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INFLUENCE OF ORDER ON MAGNETIC PROPERTIES

By R. SMOLUCHOWSKI.

Sommaire. — Une nouvelle théorie de saturation magnétique dans les alliages binaires est présentée. Dans cette théorie on considère les fluctuations de concentration électronique dans tous les groupes équivalents des atomes. Dans le cas d'un réseau du cube centré ces groupes contiennent les premiers et les seconds voisins et la théorie est en accord avec les données expérimentales pour Fe-Co. Pour les alliages à faces centrées, comme Fe-Ni, on emploie un groupe contenant les premiers voisins.

Cette théorie permet aussi de calculer l'influence d'ordre sur les propriétés magnétiques comme le moment de saturation et la magnétostriction et elle est en accord avec les expériences dans les cas connus. L'influence d'ordre sur la température de Curie, sur l'anisotropie magnétique, sur la force coercitive et sur la perméabilité est aussi discutée. Enfin l'influence de propriétés magnétiques sur les phénomènes d'ordre est considérée.

1. General characteristics. — *a. The order-disorder phenomena.* — A brief summary of the important features of the ordering phenomena may not be out of place here. In many binary alloys, usually those which exhibit complete or nearly complete miscibility, at particular compositions there can exist below a critical temperature, T_c , an « ordered » lattice. In the ordered lattice each kind of atom occupies a specific kind of lattice site in the unit cell. Ideally, at sufficiently low temperatures this « long range order » should extend throughout each single crystal. However, at low temperature the ordering process is too slow and at higher temperature the disturbing thermal agitation too large to allow the ideal condition ever to be attained. The ordered state in an actual single crystal (or grain) should be imagined as consisting of many small volumes within which the order is very high but varying in a discontinuous manner at the boundary between these volumes. Each of these volumes can be thought of as separately nucleated during the transition from a random to an ordered solid solution. Clearly, the over-all degree of order in a crystal at equilibrium depends upon the size of these blocks of high order and it changes with temperature and with deviation from the stoichiometric composition which corresponds to an ideal complete order.

For some time it was believed that the order-disorder transformation is a homogeneous transformation; i. e., the two states cannot coexist in equilibrium. Recently, mounting evidence [2] points to the conclusion that this is not true and that many, if not all, ordering reactions are heterogeneous and similar to the conventional phase transitions.

The ordering process is very conveniently described in terms of a change in the number of nearest neighbors of each kind of atoms. The ordering usually leads to a preferential formation of « mixed bonds », AB rather than AA or BB. The opposite tendency leads to a separation of an A-rich and a B-rich phase. This concept of bonds is intuitively and mathematically convenient, but it should not be assigned much physical significance since we

know that metallic bonding has a much more complicated origin and also that there are ordering reactions in which the average number of bonds of each kind does not change at all.

Finally, it should be pointed out that above the critical temperature, T_c , the crystal exists in an essentially random state. There is much good evidence that at least near the temperature, T_c , there is a tendency for atoms A to seek a B-rich neighborhood, and vice-versa. This tendency, the so-called « short range order », is best described as a general decrease in the probability of local concentration fluctuations as compared to those in a purely random solid solution.

b. Saturation magnetization. — When considering the influence of order on magnetic properties [1], it is

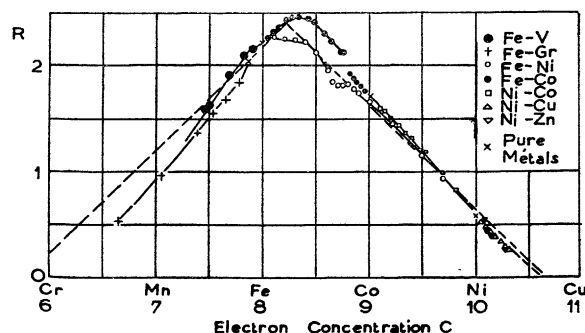


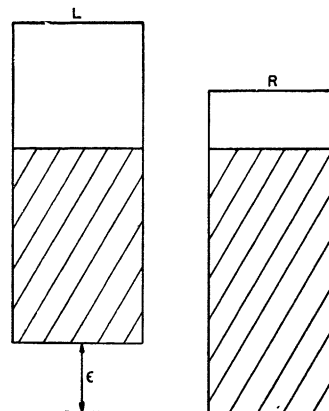
Fig. 1. — Saturation magnetization of transition elements and their alloys (after Pauling).

necessary to know the dependence of saturation magnetization on the position of the elements in the periodic table and of the interpolated positions of their binary alloys. This dependence is illustrated in figure 1 where the saturation moment of several alloy series is plotted against the number of electrons in the combined $3d$ and $4s$ shells. The striking regularity of this diagram found an early interpretation in the work of Pauling [3] which can be expressed, according to Shockley [4], in terms of band theory as follows: let us assume that the

3 *d* band is split into two parts, the higher one containing 4.88 and the lower one 5.12 electrons. Half of the states in each of these parts correspond to electrons which are parallel to each other and anti-parallel to the other half, and we imagine them occupying separate bands which we shall denote R (right) and L (left). In ferromagnetic metals due to the exchange interaction, the R and L bands are displaced with respect to each other, and thus an unbalance of R and L spins is produced. According to this model, in a ferromagnetic metal the top of the band containing the R spins, say, is lower than the bottom of the upper part of the band containing the L spins. Progressing from nickel towards iron, the electrons are gradually drained off from the upper L band, and thus the number of unbalanced spins reaches a maximum value of 2.44 at about 8.2 electrons per atom. Further reductions of the total number of electrons lower the number of the R spins, and thus the unbalance is now gradually reduced in accordance with figure 1. This model, although rather artificial and without much additional support, is very convenient in correlating the properties of the various alloys.

Perhaps a more satisfactory interpretation of figure 1 is based on the differences of the 3 *d* shells in the various atoms. Electrons in the 3 *d* band are far from free and, in fact, the identity of 3 *d* shells is to a great extent preserved. In the band theory, the exchange interaction tends to separate the R and L bands, and this is counteracted by the increase of the Fermi energy ΔE_F . The actual separation of the R and L bands is determined by a balance between these two tendencies which depends on many factors which in turn depend upon the position among the transition elements. One of the important factors is the fact that the increase of energy due to a transfer of an electron from the L to the R band is greater the greater is the width of the 3 *d* band. This width is greater for lower *Z* since then the lower charge of the nucleus allows the 3 *d* shell to expand more, and thus the overlap and interaction between neighboring 3 *d* shells is greater. In comparison with the change in the size of the 3 *d* shell, the interatomic distance remains practically constant for the transition elements in the ferromagnetic group. This allows us to estimate how ΔE_F varies within the group of elements which are of interest here. The situation can be thus qualitatively understood in the following way, illustrated in figure 2. In nickel, all vacancies are in L, and the bands are widely separated since the 3 *d* shell and the ΔE_F are relatively small. The unbalance of spins is thus equal to the number of missing electrons. In cobalt, the smaller number of electrons leaves a still larger number of unpaired spins than in nickel. At an electron concentration 8.2, however, the separation of the L and R bands has decreased to such an extent that the top

of the R band reaches the highest occupied state in the L band. From here on proceeding to iron and beyond it towards manganese, the separation of



DISPLACEMENT OF BANDS ACCORDING TO THE DIRECTION OF SPIN.

Fig. 2. — Schematic presentation of partly filled bands in a ferromagnetic material.

the two halves will further decrease with increasing ΔE_F , and both halves will have unoccupied states. This causes a progressive decrease of the number of unpaired spins, if the separation decreases linearly with *Z*, in accordance with experiment.

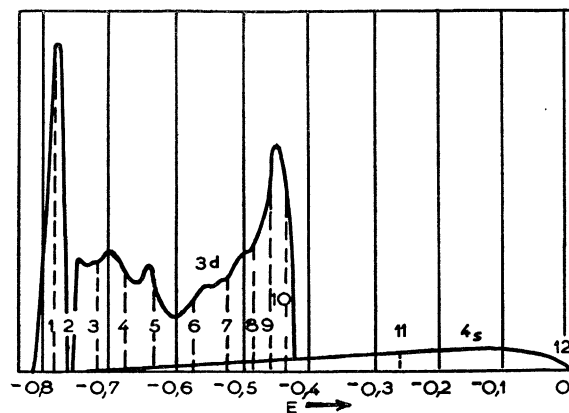


Fig. 3. — Density of electronic states in the 3 *d* band of copper (after Slater).

The above reasoning can be put into a very rough quantitative form : let us make the assumption that Slater's calculations [5] of the 3 *d* band in copper apply qualitatively to other transition elements (fig. 3) when the proper change of the width of the band is taken into account. In other words, the distribution $n(E)$ of electronic states in the band remains the same although the vertical energy scale changes. By integrating the $n(E)$ curve we obtain an expression for the total energy of *n* elec-

concentration as understandable in terms of one of the models and will approximate it by an idealized linear relationship.

The influence of the size of the 3 *d* shells on the exchange forces has been frequently considered. In particular, Slater [6] plotted the energy of magnetization against the ratio of the interatomic distance to the diameter of the 3 *d* shell. Néel [7] used a somewhat different method and, from the point of view of the influence of order, a more convenient approach by plotting the molecularfield, as deduced from the paramagnetic behavior, against the distance between the 3 *d* shells (*fig. 5*). We

shall use this result in the following discussion.

2. Saturation moment of random alloys. —

It is clear that since the saturation moment in alloys is influenced by order, the relationship shown in *figure 1* should not be interpreted, as it usually is, in terms of the *average* electron concentration but rather in terms of *local* electron concentration. Thus we consider the saturation moment of a random alloy to be a sum of the saturation moments of the various local concentration fluctuations. The size of the latter are, of course, strongly dependent upon the degree of order.

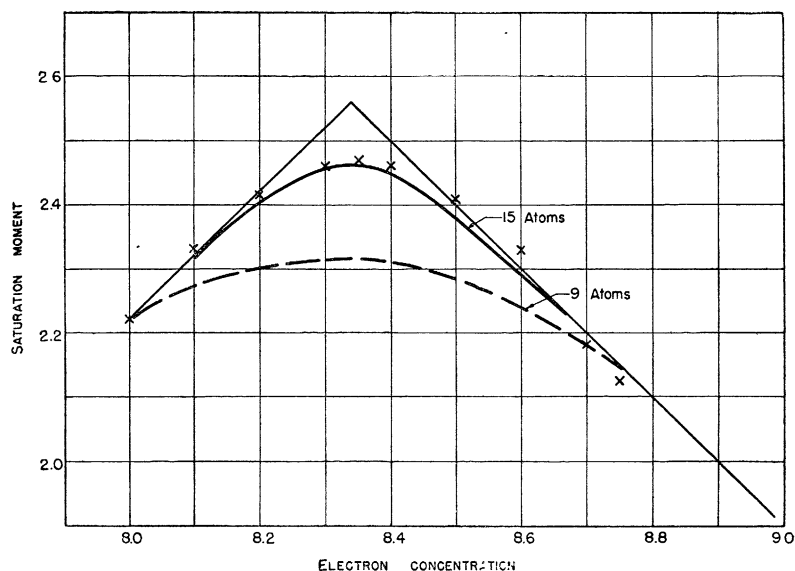


Fig. 6. — Calculated and observed saturation moments in iron-cobalt alloys.

In many of the binary ferromagnetic alloys there are changes of crystal structure and variations of lattice constant within each phase which may make a check of the theory difficult. It was thus thought advisable to use a system which is particularly simple. The bodycentered range of the iron-cobalt alloys offers an excellent possibility: the lattice constant changes very little, the maximum moment occurs in that alloy, and the effect of order is known. The next question to decide is the number of atoms which should be considered as forming a fluctuation of concentration [8]. It seems natural to choose for that purpose a group of fifteen atoms consisting of an atom, its eight nearest neighbors, and its six second nearest neighbors, which are only 15 per cent further away. Assuming perfect randomness, the probability of a given concentration of iron and cobalt atoms can be calculated from the expression

$$P_{n,r} = \binom{n}{r} p^{n-r} q^r; \quad (4)$$

where *n* is the total number of atoms in the group, *r* the number of iron atoms, *q* the average concentration of iron atoms in the random alloy, and *p* = 1 − *q* is the concentration of cobalt atoms. The average electronic density per atom in a fluctuation is then computed and the corresponding contribution to the total saturation moment assigned on the basis of a curve similar to that in *figure 1*. Since the experimental points on which *figure 1* is based were obtained on presumably random alloys, it is necessary to choose a proper relation for local concentrations. This is done in the following way: the saturation moment for iron, which is body-centered, is 2.22, the corresponding value for a hypothetical body-centered cobalt is not known, and so we use the value 1.90 which can be obtained by extrapolating the observed saturation moments for the body-centered phase. The local saturation moments for all compositions in between are determined by two straight lines of slope one, as illustrated in *figure 6*. They reach the maximum value

of 2.56 at a concentration 8.34. Typical results indicating the contributions from various fluctuations in a random 50 : 50 alloy are shown in figure 7,

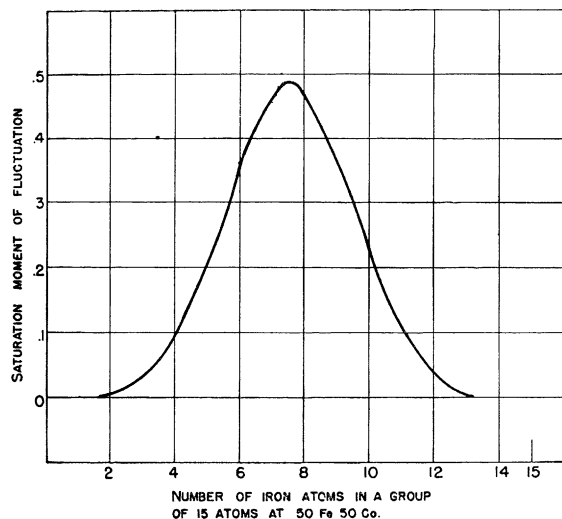


Fig. 7. — Contributions of various local fluctuations to the total saturation moment in a random 50 Fe 50 Co alloy.

the total moment being 2.38. The results for the whole range of compositions are plotted and compared with experimental data in figure 6. The agreement is within 1.5 per cent, which is quite good in view of the highly approximate character of the theory. It is interesting to note that a similar calculation based on fluctuations of concentration in a nine-atomic group leads to a rather strong disagreement with the experimental data as illustrated by a dashed line in figure 6.

In iron-nickel alloys a similar calculation can be made for the body-centered phase. In the face centered phase a group containing thirteen atoms, an atom and its twelve nearest neighbors, has to be used and it leads to a similar, though less good, agreement with experiment, which is not too surprising in view of the large change in lattice constant and other irregularities in that system.

The general procedure for interpreting and predicting the influence of order on magnetic properties is thus follows : for a body-centered lattice one takes a group of fifteen atoms, for a face-centered lattice a group of thirteen atoms, and calculates the corresponding electronic concentration. A linear dependence of local saturation moment upon electron concentration similar to that in figure 6 gives then the contribution to the observed total moment. If, according to figure 5 (or for some other reason), between certain pairs of atoms there is no magnetic interaction then the contributions of various fluctuations have to be decreased in proportion to the number of inactive neighbors.

3. Influence of order on volume properties. —

In the previous sections we have discussed order phenomena and the statistical interpretation of saturation moments. The procedure outlined above should allow us to make now a critical comparison with experimental data. It is convenient to consider separately the influence of order on the so-called structure independent and structure dependent magnetic properties. Among the first we shall deal with saturation magnetization, Curie temperature, anisotropy, and spontaneous magnetization.

a. The saturation magnetization. — The saturation magnetization is known to change with order in FeCo, FeNi₃, Ni₃Mn, CrPt, and others. In terms of the theory here presented these differences in saturation moment in ordered and random alloys should be accountable for by a change in the fluctuations. This seems to be indeed the case :

FeCo. — In the iron-cobalt system, at 50 : 50 per cent there occurs a well-known ordering reaction in which each atom of one kind has eight nearest neighbors of the other kind. According to figure 6 the saturation moment in a random alloy is 2.38. In the perfectly ordered alloy there are no fluctuations of composition, and in the previously considered group of fifteen atoms there can be either seven iron and eight cobalt atoms or vice versa. These two have an average electron concentration of 8.467 and 8.533 corresponding to 2.43 and 2.37 saturation moments, respectively. The moment of the ordered alloy is thus 2.40 which is about 1 per cent higher than the moment of the random alloy. Experiment indicates this difference to be about 4 per cent [9].

An important consequence of the above calculation is that the local saturation moment in the neighborhood of an iron atom in that alloy differs from that near a cobalt atom only by about 3 per cent while the usual atomic moments differ by about 15 per cent. This has an interesting bearing upon the recent work of C. G. Shull [10], who studied the neutron diffraction in these alloys. The diffraction of neutrons depends not only on the purely nuclear scattering but also upon the interaction between the magnetic moment of the neutron and the magnetic moments of the atoms. In the case of these iron-cobalt alloys diffraction seems to occur as if there were no difference, within the limits of experimental error, between the magnetic moments of the lattice sites occupied by iron and by cobalt atoms. This result is in agreement with the theory here outlined.

Fe-Ni₃. — This face-centered cubic alloy corresponds to "permalloy" composition in which saturation moment increases by about 6 per cent on ordering [11]. According to the outlined procedure the proper size of the group of atoms in this case is thirteen and for a random alloy the contributions

of the various fluctuations are easily calculated. However, it is here necessary to take into account the fact that iron, in a face-centered lattice, is non-magnetic, a fact which agrees with the position of the corresponding point for the nearest neighbors on the curve in figure 5. (In fact Néel suggested that in body-centered iron the interaction between nearest neighbors may be very small compared to the interaction between second neighbors.) It follows thus that the various contributions to the saturation moment have to be decreased in proportion to the iron-iron pairs occurring in each fluctuation. The resulting moment is 1.02. For the ordered alloy the situation is much simpler: there are no iron-iron nearest neighbors (fig. 8) and one

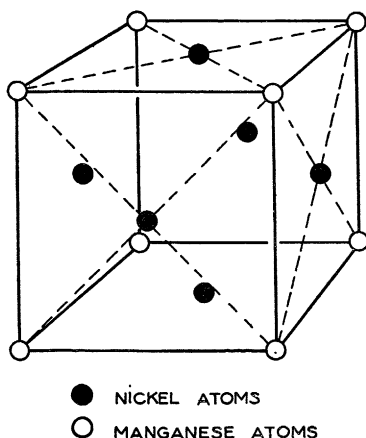


Fig. 8. — Ordered face-centered cubic lattice AB_3 .

obtains only two kinds of neighborhoods, an iron atom surrounded by twelve nickels and a nickel atom surrounded by eight nickels and four irons. The corresponding electronic concentrations of these groups give the saturation moments 0.750 and 1.21, respectively. Taking the proper ratio 1:3 of the frequency of their occurrence one obtains for the ordered lattice the total moment 1.10 which is about eight per cent higher than the moment 1.02 calculated above for the random alloy. This is in fair agreement with the difference of 6 per cent in the experimentally measured moment 1.18.

Ni₃Mn. — This alloy is also face-centered cubic and is strongly ferromagnetic in the ordered condition, having saturation moment of about 0.9 Bohr magnetons, while in the random condition it is only weakly ferromagnetic [12]. In considering this alloy according to our procedure it is important to take into account the sizes of the 3 *d* shells. Figure 5 indicates that a Mn-Mn pair will have a negative contribution to magnetism, while a Ni-Ni pair will have a positive contribution. The Ni-Mn pair, on the other hand, corresponds to a point near zero interaction. If we make a calculation analogous

to that for FeNi₃, i. e., put the contributions of the Mn-Ni interactions equal to zero, we obtain for the ordered structure a moment 0.91 in good agreement with experiment. For the random alloy we consider as before the fluctuations of concentration within the groups of thirteen atoms and take into account their contribution to the total saturation moment, obtaining a positive contribution 0.71 from the Ni-Ni interaction and an unknown negative contribution from the Mn-Mn interaction. Whether the latter is big enough to “compensate” for most of the Ni-Ni contributions is difficult to say [9] but one can expect the saturation moment for the random alloy to be small, in accordance with experiment. The scatter of the experimental data for a quenched alloy is quite likely due to an imperfect randomness.

b. Magnetostriction. — Numerous experiments indicate a large change of spontaneous magnetostriction in various alloys on ordering. The outstanding examples are FeCo, Ni₃Fe, Fe₃Al, and certain Fe-Si alloys. The difficulty in treating these effects theoretically is the lack of a good general theory of magnetostriction. Becker based his theory [13] on an interaction of magnetic dipoles located at lattice sites. Although this point of view is certainly superseded by more recent quantum mechanical developments, it is rather well suited from a descriptive, qualitative point of view [14] and in particular, it is convenient for the treatment of the effects of order. It should be remembered, however, that this theory gives at best reasonable values of magnetostriction. Since ordering produces radical changes only in the immediate surroundings of an atom, we shall consider only interactions of nearest and second nearest neighbors.

The magnetostriction calculated, as described below, from first and second neighbors only, appears to differ only slightly from the magnetostriction obtained from a summation over all atoms in the crystal, indicating that the contributions of the more distant atoms nearly cancel out. Another interesting conclusion is the fact that on this dipole model the only negative contribution to the free energy, due to positive magnetostriction λ , in a body centered lattice comes from the angular displacement of the nearest neighbors which remain at fixed distance from the central atom, within the approximation of terms linear in λ . All other displacements, and of course, the strain energy oppose magnetostriction. The final formula [14] for a body-centered cubic lattice is:

$$\lambda = \frac{N^2}{G} \frac{64\sqrt{3}\mu_1^2 - 81\mu_2^2}{54} \quad (5)$$

in which N is the number of dipoles per cubic centimeter, G is the shear modulus and μ_1 and μ_2 stand for the “effective moments” between nearest

and between second neighbors, respectively. In the case of a random alloy $\mu_1 = \mu_2 = 2.38$ as computed previously in connection with the study of the variation of the saturation moment with order. For an ordered alloy, we have to consider the moments characteristic of an interaction between pairs of atoms. For the nearest neighbors, a Ni-Fe pair, we have on the basis of their electron concentration $\mu_1 = 2.40$, while for the second nearest neighbors we have either 2.22 or 1.90 depending upon whether the central atom is iron or cobalt. The average is thus $\mu_2 = 2.06$. Substituting these values in (5) we obtain :

$$\lambda(\text{ord.}) = 1.73 \lambda(\text{disord.})$$

which has to be compared with an experimentally observed factor 1.40. The difference is not surprising in view of the very simple theoretical assumptions and also in view of the difficulty in obtaining perfect order and complete disorder experimentally. The latter conclusion has been confirmed by means of neutron diffraction since X-rays are not suitable in that case. Since magnetostriction data were available for a 45 Co-55 Fe alloy, the calculation was made also for that composition. The ordered lattice was considered as a perfectly ordered 50 : 50 lattice with 10 per cent of the cobalt atoms randomly displaced by iron atoms. The calculated ratio is 1.60 as compared to an experimental factor 1.30 which, for similar reasons as before, can be considered as a satisfactory agreement.

Fe-Si. — A large effect of order on magnetostriction has been recently observed by Carr [15], who, in his study of single crystals of various Fe-Si alloys, compared values for annealed and quenched crystals. It appears that around 11 atomic per cent silicon the magnetostriction in the cubic direction is about two times larger in the quenched alloy than in the annealed condition. Although the structure and properties of these alloys are still not well understood, it seems plausible that the effect is due to an ordering reaction which is supposed to occur at 25 per cent silicon. A comparison with theory is complicated due to the known rapid change of mechanical and, presumably, elastic properties with composition and with heat treatment. Thus, not only μ but also perhaps G may be affected although the energy of ordering is small compared to the energy of binding (approximately heat of sublimation). Changes of magnetostriction on ordering have been recently observed in FeNi₃ and Fe₃Al by Goldman [16] who obtained an increase of about 100 per cent in the former.

c. Curie temperature. — There are a few cases in which the Curie temperature for an ordered and a disordered lattice of the same composition is known, and it is, therefore, interesting to see whether that effect could be interpreted in a simple manner.

Since there is no such simple relation between the Curie temperature and composition as there is for the saturation moment, we have to use another approach. This is based on the admittedly uncertain assumption that the exchange integral to which the Curie temperature according to modern theories is proportional (the constant of proportionality being determined by the type of lattice) can be represented in a binary A-B alloy as a sum of contributions \mathcal{J}_{AB} , \mathcal{J}_{AA} and \mathcal{J}_{BB} of the individual pairs of atoms. This is analogous to the simple "bond" interpretation of the total binding energy of a crystal which is made up of positive contributions V_{AB} , V_{AA} and V_{BB} from each pair of atoms. A stronger bond implies, thus, a lower free energy.

If any two atoms A and B are interchanged, then the total binding energy in a crystal changes by a multiple of

$$V = 2V_{AB} - (V_{AA} + V_{BB})$$

while the average exchange integral changes by a multiple of

$$\mathcal{J} = 2\mathcal{J}_{AB} - (\mathcal{J}_{AA} + \mathcal{J}_{BB}).$$

In an ordered alloy $V > 0$ and the free energy is lower when there are more A-B bonds. If the corresponding magnetic interactions are such that $\mathcal{J} = 0$, then the state or order would have no influence on the Curie temperature. For $\mathcal{J} > 0$ on the contrary, the order would promote strong exchange interaction and a high Curie temperature. The opposite would be the case for $\mathcal{J} < 0$. These arguments hold not only in the case of long range order, but they are applicable also to alloys in which only short range order has developed.

An example of the case when the Curie temperature of the ordered state is higher than in the disordered state is Ni₃Mn and FeNi₃. In the first [12], the Curie temperature is raised from around room temperature to near 500° C. Lowering of the Curie temperature on ordering occurs in Fe₃Al (see paper by Sucksmith in the report) and CoPt alloys. In the first alloy the Curie temperature is lowered [17] from 550° C to 500° C while in the latter, the ordered phase is non-magnetic [2], although the random phase has a Curie temperature near 600° C.

These observations can be compared in a qualitative manner with the conclusions which we can draw about the various exchange integrals. We know that the Curie temperature in the face-centered iron-nickel alloy reaches a broad maximum around 60 per cent nickel and falls off very rapidly on the iron side and less rapidly on the nickel side. This behavior is similar enough to the existence of a maximum at 50 : 50 and it indicates that $\mathcal{J}_{\text{Ni-Fe}}$ is larger than either $\mathcal{J}_{\text{Fe-Fe}}$ or $\mathcal{J}_{\text{Ni-Ni}}$ in accord with the requirement, $\mathcal{J} > 0$. In the nickel-manganese alloy, one expects the $\mathcal{J}_{\text{Mn-Mn}}$ to be negative (fig. 5) and compensate almost exactly the $\mathcal{J}_{\text{Ni-Ni}}$ so that the necessarily small $\mathcal{J}_{\text{Mn-Ni}}$ appears as positive

and $\mathcal{J} > 0$. In the iron-aluminum alloy, the only positive interaction is undoubtedly due to the Fe-Fe pair, while the others are zero, thus $\mathcal{J} < 0$, again in accord with experiment. The CoPt alloy in the ordered state is tetragonal with alternate layers of Co and Pt atoms. It is a well-known result of modern theories of cooperative phenomena that there are no two-dimensional ferro-magnets, the interaction between the cobalt layers across the platinum layers being negligible. In the random CoPt alloy, on the other hand, there are enough three dimensional cobalt clusters to make the alloy ferromagnetic.

d. Magnetic anisotropy. — A good example of the change of anisotropy on ordering is FeNi₃ which in a random condition is essentially isotropic [11], while in the ordered state the [111] direction becomes the direction of easy magnetization. The theory of magnetic anisotropy is, in spite of much recent progress, not sufficiently well developed to allow a speculative analysis of the ordering effect [18].

4. Structure dependent properties. — So far, we have been concerned only with the influence of order on structure independent properties. There are, however, several structure dependent properties which change on ordering. Among them, we shall consider only coercive force and briefly permeability.

a. Coercive force. — There are many theories of coercive force; the one best applicable here is that given by Becker [8], who relates it to internal stresses σ , magnetostriction λ and saturation moment M in the formula :

$$H_c = p \frac{\sigma \lambda}{M},$$

where p is a proportionality constant. On ordering, all three quantities may change, and so it is difficult to see which one is the most important. However, one would expect both λ and M to reach their extreme values when the order is complete while σ can reach very high values during ordering and, in fact, it may be again lowered when the order is reached. We shall discuss here only the influence of order on coercive force through a change of σ since a change of λ or M is really a special instance of a change of a structure independent quantity. High coercive force is usually produced in alloys by high stresses due to precipitation, ordering reaction or both. Typical examples of the role of ordering are found in CoPt, FePt, FeCo powder, and in numerous commercial alloys. The CoPt which was recently investigated [2], shows that during the process of ordering platelets of the tetragonal ordered phase form and grow within the random cubic phase in such a way that they are parallel to the (110) planes. The stresses set up by this condition are very high and lead to a maximum coercive force of around 3000 Oe

and $(BH)_{\max}$ over 6.4×10^6 for a partially ordered alloy (20 h at 600° C).

A similar situation presumably occurs in FePt [20]. On the other hand, in the FeCo pressed powder [21], the situation is more complicated since in that case the coercive force depends on many additional factors.

b. Permeability. — Initial permeability is rather closely related to coercive force and depends on magnetostriction λ , strains σ and magnetization M in the following way

$$\mu_0 = 1 + \frac{c M^2}{\lambda \sigma}$$

where c is a constant. Usually a high permeability is interpreted as due to low strains. It appears, however, that the other factors may play a very important role and, as shown by Goldman in FeNi₃, permalloy, the high permeability [22] can be attributed to low magnetostriction. The heat treatment of permalloy is such as to suppress the ordering reaction which occurs at that composition and which is accompanied by a large increase of magnetostriction.

5. Influence of Magnetic properties on order.

— In our discussion of the influence of order on Curie temperature, it was tacitly assumed that the distribution of atoms in an alloy will be governed by the binding energies and the magnetic interactions will adjust themselves to the existing conditions. This was justified, since near the Curie temperature the magnetism is weak and would not exercise much influence on the binding. However, there are many opposite instances where the critical temperature T_c of the ordered lattice is much below the Curie temperature, as for instance in FeCo where the corresponding values are 760° C and 1100° C (extrapolated) respectively. Under these conditions, one might expect an important contribution of the magnetic interactions to the preferential distribution of the two kinds of atoms.

This magnetic interaction may appear in two ways : first, the energy of the bonds V_{AB} , etc. is, in most theoretical approximations, independent of temperature, and it is only the thermal agitation which counteracts order. On the other hand, the magnetic interaction, which is now part of the ordering energy, may be strongly temperature dependent and so it may alter the dependence of order on temperature as compared to the behavior in a non-magnetic alloy. No such studies have been reported. Secondly, the bond energy in the idealized theory, or V , is essentially symmetric with respect to the 50 : 50 composition, while the Curie temperature, and thus the exchange integrals, are known to vary very rapidly across the phase diagrams. Thus, since the regions of order usually extend over 10, 20 and more per cent composition, one may expect a strong asymmetry of these regions

with respect to the stoichiometric compositions. Some of the binary alloys between metals of the iron group should provide an excellent check of these conclusions, unfortunately the ranges of existence of order are mostly unknown because of difficulties with the X-ray methods. The neutron diffraction work should be very useful in this field. Certain predictions can be made using as a guide the dependence of Curie temperature on composition : one would expect the FeCo ordered phase to be symmetrical because the true (extrapolated) Curie temperatures in that system seem to be symme-

an important factor. The effect is, however, in accord with expectation : the ordered phases are non-magnetic and $\mathcal{J} = -\mathcal{J}_{AA} < 0$, where A stands for Co or Ni; thus the stronger the magnetism at a given temperature, the stronger is the tendency to randomness in that system.

It is interesting to compare the above mentioned assymetry of the ordered region in the NiPt system (similar to Co-Pt, *fig. 9*) with the assymetry of the miscibility gap in the Ni-Au system. There the minimum temperature of complete miscibility occurs at about 30 at. per cent nickel and the miscibility gap extends more towards nickel than it does towards gold. Both these assymetries can be considered as due to the same cause, namely to the preference of nickel atoms for a nickel-rich neighborhood. By forming either a solid solution with gold or an ordered lattice with platinum the nickel-nickel distances are increased by 10 to 15 per cent. Thus by splitting into a nickel-rich and a gold-rich phase in the Au-Ni system or by preferring a random solution to an ordered phase on the nickel-rich side of the 50:50 composition in the Pt-Ni system the number of the more normal distances between nickel atoms is increased. In the Pt-Ni and Pt-Co systems this factor may be more important than the magnetic effect previously considered.

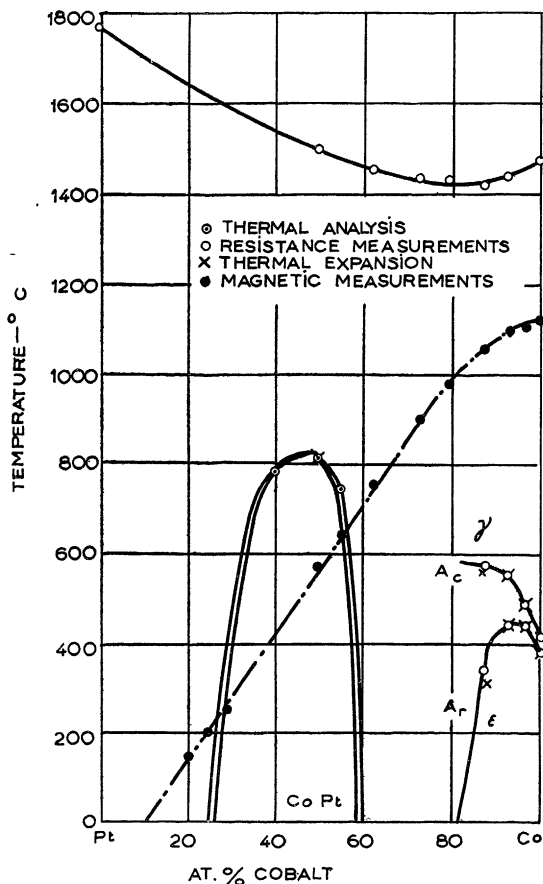


Fig. 9. — The cobalt-platinum diagram (after Köster and Gebhardt, revised by J. B. Newkirk).

trical [7] around the 50:50 composition. By similar reasoning in FeNi, the ordered region, if any, should be broad on the nickel-rich side, while in FeNi₃ the iron-rich side would be broader. A symmetrical behavior may be expected in the cobalt-nickel system. Other alloys as CoPt and NiPt show a very pronounced assymetry (*fig. 9*). However, in these cases the Curie temperatures are below T_c , and it is not certain whether the "short-range order" of spins which exists above the Curie temperature is

Remarque de M. Goldman. — Some of the ideas presented in this paper by Smoluchowski can be extended to the case of alloys of ferromagnetic elements with nonferromagnetic elements. For example, in Fe-Si alloys Fallot finds discontinuities in the moment vs composition curve at compositions at which the onset of a superlattice is suspected. For low silicon content, the silicon atoms simply replace Fe-atoms and decrease the moment linearly. However, at higher silicon contents, the moment decreases more rapidly. We think this can be understood on the basis of Néel's theory. In body-centered cubic structures, Néel finds that for atomic spacings found in iron and some of its alloys, positive exchange results only from next nearest neighbor interactions. In Fe₃Si, however, 1/3 of the Fe-atoms have only Si atoms as next nearest neighbors. Hence, they will not contribute to the magnetic moment. According to this interpretation, the anomalous decrease in moment would commence at a composition where the probability of finding an iron atom with silicon atoms as next nearest neighbors becomes significant.

Remarque de M. O. Berg. — It is essential to distinguish between just ordered phases and intermetallic compounds. FeCo is not an intermetallic compound whereas Fe₃Si, FeSi, Fe₃Al, FeAl, and Ni₃Mn are. In all cases of intermetallic compounds to my knowledge, the magnetic moment of the

ordered phase, i. e. the intermetallic compound, is considerably lower than that of the disordered phase. This is particularly apparent in the case of Fe_2W . Quenched specimens which do not contain Fe_2W have a higher magnetic moment than annealed specimens which contain Fe_2W . The pure compound Fe_2W is non-magnetic, at least at room temperature. Data given on Ni_3Mn by various authorities spread to the extent that it is difficult to draw safe conclusions. It is probable however that the ordered phase Ni_3Mn is an intermetallic compound the formation of which decreases the magnetic moment.

Réponse de M. Goldman. — In the measurements on Fe-Co the state of order was estimated by means of neutron diffraction and I agree with Dr Berg that this system is not of the intermetallic type of order. However, the applicability of this theory to such alloys as Fe-Co seems to make plausible the notion herein introduced that, at least as regards magnetic properties, specifically the magnetic moment, a nearest and next nearest neighbor approximation, which has certain features similar to an intermetallic compound treatment, is valid.

Réponse de M. Guillaud. — J'ai étudié un MnNi_3 , en surstructure, obtenu en partant d'éléments très purs. Le recuit nécessaire pour obtenir le maximum de moment est très long (trois semaines à 450°C). Dès qu'on dépasse 480°C , l'aimantation spontanée disparaît et au refroidissement MnNi_3 n'est plus ferromagnétique (état désordonné).

Remarque de M. Went. — Nous avons trouvé que l'ordre peut aussi se manifester dans la forme des courbes de l'aimantation spontanée σ en fonction de la température T . Les courbes (σ, T) ont été déterminées pour le nickel pur et pour des solutions solides de nickel avec Al, Si, V, Cr, Cu, Mo, Sn, W, Mn, Pd, Fe ou Co. On sait que pour le nickel pur cette courbe coïncide d'une manière satisfaisante

avec la courbe théorique bien connue correspondant à $s = \frac{1}{2}$. Pour tous les systèmes binaires mentionnés la courbe (σ, T) est moins concave vers l'axe des températures. Les déviations sont proportionnelles à la teneur de l'élément ajouté; elles dépendent de la nature de cet élément. Dans la série Co, Fe, Mn, Cr la déviation par atome ajouté augmente du Co au Cr. Nous croyons que ces phénomènes sont étroitement liés aux fluctuations dans la concentration locale des atomes magnétogènes. Par conséquent, on doit s'attendre à ce qu'une solution solide complètement ordonnée présente une courbe (σ, T) normale. En effet, nous avons trouvé, pour FeNi_3 , que dans l'état complètement ordonné, la courbe (σ, T) coïncide pratiquement avec celle du nickel pur, tandis que pour l'état trempé des déviations considérables ont été constatées.

Remarque de M. Meyer. — Il est remarquable de constater que, d'après Marian, l'alliage Ni_3Pt possède à l'état désordonné un moment supérieur à celui de l'état ordonné, tandis que le phénomène inverse se produit pour Ni_3Mn et Ni_3Fe .

Réponse de M. Smoluchowski. — The results obtained by Dr Went are most interesting and they should make it possible to check the theory here outlined. A similar case has been recently considered by T. Muto et al (*J. de Phys. Soc. Jap.*, 1948, **3**, 277-284). I cannot agree with Dr Berg that the distinction between ordered solid solutions and intermetallic compounds is so clear cut. The quoted examples represent, at best, a quantitative rather than a qualitative difference in the equilibrium condition. The kinetics of transformation show, on the other hand, a greater variety and there a more close analysis is necessary [see for instance NEWKIRK J. B., SMOLUCHOWSKI R. et al., *Trans. A. I. M. E.*, 1950, **188**, 1249; *J. Appl. Phys.* (in press) and *Acta Cryst.* (in press); also H. SATÔ, *Sc. Rep. Res. Inst. Tôhoku Univ.*, 1949, **1**, 405].

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