same as in the pure transition metal, thus less than one, and that it does not change until the d-band is filled. This is not necessarily correct: the availability of electrons contributed by the noble metal will depend not only on the number of electrons but also on such factors as the ionization potential and differences in energy of the possible electronic states. It has been pointed out elsewhere[8] that these factors play an important role for instance in the anomalous influence of manganese on the α-γ transformation in iron, etc.

TABLE I. Ionization potentials.

	I	II		I	II
Cu	7.68	20.18	Ni	7.61	18.4
Ag	7.54	21.9	Pd	8.3	19.8
Au	9.19	20.0	Pt	8.9	18.47

A comparison of the first and second ionization potentials[9] for several elements shows clearly, Table I, the unusually loose binding of the valence s-electron in silver and the equally striking strong binding of the d-shell in silver and in palladium. It is very likely that these differences have an important effect on the electronic structure in alloys. For instance, it would be natural to expect in palladium alloys a stronger tendency to fill up the d-band than in nickel or platinum alloys. An example here is the disappearance of paramagnetic susceptibility in Au-Pd and Au-Pt alloys at 50 and at 65 percent gold respectively. Similarly, silver alloys would show a stronger tendency to fill up the d-band than copper or gold alloys. An example here is provided by the Pd-Ag and Pd-Au alloys, in which the minima of the thermoelectric power and of the temperature coefficient of electrical resistivity occur near 38 and 48 atomic percent of the noble metal respectively. Thus there are differences in the critical compositions without necessarily implying different numbers of holes in the d-bands in pure metals. The great similarity in the relative magnitude of the first and second ionization potentials of nickel and palladium makes it plausible to conclude that both metals have 0.6 hole in the d-bands. This agrees well with the final equilibrium concentration of hydrogen in palladium, which corresponds to 0.6 hydrogen atom per one atom of palladium.[10] It seems thus that as silver is added to palladium, the original number of 0.6 hole in the d-band is filled up in such a manner that at 50:50 there are no holes in the d-band (in the absence of fluctuations) and there are 0.5 electron in the s-band. This decrease in the number of s-electrons from 0.6 at pure Pd to 0.5 at the Ag-Pd composition is quite compatible with the simultaneous lowering of the average ionization potential of the s-electrons from 8.3 to $7.92=\frac{1}{2}(8.3+7.54)$ and raising of the corresponding quantity for the d-electrons from 19.8 to $20.35=\frac{1}{2}(19.8+21.9)$.

[8] R. Smoluchowski, Metal Progress **41**, 363 (1942); Phys. Rev. **61**, 390 (1942); R. Smoluchowski and J. S. Koehler, Ann. Rev. Phys. Chem. (1951).
[9] W. F. Meggers, J. Opt. Soc. Am. **31**, 39, 605 (1941).
[10] A. Sieverts and G. Zapf, Z. physik. Chem. **172**, 314 (1935).

5. THERMOELECTRIC POWER

As shown by Mott,[6] thermoelectric power of transition metals is closely related to the density of states near the top of the filled d-band; whenever the latter varies as the square root of the energy, the absolute thermoelectric power in a solid solution of a transition and a nontransition metal is given by:

$$S=\text{const}T(c-c_c)^{-\frac{1}{2}}\left\{\alpha+\left(\frac{c-c_c}{1-c_c}\right)^{\frac{1}{2}}\right\}^{-1};\quad c>c_c \quad (7)$$

where $\alpha=0.25$, c is the concentration of the transition metal and c_c is the critical concentration at which the d-band is filled. Similarly to the temperature coefficient of electrical resistance, the thermoelectric power reaches extreme value near the critical composition.

a. Palladium-Silver Alloys

As concluded previously, the d-band in palladium-silver alloys is filled up near the 50:50 composition. The thermoelectric power S obtained from (7) is shown in Fig. 8 as curve I, which represents the local thermoelectric power characteristic of individual fluctuations. The constant of proportionality was chosen to give agreement with experiment[11] for pure palladium at 900°C. The statistical procedure based again on a 13-atomic group gives the average thermoelectric power as indicated by curve II. Formula (7) assumes that neither s-electrons of palladium or of silver contribute to S. This is not strictly correct since, for instance, the thermoelectric power of silver, which is all due to s-electrons, though small, is not negligible. In view of this approximation, the agreement between calculation and theory is quite good.

b. Palladium-Gold Alloys

The calculations follow the same pattern as for palladium-silver alloys. As indicated previously, gold fills up the d-band in palladium at a slower rate than silver and thus it was first assumed that, as in the nickel-copper system, $c_c=0.40$. The result is shown in Fig. 9 by curve II which does not agree too well with experiment.[11] Putting $c_c=0.32$, a better fit, especially in the position of the minimum, is obtained, curve III. The corresponding local thermoelectric power is shown by curve I.

6. PARAMAGNETIC SUSCEPTIBILITY

The high paramagnetic susceptibility of transition metals is also related to the unfilled d-band and, in alloys with nontransition metals, it disappears at a concentration corresponding to a filled d-band. The theory[4] requires that the susceptibility be proportional to the density of states at the top of the band. However, the relative rate of decrease of the susceptibility with increasing content of the nontransition element as observed, for instance, in palladium-gold alloys is much too rapid for such a simple relation. The statistical method does not seem to improve the situation except for explaining the persistence of weak paramagnetism beyond the critical concentration. It seems thus that a change in the theory of paramagnetism of transition metals is necessary before a statistical method can be applied.

A similar conclusion follows from consideration of susceptibility of copper-nickel alloys below 40 percent nickel.[5] The variation of susceptibility with composition and temperature in that system is hard to reconcile with present theoretical explanations based on band theory. Some light on this problem may have been shed by the results of the statistical treatment of saturation magnetization in these alloys as discussed earlier.

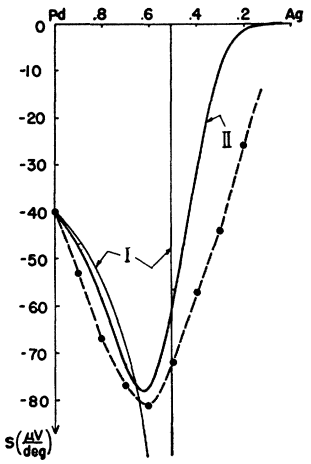

FIG. 8. Thermoelectric power of Ag-Pd alloys.

7. OTHER PHENOMENA

a. Magnetostriction

Consideration of the influence of order on magnetostriction is based on the calculation of the change of the

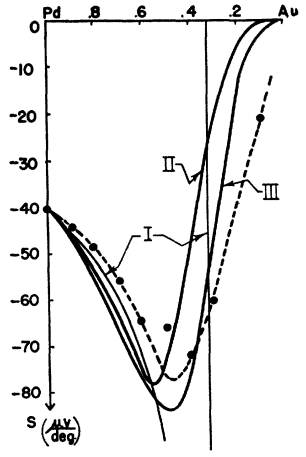

FIG. 9. Thermoelectric power of Au-Pd alloys.

[11] W. Geibel, Z. anorg. u. allgem. Chem. **69**, 38 (1910); **70**, 240 (1911).

effective magnetic moments[2] situated on the interacting lattice sites. The method here described gives good agreement with experiment.[1]

b. Electronic Specific Heat

A typical example of a possible application of the theory is the electronic specific heat of alloys which depends on the density of states $n(E_F)$ at the Fermi surface. To each local concentration fluctuation corresponds a local density of states with its characteristic electronic specific heat C_e. The total electronic specific heat is then easily obtained in an additive manner by taking into account the probability factor (1). The actual quantitative relation between $n(E_F)$ and C_e involves the effective electron mass, which is usually unknown and which may vary with local electronic density. Thus the validity of a strict comparison with experiment may be questionable. In certain cases simplifying assumptions are permissible and on that basis Goldman,[12] using the method here described, obtained an interpretation of the behavior of electronic specific heat and resistance in copper-nickel alloys.

Another important application of the statistical method to electronic specific heat may arise when there is a tendency to cluster[13] or to form short-range order. Both these tendencies should show up in the temperature dependence of electronic specific heat or rather in the influence of heat treatment on the electronic specific heat as measured at low temperatures. In that case, instead of the random probability, the corresponding expressions for nonrandom solutions[14] should be used. Typical systems in which the effect may be found are Au-Ni, Au-Mn, Cu-Pd, etc.

c. Crystal Structure and Lattice Constant

The role of electron concentration in determining crystal structure is well known and here the role of fluctuations of electronic concentration is particularly striking. For instance, the transformation between the body-centered and face-centered phases in iron and its alloys is extremely sensitive to changes in electron concentration[8] and small variations in composition affect the equilibrium range of existence of the two phases. It follows thus that fluctuations of the local electron concentration play a decisive role in the formation of potential nuclei (embryos) of a new phase. They determine the balance of free energy and thus the rate of nucleation. The fluctuations will be strongly affected by small alloy additions or by deviations from randomness and in this way the unusually strong dependence of nucleation rates in iron alloys on these two factors can be understood. Other examples could be here cited.

The lattice constant is often strongly dependent on the number of electrons which overlap from one Brillouin zone to the next. This is the basis of the explanation[15] of the anomalously large lattice constant of aluminum and of the anomalies of the c/a ratio in several magnesium alloys. In particular, the concentration corresponding to the onset of such an overlap shows up often as a sharp break in the lattice constant *vs* composition curve. It is thus to be expected that when the average electronic concentration has reached this critical value, then the fluctuations of the local electron concentration will produce local fluctuations in lattice parameters. The presence of such parameter fluctuations would affect electrical conductivity, various magnetic properties and such mechanical properties as critical shear strength, hardness, etc. Not enough data are available to check these conclusions for alloys mentioned above. However, several of the well-known anomalous properties of iron-silicon alloys may be interpreted in that way.[16]

8. CONCLUSIONS

A survey of the various applications of the statistical theory of properties of solid solutions indicates that numerous experimental facts can be explained in a quantitative manner. The statistical method provides in certain instances a sensitive indicator of the concentration at which d-bands in alloys of transition metals are filled up. It may be mentioned that the choice of the basic group, an atom and its neighbors, cannot be altered appreciably without destroying the agreement with experiment.

This work was supported by an AEC contract.

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[15] W. Hume-Rothery, *Atomic Theory for Students of Metallurgy* (Institute of Metals, London, 1946).
[16] R. Smoluchowski (to be published).

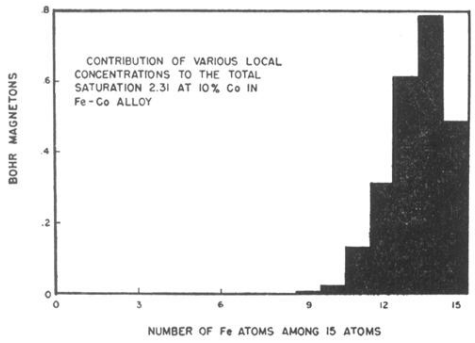

FIG. 2. Contribution of various fluctuations to the saturation moment of a random Fe-Co alloy.