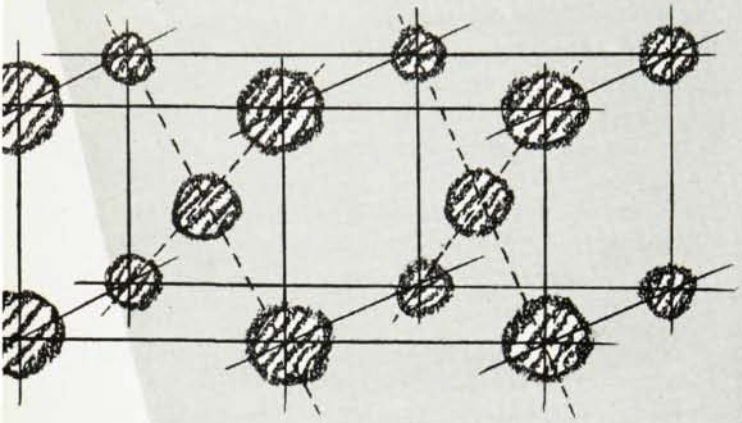
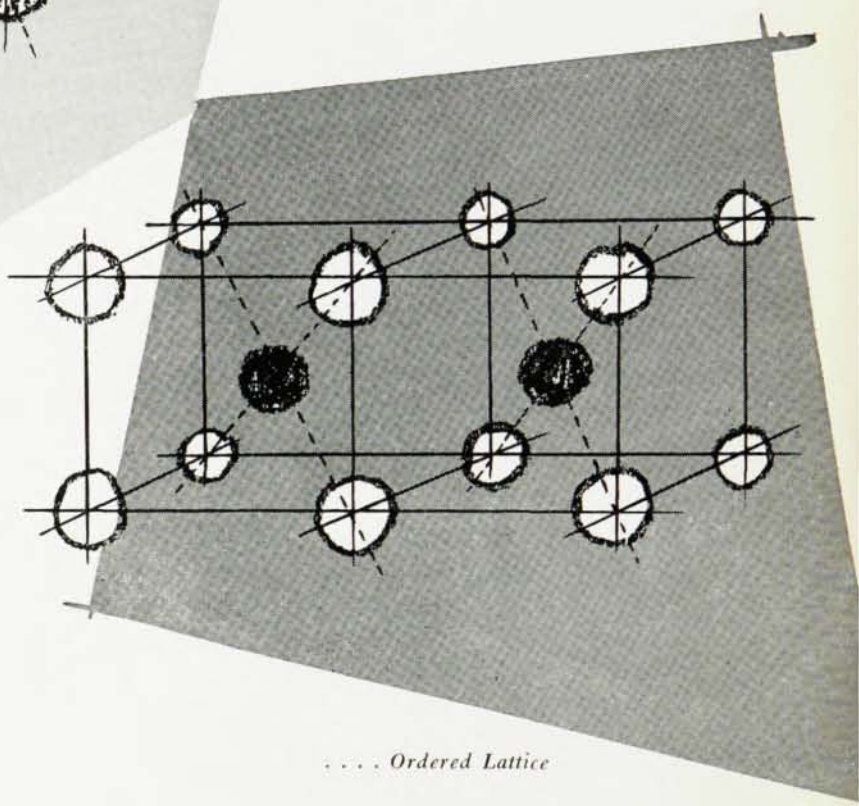
Random Lattice . . . .



Some recent findings on order and disorder.

ORDER IN



. . . . Ordered Lattice

Iron or cobalt

Iron

Cobalt

R. Smoluchowski, professor at the Metals Research Laboratory of the Carnegie Institute of Technology, came to Princeton in 1939 after having headed the physics of metals section of the metals Institute at the Warsaw Institute of Technology. He became interested in physics of solid state because so much fundamental research could be done with relatively simple instruments and because the field is in great need of theoretical investigations.

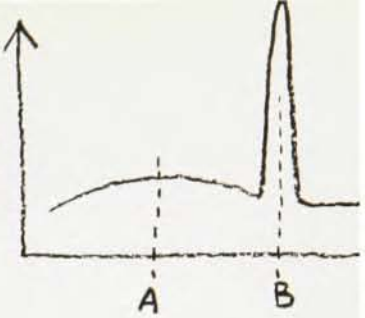


Fig. 2—Broad and sharp maxima in x-ray diffraction pattern of a gold-silver alloy (sketch after Guinier).

METALLIC CRYSTALS

by ***R. Smoluchowski***

To most people the beauty and harmony of crystalline form are synonymous with perfection and stability, and their metaphorical usage is indeed widespread. The curious and often skeptical scientists, however, long suspected that a more detailed study of crystals would reveal imperfections of various kinds; and the advent of modern research tools and, in particular, of x-ray diffraction methods has in fact opened a vast field of study in which changes, reactions, and imperfections in crystals are being investigated. At the same time, to be sure, the very same methods told physicists many of the why's and how's of the startling harmony and symmetry of the internal and external structure of crystals.

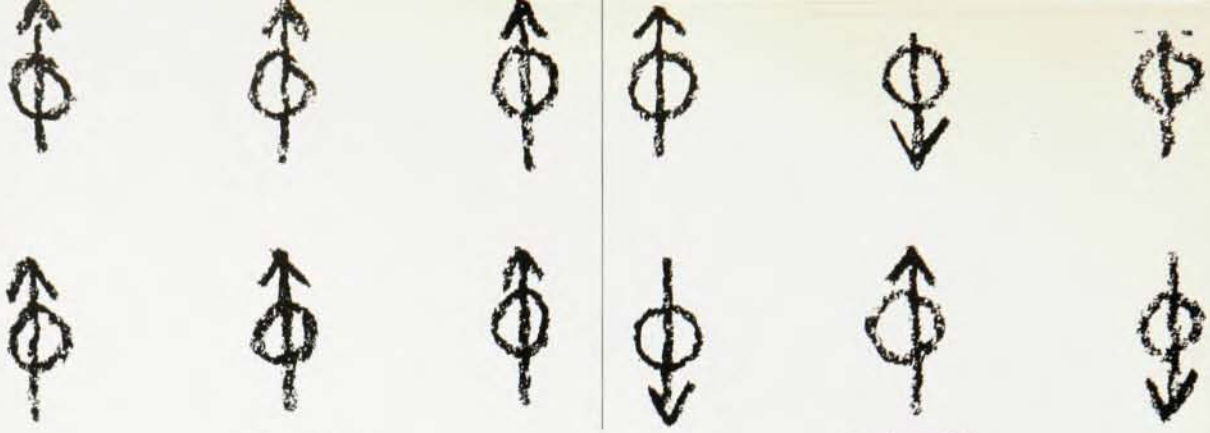
Modern theory of solids has told us much about the nature of binding forces in metals, ionic crystals, valence crystals, and so forth. In ionic crystals the binding forces are primarily due to the electrostatic interaction between the various positively and negatively charged ions. In valence crystals, the forces, or bonds, act between neighboring atoms and are rather rigid in their direction and length. Thus, these crystals allow little, if any, variability of compositions or of dimensions. On the other hand, in metals the binding is mainly due to an over-all interaction between the positive ions and the numerous negative electrons which move, more or less freely, through the metallic crystalline lattice.

Metallic binding is thus characterized by the absence of directed, fixed bonds between atoms and permits a particularly large range of deviations from perfection in metallic crystals. These deviations can occur either in the geometrical perfection of the atomic arrays in a pure metal or, in alloys, they may appear as the great diversity of distributions of the various kinds of atoms in the crystalline lattice. Some of these changes of distribution of atoms are accompanied by pronounced changes in the crystalline lattice itself—others occur in a practically unperturbed lattice. The purpose of this brief review is to summarize some of the more recent results obtained in the study of binary alloys in which a change in the distribution of the two kinds of atoms takes place. These transformations are usually referred to as the order-disorder phenomena.

Long and Short Range Order

A change in order is conveniently described in terms of the change of the number of neighbors of a certain kind. For instance, in a random body-centered cubic lattice of iron-cobalt (FeCo) each atom, whether it is iron or cobalt, is surrounded *on the average,* by an equal number of iron and cobalt atoms among its eight nearest neighbors as shown in the first figure. On the other hand, in the perfectly ordered condition, which can exist only below 770°C, each atom is surrounded by eight atoms of the opposite kind, as illustrated. Thus one can say that a random iron-cobalt crystal changes to an ordered crystal whenever the iron-cobalt bonds are sufficiently more favorable than the iron-iron or the cobalt-cobalt bonds to counteract the thermal agitation of atoms which tends to destroy the order and produce a random distribution of the two kinds of atoms.

But one should remember that this use of the concept of bonds of various energies between neigh-



Parallel *Antiparallel*

Fig. 3—Orientation of magnetic moments in a crystal lattice.

bors in a metal has not only the great advantage of being simple but also the great danger of being oversimplified since it ignores much that we know about the metallic binding and also does not take into account the differences of atomic diameters, strain, and so forth. In fact there are ordering reactions in which the average number of neighbors does not change at all.

In the long range order described above, the distribution of the two kinds of atoms in one unit cell predetermines the distribution of the atoms in every other unit cell of the crystal. With increasing temperature, this order becomes more and more disturbed and finally disappears entirely at a certain critical temperature. All that is left then is a "tendency" for an atom of one kind to surround itself with atoms of the other kind, but there is no long range correlation between the various sites of atoms. This tendency can be measured and is called short range order.

From the point of view of x-ray analysis, the long range order leads to additional diffraction lines in the powder pattern while the short range order produces only broad maxima in the diffuse background of the diffraction patterns. An early evidence of this effect obtained by Guinier is illustrated in the second figure, which shows the sharp lines of the normal random lattice and the broad diffraction maxima in a gold-silver alloy.

A more recent work of Cowley, made on single crystals of copper-gold (Cu_3Au), reveals a very pronounced short range order above the ordering temperature. These results, obtained from very exact intensity measurements, show that short range order makes itself felt across many shells of neighbors. Let us assume that the central atom is a gold atom. Then its twelve neighbors are predominantly copper atoms and their neighbors, the next shell, are predominantly gold atoms, and so on. It appears that even the tenth shell of neighbors shows a preference for a certain kind of atoms. This shell-like structure resembles strongly the well known structure of a liquid where the atoms cannot approach each other closer than their diameters. In copper-gold the sum of the diameters of a gold and a copper atom plays the role of this minimum approach.

A problem often discussed in connection with order phenomena is the true nature of the ordering transformation: some scientists believed it to be a homogeneous reaction, which means that in equilibrium at a given temperature either the ordered or the disordered phase can exist, but not both of them together. Many other scientists saw little, if any, difference between the ordering and most of the other usual phase transformations in alloys, which are heterogeneous. That is, the new phase forms locally within the old phase and under proper conditions the two can coexist in equilibrium.

It appears now that the confusion was due primarily to insufficiently refined x-ray techniques on one hand and to an overestimate of their accuracy on the other. The work of Borelius on gold-copper alloy and especially the more recent work of Newkirk on cobalt-platinum alloys indicate that the slightly tetragonal ordered phase is formed locally within the cubic disordered phase and that the two can coexist, both during the process of ordering and in equilibrium. This behavior is thus quite analogous to a usual heterogeneous transformation. The x-ray methods fail if the ordering temperature is low, because then the ordered phase is too finely dispersed to form a clear diffraction pattern. At the same time, it has been shown that at a certain stage the ordered phase appears as small platelets about 100 Å on the side and 10 Å thick and that these platelets have a special orientation with respect to

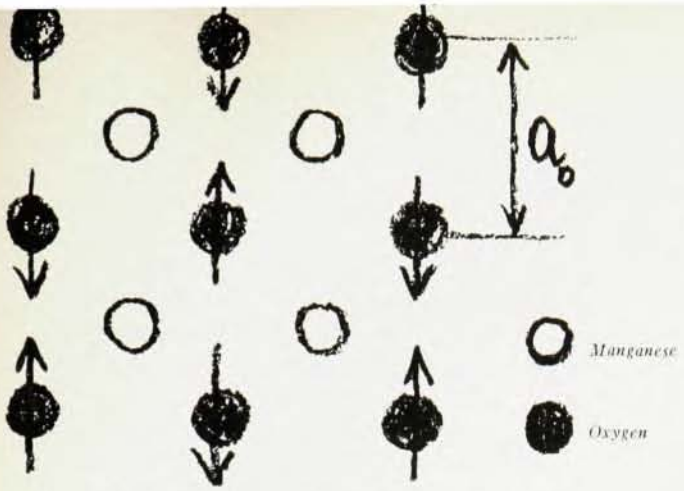


Fig. 4—Arrangement of atoms and magnetic moments of manganese atoms in manganese oxide.

the crystal lattice of the random phase.

These small volumes of order do not fit too well into the surrounding random lattice, and so they produce strains which cause a remarkable change in the magnetic properties of the alloy: the coercive force which is so important in all permanent magnets is here greatly increased while in a completely random or a completely ordered lattice it is low. This effect is in agreement with the well known relation between internal strains and coercive force in magnetic materials.

"Magnetic" Order

Ordering seems to influence certain magnetic properties of alloys not only in the two-phase stage, but also when the ordering reaction is brought to completion. An iron-cobalt alloy is ferromagnetic both in the ordered and in the disordered state but, as a recent study by Goldman and Smoluchowski has shown, the magnetostriction (the small change of dimension during magnetization) is nearly fifty percent higher in the ordered alloy than in the random case.

It has been possible to devise a simple theory of this effect based on the fact that, as illustrated in the first figure, the neighborhood of an atom changes during ordering and thus the interactions between the elementary magnetic dipoles are altered. This change leads to a change in the distribution of electronic density in the crystal lattice and to a theoretically predictable increase of magnetostriction by eighty percent. In view of the simple model used in this theory, and the imperfect randomness and imperfect order of the alloys, the agreement with experiment is reasonably good. The states of randomness and of order in those alloys have been checked using the new technique of neutron diffraction, which is particularly suitable for the iron-cobalt alloys. The theory also predicted a change in the magnetic saturation on ordering; this has been experimentally confirmed.

Many other interesting changes of physical properties due to ordering phenomena can be explained at least qualitatively if not quantitatively. The theory becomes a little too involved for this brief presentation and so only a few examples will be mentioned: the change of the feebly magnetic nickel-manganese (Ni_3Mn) to a strongly magnetic alloy on ordering and also the increase of saturation moment of iron-nickel ($FeNi_3$), the famous permalloy, on ordering can be satisfactorily explained, similarly to the above treatment of iron-cobalt.

An entirely new kind of order has been recently studied by Shull using diffraction of a beam of neutrons instead of x-rays. According to modern physics, a beam of neutrons, or any other particle, behaves in certain respects as if it were a wave and thus it produces diffraction effects. The interesting aspect of a neutron diffraction study of order is that the diffraction depends not only upon the distribution of the two kinds of atoms, but also upon the direction of the small magnetic moments which are associated with an atom. These moments can be oriented at random or they can be parallel or antiparallel to each other, as illustrated in figure 3. We have, thus, a "magnetic" order of the orientation of magnetic moments, which in an alloy or compound can be superimposed on a "chemical" order. This magnetic order leads to the appearance of additional "magnetic" lines in the diffraction pattern of neutrons just as the "chemical" order leads to additional diffraction lines of x-rays.

Shull has shown that in manganese oxide, which is schematically represented in figure 4, the smallest distance between chemically equivalent atoms is a_0 while the smallest distance between magnetically equivalent atoms, in the cubic direction, is twice that distance, or $2a_0$. Thus, the chemical periodicity of the lattice is different from its magnetic periodicity.

These are only a few of the numerous, extremely interesting, recent investigations, both experimental and theoretical, in the domain of order phenomena in metals. Their study seems to indicate a very fruitful path towards a better understanding of the internal mysteries of crystals.