

Statistical Theory of Superlattices

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1—INTRODUCTION. ANALOGY TO FERROMAGNETISM

In a recent paper, Bragg and Williams* have pointed out that the arrangement of the atoms in an alloy depends in a striking way on the temperature. At high temperatures, the atoms are distributed practically at random among the lattice points of the crystal, but at low temperatures a superlattice may be formed such that the atoms of one kind are arranged in a regular lattice of their own and the atoms of the other kind occupy the remaining "sites" in the crystal. The transition from the ordered to the disordered state occurs in a fairly small temperature range, and is accompanied by a large specific heat, an increase in electric resistance, etc.

The mathematical method employed by Bragg and Williams is similar to that used in Weiss's theory of *ferromagnetism*. Both involve the assumption that the "force" tending to produce order at a given point is uniquely determined by the average state of order throughout the crystal. Actually it will depend on the configuration of the atoms in the immediate neighbourhood of the point under consideration. The order of the crystal as a whole determines this configuration only on the average. In the present paper, the effect of fluctuations in configuration, which was neglected by Bragg and Williams, will be taken into account.

For our investigation, we shall assume that only nearest neighbours interact. This assumption is essentially the same as that which underlies the modern theory of ferromagnetism.† There we have an interaction energy (electron exchange) between the spins of neighbouring atoms which tries to set them parallel. This interaction, although only acting between neighbouring spins, is nevertheless capable of setting all spins throughout the crystal parallel at low temperatures, thus establishing perfect order. In addition, experimentally a sharp Curie point is found at which the "order," *i.e.*, the permanent moment, of the crystal as a whole dis-

* 'Proc. Roy. Soc.,' A, vol. 145, p. 699 (1934).

† Bloch, 'Z. Physik,' vol. 61, p. 206 (1930); Bethe, 'Handbuch der Physik,' vol. 24, 2, p. 607.

appears. Super-lattices should be similar, and one may even hope that it is simpler to treat since it involves no quantum mechanics but only classical statistics.

2—ORDER AT LARGE AND SMALL DISTANCES. INFLUENCE OF THE NUMBER OF DIMENSIONS

Phenomena analogous to ferromagnetism, such as the one treated in this paper, are essentially restricted to three (or more) dimensions.* In a linear chain, the interaction between neighbours could never establish order through large distances; there will only be small regions that are ordered. This can be seen very easily for a "linear chain alloy" as follows.

Consider a linear chain containing an equal number of atoms of two different kinds A and B. If there is perfect order, the atoms A and B should simply alternate, giving the arrangement A B A B A B At low temperatures, it will indeed be much more probable that two neighbouring atoms should be unlike than like. Still at any finite temperature there will be a finite number of pairs of neighbours of the *same* kind. Consider such a pair, *e.g.*, two neighbouring A-atoms $A_1 A_2$. Then the atoms on the right of A_2 will probably be ordered with respect to A_2 , because there is no interaction between them and A_1 . The atoms on the left will be ordered with respect to A_1 , so that the arrangement

$$\dots A B A B_1 A_1 A_2 B_2 A B A B \dots$$

arises. The chain falls into two parts which are disordered with respect to each other, *e.g.*, the third atom on the right of B_1 is the B-atom B_2 , whereas in an ordered crystal the third neighbour of a B-atom would be always an A-atom. Thus one single pair of equal neighbours destroys completely the order of the chain as a whole, and only small portions of the chain can be ordered, namely, the portions between any two pairs of like neighbours.

This is completely different for two or three dimensions. Consider in two dimensions again a pair of like neighbours $A_1 A_2$. Then it is by no means certain whether a given neighbour of atom A_2 , *e.g.*, the atom x in fig. 1*a*, is more likely to be a B or an A-atom. For in contrast to the linear chain, x interacts not only with the atom A_2 which would require it to be a B-atom, but also with y , which, being a neighbour of A_1 , should be a B-atom and therefore requires x to be an A-atom. Thus the (prob-

* Bloch, *loc. cit.*

able) nature of x depends on the arrangement of *all* the atoms surrounding it, not only on A_2 . Three alternatives are possible: either

- (1) the atoms surrounding $A_1 A_2$ "fit" to A_1 , so that A_2 is simply a single "wrong" atom in perfectly ordered surroundings, fig. 1*b*;
or
- (2) the surrounding atoms fit to A_2 , so that A_1 is a "wrong" atom; or
- (3) there is a real break in the order, similar to the linear chain. The crystal falls into two halves, each being completely ordered in itself but completely disordered with respect to the other half. The halves are separated from each other by a "boundary" which passes between A_1 and A_2 and also between other pairs of neighbouring like atoms, fig. 1*c*.

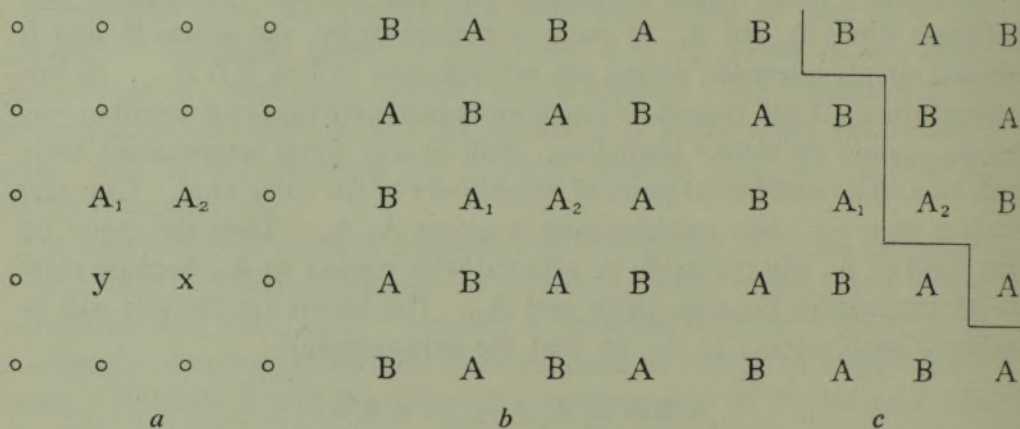


FIG. 1

It is clear at once that—given the existence of the pair $A_1 A_2$ —the arrangements (1) and (2) have lower energy than (3). For in the first two cases we need only have four pairs of like neighbours, *e.g.*, in case (1) A_2 is surrounded by 4 A-atoms whereas everywhere else we have only pairs of unlike neighbours. In case (3), on the other hand, we have one pair of equal neighbours *per unit length of the boundary*, and this makes an enormous number of pairs if we want the boundary to extend through the whole crystal, thus really destroying the correlation between left-hand side and right-hand side of the crystal, in analogy to the linear chain.

At low temperatures, only the states of low energy are realized, therefore we expect that at low temperatures the crystal is ordered as a whole, only containing the few atoms at wrong places inside it, *e.g.*, a cubic body-centred crystal would have nearly all corners of the cubes occupied

by A-atoms and almost all centres by B-atoms; only a small fraction of the A-atoms (increasing with temperature) goes into the centres and a corresponding number of B-atoms occupies corners.*

We have at low temperatures a "correlation" between distant atoms, however far away. If we know the nature of the atom situated at a given place, we can predict whether another atom 1000 atomic distances away is likely to be an A- or a B-atom.

This will not be true for high temperatures. For then the number of possible realizations of a given arrangement of atoms is more important than the energy of the arrangement. Given only the two atoms A_1 and A_2 , there is only one single arrangement of the atoms in the crystal corresponding to case (1) above, since the positions of all atoms are fixed by requiring that there should be perfect order with respect to A_1 . But there is an immense number of ways in which a boundary may be laid through the crystal; therefore, at sufficiently high temperatures, case (3) is the more probable *in spite of its higher energy*. Thus the "correlation of distant atoms" disappears at high temperatures (§ 6).

This does not mean that there is no order at all at high temperatures. At any finite temperature, it will be more likely to find a B-atom beside a given A-atom than to find another A-atom there, because the energy is smaller in the former case and the *a priori* probability is the same. Only the order does not extend through the whole (and not even through large portions of the) crystal. Thus we are led to distinguish between two different types of order: the order of neighbours and the order of the crystal as a whole (order at large distances).

3—DEFINITION OF THE TWO DEGREES OF ORDER

The "order of neighbours" σ is defined as the difference of the probabilities of finding an unequal and an equal neighbour beside a given atom. Thus the probability for finding a B-atom beside a given A-atom is $\frac{1}{2}(1 + \sigma)$, that for finding another A-atom is $\frac{1}{2}(1 - \sigma)$. If N is the total number of atoms, z the number of neighbours of each atom, then there will be

$$\frac{1}{4}Nz(1 + \sigma) \text{ pairs of neighbours A B,}$$

$$\frac{1}{8}Nz(1 - \sigma) \text{ pairs A A and equally many B B.}$$

If the interaction energy between an A and a B atom is V_{ab} , and V_{aa} and

* Of course, the B-corners and A-centres in the equilibrium state will *not* in general be beside each other.

V_{bb} that between A A and B B respectively, the total energy of our crystal becomes

$$E = \frac{1}{4}NzV_{ab}(1 + \sigma) + \frac{1}{8}Nz(V_{aa} + V_{bb})(1 - \sigma) = \text{const} + \frac{1}{4}NzV(1 - \sigma), \quad (1)$$

where

$$V = \frac{1}{2}(V_{aa} + V_{bb}) - V_{ab}. \quad (2)$$

Thus the order of neighbours σ is directly proportional to the energy of the crystal (apart from a constant). V is the difference of the interaction energies between two equal and between two unequal neighbours. V must be positive in order to make a superlattice possible (otherwise the atoms A and B would segregate). Its magnitude determines the temperature at which the transition from the ordered to the disordered state takes place. $\sigma = 1$ corresponds to perfect order, $\sigma = 0$ to perfect disorder. For any finite temperature σ lies between these limits.

To define the long-distance order, we divide the lattice points in the crystal into two groups, a and b , the points of each group forming a lattice of their own, *e.g.*, in a cubic body-centred lattice, a and b are the corners and the centres of the cubes; in a simple cubic lattice the a 's and b 's form a rocksalt structure, the positions of the Na atoms being denoted as " a ," the Cl positions as " b ." Then the long-distance order S is the probability for finding an A-atom in an " a " position minus the probability for finding a B-atom there. This definition of order is equivalent to that used by Bragg and Williams. $S = +1$ or -1 corresponds to perfect order, $S = 0$ to perfect disorder. Above a certain critical temperature Θ (Curie point) we expect S to be zero (§ 2), below Θ the "distant order" S is finite.

If S is to have a physical meaning, it is necessary that the temperature at which the distant order disappears should be independent of the size of the crystal; in other words that the question of stability or non-stability of breaks in the order should not depend on the number of atoms in the crystal but only on the temperature. This can be proved for two- and three-dimensional lattices.*

4—QUALITATIVE DISCUSSION OF THE TRANSITION POINT

For a given value of S , there is a great number of possible distributions of the atoms over the various sites. We know only that there are

* The probability for a boundary is of the order $\exp\left(e^{-\frac{NV}{k}}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)$, N being the number of atoms in one crystal plane, T_0 a critical temperature and k Boltzmann's constant.

$\frac{1}{4}N(1 + S)$ A-atoms and $\frac{1}{4}N(1 - S)$ B-atoms in a -positions. But they may be distributed over the $\frac{1}{2}N$ available a -positions in $\binom{\frac{1}{2}N}{\frac{1}{4}N(1 - S)}$ different ways, and there is an equal number of possible distributions of A- and B-atoms over the b -positions. Each distribution corresponds to a certain energy. The lowest energy is obtained if all "wrong" atoms, *i.e.*, the B-atoms in a -positions and the A-atoms in b -positions, are put together. They then form a cluster inside which there is perfect order, and only on the surface are there then pairs of like neighbours. The energy is only of the order $N^{2/3}(1 - S)^{2/3}V$ if the constant in 1 is put equal to zero. It is, however, clear that this distribution is most unlikely, and that it is much more probable that the "wrong" atoms are more or less isolated from each other. For complete isolation, we obtain the maximum possible energy, *viz.*, $\frac{1}{2}NzV(1 - S)$. There is a great number of states having energies between these two limits.

We may suppose the number of states having a given S and a given energy (or σ) to be given; let us denote this number by $n(S\sigma)$. Then we can calculate the partition function for any value of S at a given temperature T

$$P(S) = \sum_{\sigma} n(S\sigma) e^{-E(\sigma)/kT}.$$

By symmetry we have $P(-S) = P(S)$. At very low temperatures the partition function will have two maxima at $S = \pm 1$ and a minimum at $S = 0$. As the temperature increases, the maxima move to lower (absolute) values of S , *i.e.*, the long-distance order decreases gradually. This goes on until the two maxima merge into each other at $S = 0$, at a certain critical temperature Θ .*

The energy of the crystal increases with temperature for two reasons: Firstly, for a given S the average energy increases (σ decreases) with temperature. In other words, if S is kept fixed, the "wrong atoms" cluster together at low temperatures and become isolated at high temperatures. The specific heat due to this process (*i.e.*, the rate of change of the energy with temperature) almost certainly decreases with increasing temperature for any given value of S .

* These statements cannot be proved rigorously, but seem highly probable. An alternative assumption would be that a secondary maximum develops at $S = 0$, increases gradually with increasing temperature and becomes higher than the two maxima at large S , before the latter have merged together. In this case, there would be a real point of transformation, with latent heat, jump in the physical properties, etc. But there seems to be neither a theoretical nor an experimental reason for such an assumption.

Secondly, the most probable large-distance order decreases with increasing temperature until it reaches zero at $T = \Theta$. Since for small S there are many states with rather high average energy, for large S few states with low energy, the change of S means also an increase of energy. The corresponding specific heat should increase with increasing temperature, since the long-distance order changes (decreases) the more rapidly the smaller it is already, *i.e.*, the nearer the temperature comes to Θ (*see* Bragg and Williams, *loc. cit.*, and § 6 of this paper). When the critical temperature Θ is reached, this second kind of specific heat suddenly disappears altogether. Therefore we should expect (1) a jump in the specific heat at $T = \Theta$, *i.e.*, a higher c_v for $T < \Theta$ than for $T > \Theta$, (2) the specific heat should increase with increasing temperature on the low-temperature side of the critical temperature, since it contains the specific heat due to change of long-distance order on that side, (3) it should decrease on the high-temperature side, because there it is entirely due to the change of average energy for the fixed value $S = 0$.

All these features are shown by the curves d and e in fig. 6, which give the results of the quantitative calculation. The contribution from the disordering to the specific heat above the "Curie point" is seen to be exceedingly small, only about 5% of that below Θ . The theory of Bragg and Williams gives zero specific heat above Θ , because it considers only the specific heat due to change of S .

All physical properties which depend on the order at long distances, such as electric conductivity, and more so the intensity of the superlattice lines in X-ray spectra, should show a rapid change below $T = \Theta$, and have practically the value for a perfectly disordered crystal above Θ . There should be no jump in these quantities at $T = \Theta$, but only a kink in the curves representing them as functions of T .

5—APPROXIMATION FOR VANISHING LONG-DISTANCE ORDER

At high temperature there is no order at long distances. There is, however, a considerable correlation between neighbours which we shall calculate.

Let $w = \frac{1}{2}(1 - \sigma)$ be the probability that a neighbour of a given "central" A-atom is itself an A-atom. For a first approximation, we could assume this probability to be independent of the nature of the other neighbours of the central atom. Then obviously the ratio of the probabilities that the neighbour is A or B respectively is given by the Boltzmann factor

$$e^{-V/kT} = x, \quad (3)$$

viz.,

$$w/(1 - w) = x,$$

from which we find

$$\sigma = (1 - x)/(1 + x). \tag{4}$$

This means a very slow increase of the order with decreasing temperature (decreasing x) which is shown in fig. 4, curve a . There is no sign whatever of a "transition temperature."

The assumed mutual independence of the neighbours of one central atom is, however, only true for a linear chain of atoms. For two- or three-dimensional lattices, the nearest neighbours of a central atom ("atoms in the first shell") are connected with each other not only by their interaction with the central atom but also by interaction with the "second shell" which is defined as containing all the nearest neighbours

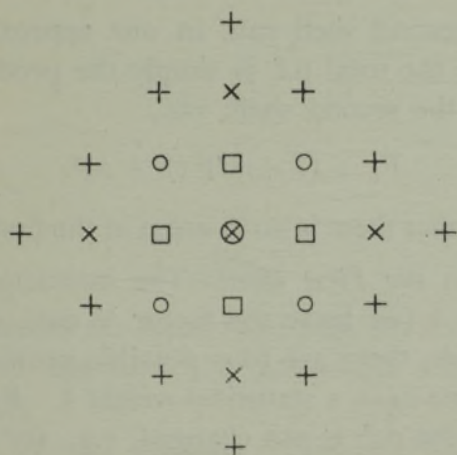


FIG. 2—Quadratic lattice. ⊗ Central atom; □ first shell; × corner atoms in second shell; ○ medium atoms, second shell; + third shell

of the atoms in the first shell, fig. 2. This interaction tends to make all atoms in the first shell equal, and thus supports the ordering force exerted by the central atom. Therefore the order is greater than in our first approximation for any temperature and the order-temperature curve is steeper.

The effect of the second shell can be taken into account by the following method (second approximation). Take a given distribution of A- and B-atoms over the first shell and calculate the partition function for this distribution, including the interaction with the second shell. We shall explain this for the quadratic (two-dimensional) lattice, fig. 2. Each lattice point has, in this system, four nearest neighbours, this is therefore the number of atoms in the first shell. The second shell contains 8 atoms, 4 of which lie at the corners of a square and 4 at the middle of its sides ("medium atoms"). The following distributions are possible.

(1) *No A-atoms in the First Shell*—Then the interaction energy of the first shell with the central atom is zero.* If any corner-atom in the second shell is A, its interaction energy with its neighbour in the first shell (which is certainly a B-atom) is zero as well. If the corner-atom is B, the interaction energy is V. Therefore, each corner-atom has the partition function (p.f.).

$$1 + e^{-V/kT} = 1 + x.$$

If a medium position of the second shell is occupied by an A-atom, the latter's interaction energy with the first shell is again zero, while a B-atom would have the interaction energy 2V, because it interacts with two B-atoms in the first shell. Therefore its p.f. becomes

$$1 + e^{-2V/kT} = 1 + x^2.$$

Each atom in the second shell can, in our approximation, be treated separately; therefore the total p.f. is simply the product of the p.f.'s for the single atoms in the second shell, viz.,

$$P_0 = (1 + x^2)^4 (1 + x)^4.$$

The index 0 signifies that there is no A-atom in the first shell.

(2) *One A-atom in the First Shell*—The interaction energy with the central atom is now 1 (we leave the factor V out), giving a factor x in the p.f. Furthermore, there are four possible positions for the A-atom in the first shell, so we have a statistical weight 4. For the corner-atoms in the second shell, the p.f. is not changed, e.g., for the corner near the A-atom of the first shell, the energy is now 0 if the corner is occupied by a B-atom and 1 if the atom is A, but the p.f. remains $1 + x$. For the medium atoms, however, two positions are to be distinguished: two medium atoms, marked \circ in fig. 3a, have still got two B-atoms as neighbours and have thus the p.f. $1 + x^2$. The two others, marked \times , each have one A and one B neighbour; it is therefore irrelevant whether they are A or B, in any case their interaction energy with their neighbours in the first shell will be 1, which makes the p.f. for them $2x$. Therefore the total partition function is

$$P_1 = 4x(2x)^2(1 + x^2)^2(1 + x)^4.$$

(3) *Two Atoms in the First Shell*—They can lie (a) side by side, para-position, fig. 3b, or (b) opposite each other, ortho-position, fig. 3c. The

* We fix the interaction energy of two unequal neighbours to be zero, that of two equal neighbours has then to be taken equal to V (cf. equation (2)). The constant in (1) is then zero.

interaction with the central atom is 2 in both cases, giving factor x^2 . The statistical weight for para 4, for ortho 2. Partition function for each corner atom $1 + x$. Medium atoms of second shell:

(a) for para two medium atoms have two like neighbours (one A A the other B B) and therefore p.f. = $1 + x^2$, the other two have neighbours A B, p.f. = $2x$. Consequently,

$$P_{2P} = 4x^2 (2x)^2 (1 + x^2)^2 (1 + x)^4;$$

(b) for ortho each medium atom has one A- and one B-neighbour, giving $2x$ for its p.f., therefore

$$P_{20} = 2x^2 (2x)^4 (1 + x)^4.$$

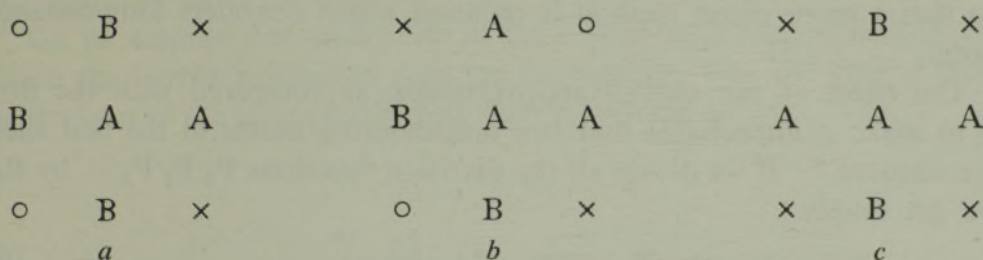


FIG. 3

(4) For three A-atoms the interaction with the second shell is the same as for one A in the first shell, the interaction with the central atom is 3 instead of 1, giving

$$P_3 = 4x^3 (2x)^2 (1 + x^2)^2 (1 + x)^4.$$

(5) Four A-atoms are identical with no one as regards interaction with the outside, the interaction with the centre is 4 instead of 0, therefore

$$P_4 = x^4 (1 + x^2)^4 (1 + x)^4.$$

The probability that a "central" A-atom has no A-atom among its neighbours is now

$$p_0 = P_0 / (P_0 + P_1 + P_{2P} + P_{20} + P_3 + P_4).$$

The average number of A-atoms near a central A-atom is

$$w = \frac{P_1 + 2(P_{2P} + P_{20}) + 3P_3 + 4P_4}{P_0 + P_1 + P_{2P} + P_{20} + P_3 + P_4} = p_1 + 2(p_{2P} + p_{20}) + 3p_3 + 4p_4,$$

and the degree of order

$$\sigma = 1 - \frac{1}{2}w = p_0 - p_4 + \frac{1}{2}(p_1 - p_3). \tag{5}$$

The order calculated by this method is considerably larger than in the first approximation (formula (4)), and increases with temperature more steeply. For the quadratic lattice we have

$x =$	0.1	0.2	0.3	0.4	0.5	0.6	0.8	1.0
(first approx.) ..	81.8	66.7	53.8	42.9	33.3	25.0	11.1	0
(second approx.)	99.03	91.71	75.6	56.6	40.4	28.2	11.9	0

For the simple cubic lattice the order is given in fig. 4 (curve *b*) as a function of temperature.

It would in principle be possible to reach the exact value for the order at any temperature by calculating the higher approximations of our method. Actually, already the third approximation is extremely tedious, so that a more direct method is required which considers long-distance order.

The effect of our second approximation as compared with the first is to make it improbable that two neighbouring atoms in the first shell are unequal.* If we divide all the partition functions $P_0 P_1 P_2 \dots$ by P_0 , we get simply

$$P_{mn} = g_{mn} x^n \left(\frac{2x}{1+x^2} \right)^m \quad (6)$$

where n is the number of A-atoms in the first shell, g_{mn} the statistical weight and m the number of pairs of unequal neighbours in the first shell, *i.e.*, for each such pair the partition function has to be multiplied by the factor

$$\mu = \frac{2x}{1+x^2} \quad (7)$$

which takes account of the interaction with the second shell.

6—FIRST APPROXIMATION INCLUDING LONG-DISTANCE ORDER

With the notation of § 3, we may divide the atoms into "right" ones, (R-atoms) and wrong ones (W-atoms). An A-atom in an "a" position or a B-atom in a "b" position are "right," and A-atom in "b" or a B-atom in "a" are to be termed W. Two neighbouring R-atoms or two neighbouring W-atoms have the interaction energy zero; a pair of neighbours R W has the interaction energy V.

* Two neighbours in a given shell are, of course, never nearest neighbours but only second nearest. The nearest neighbours of an atom in the n th shell lie all in the $n-1$ st and $n+1$ st shells. Nearest neighbours have to be unlike, second nearest like if the crystal is perfectly ordered. The number of pairs of *unequal neighbours in a given shell* is therefore the smaller the greater the order.

We consider again a central atom and the various shells round it (§ 5). In the first approximation, we assume that the only effect of the "outer shells" is to make R-atoms in the first shell more likely than W-atoms. This is due to the fact that the outer shells themselves contain more R-atoms than W's, according to our assumption, and that the energy is smaller if an R-atom lies beside another R than if a W-atom lies there. To take account of this fact we introduce a factor ε into the partition function for each wrong atom in the first shell. We can then calculate the probabilities (a) that the central atom is wrong, (b) that any atom in the first shell is wrong, as functions of x (temperature) and ε . The parameter ε is then fixed by the condition that the two probabilities (a) and (b) must be equal, because the "central" atom is in no way distinguished from the others.

Let us suppose that each atom in the crystal has z nearest neighbours. Then the partition function (relative probability), that the central atom is R and n of the atoms in the first shell are wrong, is

$$r_n = \binom{z}{n} x^n \varepsilon^n. \quad (8)$$

Here $\binom{z}{n}$ is the statistical weight (number of distributions of the n wrong atoms over the z sites), one factor x is introduced for the interaction of the central R-atom with any one W-atom in the first shell, and ε^n takes account of the interaction with the outside. If the central atom is wrong, its interaction energy with the first shell is $(z - n)V$, because it has the interaction energy V with each R-atom. Therefore the probability that the centre is W and n wrong atoms are in the first shell, becomes

$$w_n = \binom{z}{n} x^{z-n} \varepsilon^n. \quad (8A)$$

Accordingly, the total relative probabilities that the central atom is right or wrong are respectively

$$\left. \begin{aligned} r &= \sum_{n=0}^z r_n = (1 + \varepsilon x)^z \\ w &= \sum w_n = (\varepsilon + x)^z \end{aligned} \right\}. \quad (9)$$

On the other hand, the relative probability that an atom of the first shell is wrong is given by

$$w' = \frac{1}{z} \sum n(r_n + w_n) = \frac{1}{z} \varepsilon \frac{\partial}{\partial \varepsilon} (r + w) = \frac{\varepsilon x}{1 + \varepsilon x} r + \frac{\varepsilon}{\varepsilon + x} w. \quad (10)$$

The condition

$$w' = w \quad (11)$$

therefore reduces to

$$\left. \begin{aligned} \frac{x}{\varepsilon + x} w &= \frac{\varepsilon x}{1 + \varepsilon x} r \\ \frac{w}{r} &= \frac{\varepsilon(\varepsilon + x)}{1 + \varepsilon x} \end{aligned} \right\}, \quad (12)$$

whereas from (9) we find

$$\frac{w}{r} = \left(\frac{\varepsilon + x}{1 + \varepsilon x} \right)^z. \quad (13)$$

Comparing (12) and (13), we obtain

$$(\varepsilon + x)/(1 + \varepsilon x) = \varepsilon^{1/(z-1)}, \quad (13A)$$

therefore

$$x = (\varepsilon^{1/(z-1)} - \varepsilon)/(1 - \varepsilon^{z/(z-1)}),$$

and, putting

$$\varepsilon = e^{-2\delta(z-1)}, \quad (13B)$$

we have

$$x = \sinh(z-2)\delta/\sinh z\delta. \quad (14)$$

From this equation, ε may be determined as a function of the temperature, *i.e.*, of x , or more easily x as function of ε . One sees immediately:

(1) Two values of ε , namely, $\varepsilon = \varepsilon'$ and $\varepsilon = 1/\varepsilon'$, correspond to the same value of x . That means that "right" and "wrong" atoms may be interchanged, as is natural.

(2) The value $\varepsilon = 1$ always gives a solution, namely, $x = 0/0$. This is to be understood from the fact that the case $S = 0$, *i.e.*, no long-distance order, always corresponds to an extreme of the free energy, namely, a minimum at high, a maximum at low temperature.

(3) If ε is different from unity, x can never be larger than

$$x_0 = 1 - 2/z. \quad (15)$$

For (14) evidently increases with increasing ε (decreasing δ) as long as $\delta > 0$. The maximum value of (14) is therefore obtained by putting $\delta \ll 1$; this leads to the value (15) for x .

Order at large distances can therefore only exist below a critical temperature, which is given by (15). Above that temperature, (14) has only the one solution $\varepsilon = 1$, corresponding to $S = 0$. Below Θ , there are three solutions, ε' , 1, $1/\varepsilon'$, the first and third of which correspond to a non-vanishing order $+S$ and $-S$ at long distances and to a lower free energy than $\varepsilon = 1$.

The energy of the crystal is V times the number of pairs of neighbours RW . This number is equal to the total number of atoms N , times the

probability for right atoms, $r/(w + r)$, times the average number of wrong neighbours of a right atom, $\Sigma(nr_n)/r$. Therefore

$$E = NV\Sigma(nr_n)/(w + r).$$

Using (1), we can calculate the order of neighbours

$$1 - \sigma = \frac{4}{z} \frac{\Sigma nr_n}{w + r}, \tag{16}$$

which according to (9), (10) becomes

$$1 - \sigma = 4 \frac{\epsilon x}{1 + \epsilon x} \frac{r}{w + r}. \tag{17}$$

Now from (13) and (13A) we deduce (*cf.* 13B)

$$w/r = \epsilon^{z/(z-1)} = e^{-2z\delta}, \tag{18}$$

so that

$$1 - \sigma = 4 \frac{\epsilon x}{1 + \epsilon x} \frac{1}{1 + \epsilon^{z/(z-1)}} = \frac{2 \sinh(z - 2)\delta}{\sinh(2z - 2)\delta \cosh z\delta} \tag{19}$$

where ϵ may be expressed in terms of x , by making use of (14).

The order at long distances is simply

$$S = \frac{r - w}{r + w} = \tanh z\delta. \tag{20}$$

This reaches zero at the critical temperature ($\epsilon = 1$), whereas for the order of neighbours at that temperature we find (*cf.* (17), (15))

$$1 - \sigma_0 = 2 \frac{x_0}{1 + x_0}; \quad \sigma_0 = \frac{1 - x_0}{1 + x_0} = \frac{1}{z - 1}. \tag{21}$$

We now proceed to calculate the specific heat near the critical temperature. We find from (14), (20)

$$x = \frac{z - 2}{z} (1 - \frac{2}{3}(z - 1)\delta^2 + \dots), \tag{14A}$$

$$S = z\delta - \dots, \tag{20A}$$

and, after some calculation,

$$1 - \sigma = \frac{z - 2}{z - 1} (1 - \delta^2 z (z - \frac{2}{3}) + \dots), \tag{19A}$$

$$\frac{d(1 - \sigma)}{dx} = \left(\frac{z}{z - 1}\right)^2 \left(\frac{2}{3}z - 1\right). \tag{22}$$

For the specific heat per atom we obtain, using (1) and (3)

$$c_v = \frac{dE}{N dT} = \frac{z}{4} kx (\log x)^2 \frac{d(1-\sigma)}{dx} \left. \begin{aligned} & \\ & = \frac{z-2}{4} \left(\frac{z}{z-1}\right)^2 \left(\frac{3}{2}z - 1\right) \left(\log \frac{z-2}{z}\right)^2 k \end{aligned} \right\} \quad (23)$$

Above the critical temperature, we have according to (4),

$$\sigma = (1-x)/(1+x),$$

therefore

$$\left(\frac{d(1-\sigma)}{dx}\right)_{x>x_0} = \frac{2}{(1+x_0)^2} = \frac{1}{2} \left(\frac{z}{z-1}\right)^2, \quad (24)$$

and the ratio of the specific heat below and above Θ becomes

$$\frac{c_v(T < \Theta)}{c_v(T > \Theta)} = 3z - 2. \quad (25)$$

Numerically, we obtain the following values for the specific heat just above and below the Curie point:—

Number of neighbours	Structure	Specific heat per atom	
		Below	Above
2	linear chain	0	0
4	quadratic	2.14 k	0.214 k
6	simple cubic	1.90	0.119
8	cubic body-centred	1.78	0.081
12	cubic face-centred	1.68	0.049
∞	—	1.50	0

The long-distance order changes near the Curie point as the root of $\Theta - T$, viz., according to (14A) and (20A),

$$S = z\delta = z \sqrt{\frac{3}{2(z-1)}} \sqrt{\frac{x_0-x}{x_0}} = z \sqrt{\frac{3|\log x_0|}{2(z-1)}} \sqrt{\frac{\Theta-T}{\Theta}} \\ = \sqrt{\frac{3}{2} \frac{z^2}{z-1} \log \frac{z}{z-2}} \sqrt{\frac{\Theta-T}{\Theta}}, \quad (26)$$

e.g., for a simple cubic lattice $S = 2.09 \sqrt{(\Theta - T)/\Theta}$, for $z = \infty$, we have $S = 1.73 \sqrt{(\Theta - T)/\Theta}$. The long-distance order increases the more rapidly with decreasing temperature the smaller the number of neighbours of each atom. Accordingly, the specific heat near the Curie point also increases with decreasing z .

7—COMPARISON WITH THE THEORY OF BRAGG AND WILLIAMS

For an infinite number of neighbours z , our theory goes over exactly into that of Bragg and Williams, putting their V_0 equal to $2z$ times our V .

If we introduce δ as in (13B), $z\delta$ must be of order unity because of (20A), therefore $\delta \ll 1$, and according to (14A), (20)

$$x = \frac{\sinh(z-2)\delta}{\sinh z\delta} = 1 - \frac{2\delta}{\tanh z\delta} = 1 - \frac{2\delta}{S}.$$

On the other hand, V/kT is small in the interesting temperature range, since zV/kT is of the order unity. Therefore the definition (3) for x becomes

$$x = 1 - V/kT = 1 - 2\delta/S,$$

which means

$$\delta = VS/2kT.$$

Introducing this into (20A), we find

$$S = \tanh z\delta = \tanh (VzS/2kT) = \tanh (V_0S/4kT),$$

i.e., the principal equation of the theory of Bragg and Williams.

For the "order of neighbours" follows from (19)

$$1 - \sigma = 4 \frac{1}{(\cosh z\delta)^2}; \quad \sigma = (\tanh z\delta)^2 = S^2,$$

also identical with the assumption of Bragg and Williams. Therefore all consequences of their theory also follow from our first approximation for $z = \infty$.

8—SECOND APPROXIMATION

The "outer shells" have not only the effect of making the atoms in the first shell "right"—which we treated in § 6—but also of making them equal to each other, as we know from § 5. We now make essentially the same approximation as in § 5, only we assume in addition that the outer shells make it more probable to find an R-atom in the second shell than a W-atom. We therefore introduce, as in § 6, a factor ϵ in the partition function for each wrong atom in the second shell, and we determine ϵ from the condition that the probability to find a wrong atom is the same for the centre atom as for an atom in the first shell.

The reasoning is now exactly similar to § 5. Consider, *e.g.*, a corner atom in the second shell beside a right atom in the first. The contribution to the partition function is simply unity, if the corner atom is right, and it is ϵx if the atom is "wrong," where the factor x arises from

the interaction with the neighbour in the first shell (as in § 5), while ϵ is introduced by the interaction with the outer shells. Thus the p.f. of the corner atom is $1 + \epsilon x$ if it lies beside an R-atom in the first shell, and similarly it may be shown to be $x + \epsilon$ if the neighbouring first shell atom is W.

The factor in the p.f. corresponding to a "medium atom" in the second shell is

- $1 + \epsilon x^2$, if its two nearest neighbours in the first shell are both R;
- $\epsilon + x^2$, if both nearest neighbours are W;
- $x(1 + \epsilon)$, if one of them is a W, the other an R-atom.

For $\epsilon = 1$ these formulæ go over into those of § 5.

A given configuration of the first shell may be characterized by the number n of wrong atoms in the shell and the number m of pairs of unequal neighbours in it.* Then the number of R-atoms is $z - n$, the number of neighbouring pairs WW is $(\frac{1}{2}z - 1)n - \frac{1}{2}m$, and the number of pairs RR is $(\frac{1}{2}z - 1)(z - n) - \frac{1}{2}m$. For each atom in the first shell of a quadratic or simple cubic lattice has $z - 2$ neighbours in the first shell, viz., all atoms of that shell except the diametrically opposite and itself. Therefore we have

$$(z - 2) \times \text{number of W-atoms} = \text{number of RW-pairs} + 2 \times \text{number of WW-pairs},$$

$$(z - 2) \times \text{number of R-atoms} = \text{number of RW-pairs} + 2 \times \text{number of RR-pairs},$$

which gives the above expressions for the number of RR and WW pairs.

If we now put equal to unity, the partition function that *all* atoms of the first shell are R, we have to introduce a factor $(\epsilon + x)/(1 + \epsilon x)$ for each W-atom in the first shell (because of the interaction with corner atoms), a factor $(\epsilon + x^2)/(1 + \epsilon x^2)$ for each pair of neighbours WW, and a factor $x(1 + \epsilon)/(1 + \epsilon x^2)$ for each pair RW.

Therefore the partition function for any configuration of the first shell becomes

$$\begin{aligned} P_{nm} &= g_{nm} \left(\frac{\epsilon + x}{1 + \epsilon x} \right)^n \left(\frac{\epsilon + x^2}{1 + \epsilon x^2} \right)^{(\frac{1}{2}z-1)n - \frac{1}{2}m} \left(\frac{x(1 + \epsilon)}{1 + \epsilon x^2} \right)^m \\ &= g_{nm} \lambda^n \mu^{\frac{1}{2}m} \end{aligned} \quad (27)$$

with

$$\lambda = \frac{\epsilon + x}{1 + \epsilon x} \left(\frac{\epsilon + x^2}{1 + \epsilon x^2} \right)^{\frac{1}{2}z-1} \quad (28)$$

$$\mu = \frac{x^2(1 + \epsilon)^2}{(1 + \epsilon x^2)(\epsilon + x^2)}$$

* Cf. footnote, p. 556.

g_{nm} = statistical weight. It is more convenient to divide (27) by $\lambda^{\frac{1}{2}z}$, so that

$$P'_{nm} = g_{nm} \lambda^{n-\frac{1}{2}z} \mu^{\frac{1}{2}m}. \tag{27A}$$

It remains to consider the interaction with the central atom. The partition function that the central atom is right and that n wrong atoms occur in the first shell, becomes

$$r_{nm} = P'_{nm} x^n, \tag{29}$$

and the partition function of the same configuration with a wrong central atom is

$$w_{nm} = P'_{nm} x^{z-n}. \tag{29A}$$

The parameter ϵ has to be fixed by the condition of equal "long-distance order" at the centre and in the first shell:

$$\sum_{nm} w_{nm} = \frac{1}{z} \sum_{nm} n (r_{nm} + w_{nm}), \tag{30}$$

the order of neighbours is then given by (16).

In discussing these equations, we first consider the "Curie point." Near that point, ϵ may be put equal to $1 - \delta$ with $\delta \ll 1$. Then

$$\lambda = 1 - \delta \left[\frac{1-x}{1+x} + (\frac{1}{2}z - 1) \frac{1-x^2}{1+x^2} \right] + \dots,$$

whereas

$$\mu = \left(\frac{2x}{1+x^2} \right)^2 \left[1 + \frac{1}{4} \delta^2 \left(\frac{1-x^2}{1+x^2} \right)^2 + \dots \right].$$

Therefore, neglecting δ^2 , we have

$$\left. \begin{aligned} \mu &= \mu_0 = (2x/1+x^2)^2, \\ \lambda &= 1 - \kappa, \quad \kappa \sim \delta \ll 1. \end{aligned} \right\} \tag{31}$$

Then

$$r_{nm} = g_{nm} x^n \mu_0^{\frac{1}{2}m} (1 - (n - \frac{1}{2}z) \kappa) = p_{nm} (1 + (\frac{1}{2}z - n) \kappa), \tag{32}$$

where p_{nm} is the probability for the configuration nm as calculated in § 5, *i.e.*, assuming *no* long-distance order. It is simply a function of x (temperature), and ϵ enters the probability r_{nm} only in the factor

$$1 + (\frac{1}{2}z - n) \kappa.$$

Adding the probabilities of the various configurations having the same number n of W-atoms in the first shell, we may rewrite (32):

$$r_n = p_n (1 + (\frac{1}{2}z - n) \kappa), \tag{32A}$$

p_n is the probability that—with no long-distance order— n atoms of the first shell are *equal* to the central atom.

Similarly, we obtain

$$w_n = p_{z-n} (1 + (\frac{1}{2}z - n) \kappa) \quad (32B)$$

because, if the central atom is wrong, all the *right* atoms of the first shell are equal to it, *i.e.*, $z - n$ atoms. Summing (32A) over n , we obtain

$$r = \Sigma p_n + \Sigma (\frac{1}{2}z - n) p_n \kappa = 1 + \frac{1}{2}z\kappa\sigma_0. \quad (33)$$

For Σp_n is the sum of the probabilities of all configurations of the first shell and therefore unity, whereas

$$\Sigma \left(1 - \frac{2n}{z}\right) p_n = \sigma_0 \quad (34)$$

is the probability of finding (with vanishing long-distance order) an unequal atom beside the central atom minus that of finding an equal one there ($z - n$ of the z first shell atoms are unequal, n equal to the central atom).

Similarly to (33), we obtain

$$w = \Sigma w_{z-n} = \Sigma p_n (1 - (\frac{1}{2}z - n) \kappa) = 1 - \frac{1}{2}z\kappa\sigma_0, \quad (33A)$$

$$\frac{2}{z} \Sigma nr_n = r - \Sigma \left(1 - \frac{2n}{z}\right) r_n = r - \sigma_0 - \frac{1}{2}z\rho\kappa, \quad (35)$$

$$\begin{aligned} \frac{2}{z} \Sigma nw_n &= \frac{2}{z} \Sigma (z - n) w_{z-n} = w + \Sigma \left(1 - \frac{2n}{z}\right) w_{z-n} \\ &= w + \sigma_0 - \frac{1}{2}z\rho\kappa, \end{aligned} \quad (35A)$$

where

$$\rho = \Sigma \left(1 - \frac{2n}{z}\right)^2 p_n. \quad (36)$$

Adding (35) and (35A) and using (30), we obtain

$$\left. \begin{aligned} 2w &= \frac{2}{z} \Sigma n (r_n + w_n) = r + w - z\rho\kappa \\ r - w &= z\rho\kappa, \end{aligned} \right\}, \quad (37)$$

whereas from (33), (33A) we find

$$r - w = z\sigma_0\kappa. \quad (37A)$$

In order that these two equations should be consistent, we must have

$$\sigma_0 = \rho. \quad (38)$$

This is the *condition for the Curie point*. At high temperatures, $\rho > \sigma_0$, because ρ must be positive and σ_0 vanishes for $T = \infty$. (At $T = \infty$ ρ has

the value $1/z$.) At low temperatures, $\rho < \sigma_0$, because p_n is only large for very small n . For the simple cubic lattice, the condition (38) is fulfilled for

$$x_0 = 0.6563,$$

corresponding to $\Theta = 2.372 V/k$, whereas in the first approximation (6) we find $x_0 = 0.6667$. The Curie point is therefore slightly lowered by the improvement in the approximation.

By taking higher powers in κ into account, κ can be determined as a function of temperature. A quadratic equation is obtained in this way, viz.,

$$\begin{aligned} \kappa^2 \sum_n \left\{ \left(1 - \frac{2n}{z}\right)^4 - \left(1 - \frac{2n}{z}\right)^3 + \frac{1}{4} \frac{(1+x_0)^2}{(\frac{1}{2}z-1)(1+x_0)^2+1+x_0^2} \right. \\ \left. \times \frac{2m}{z} \left[\left(1 - \frac{2n}{z}\right)^2 - \left(1 - \frac{2n}{z}\right) \right] \right\} p_n = \sigma_0 - \rho, \quad (39) \end{aligned}$$

therefore

$$\kappa^2 \propto \sigma_0 - \rho \propto \Theta - T.$$

9—RESULTS

For the simple cubic lattice, we find (in second approximation)

$$\begin{aligned} \kappa^2 &= 35.7 (x_0 - x) \\ S &= \frac{r-w}{r+w} = 3\kappa\sigma_0 = \sqrt{19.4_5 (x_0 - x)} = 2.32 \sqrt{\frac{\Theta - T}{\Theta}}, \\ \sigma_{T=\Theta} &= 24.60\%, \end{aligned}$$

and for the specific heat

$$\left. \begin{aligned} c_v &= 2.14k \text{ just below} \\ c_v &= 0.203k \text{ just above} \end{aligned} \right\} \text{the critical temperature.}$$

The transition point is therefore a little more marked than in the first approximation, the "distant order" S increases more rapidly below Θ and so does the "order of neighbours" σ , which causes a slightly (12%) larger specific heat.

The order has been calculated numerically for various temperatures. The result is given in figs. 4 to 6, which all refer to a simple cubic lattice. Fig. 4 gives the "order of neighbours" as a function of temperature for various approximations, viz.,

- (a) for the linear chain approximation (equation (4));
- (b) for the second approximation with no long-distance order (§ 5);

- (c) for the approximation of Bragg and Williams;
 (d) and (e) for the first and second approximation with order at long distances (§§ 6 and 8).

Fig. 5 gives the long-distance order according to the approximations *c*, *d*, *e*, fig. 6 the specific heat. The latter is seen to increase near the Curie point with improving approximation.

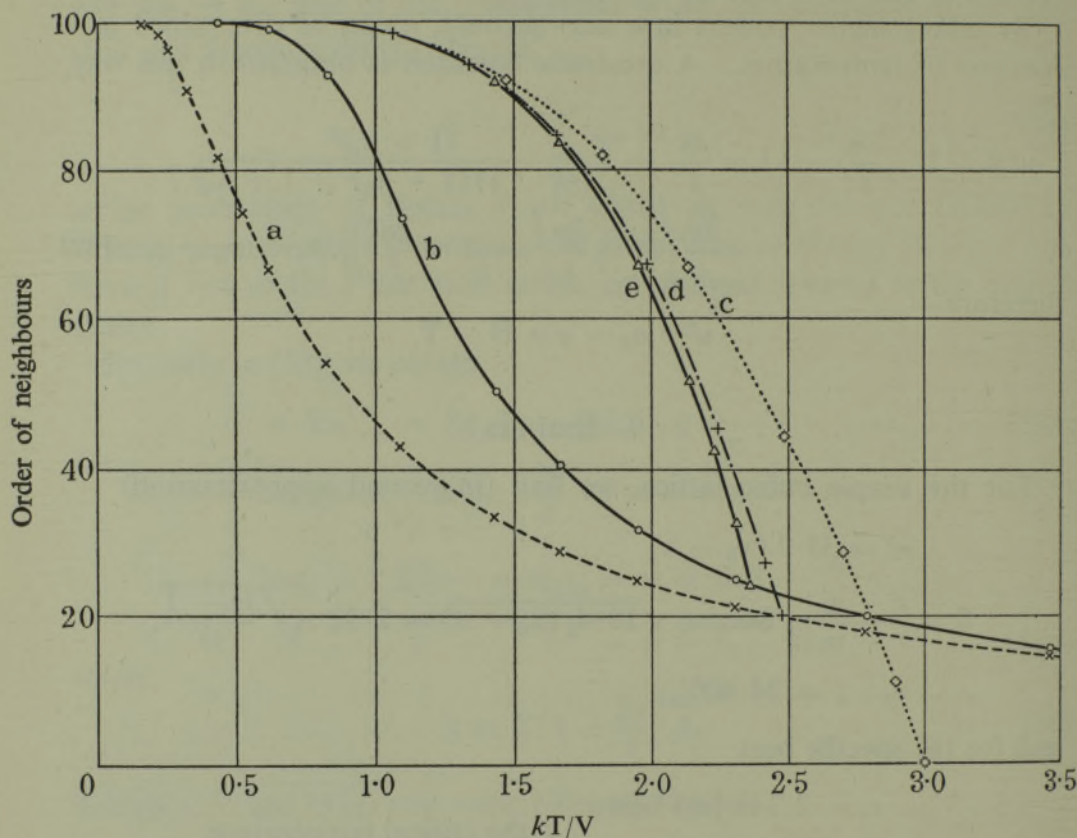


FIG. 4

The results may be checked to some extent by the following method.

It is known that the total energy of any statistical system is connected with its total partition function *P* by

$$E = - \frac{d \log P}{d(1/kT)}. \quad (40)$$

Now, for $T = 0$ the p.f. (partition function) is 2, corresponding to the two perfectly ordered states of the crystal which have energy zero ($S = 1$ and $S = -1$). For $T = \infty$, the energy is irrelevant, therefore the contribution of each state of the crystal to the p.f. is 1. The $\frac{1}{2}N$ A-atoms

and the $\frac{1}{2}N$ B-atoms may be distributed in any arbitrary way over the N lattice points, that gives

$$\binom{N}{\frac{1}{2}N} \approx 2^N$$

different distributions. Therefore

$$\log S_{T=\infty} = N \log 2; \quad \log S_{T=0} = 0 \tag{41}$$

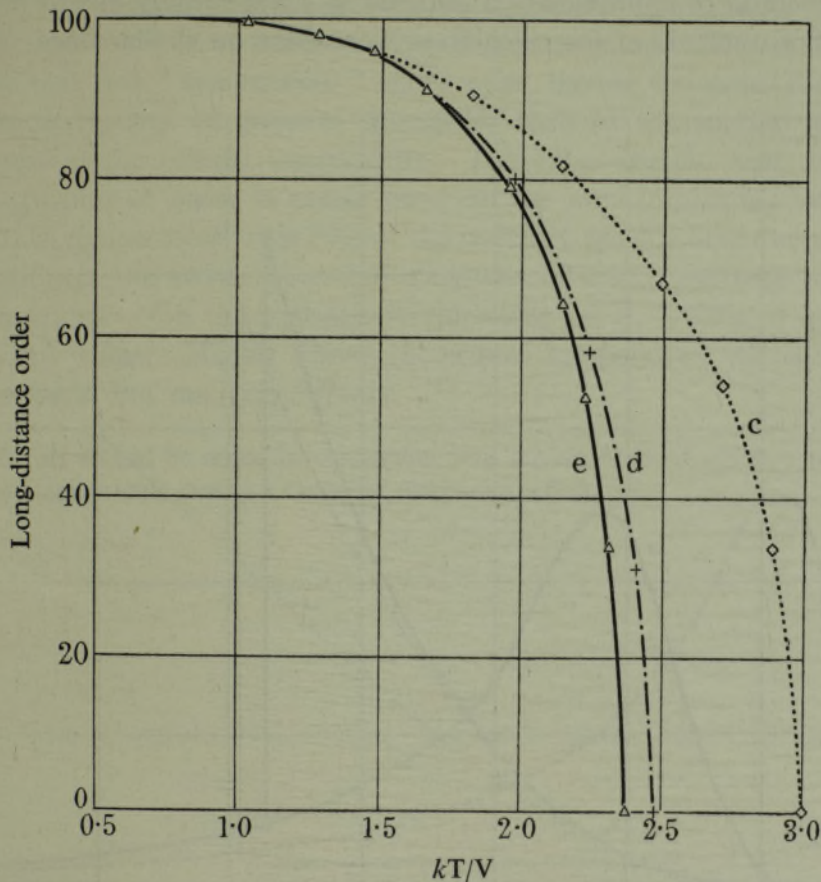


FIG. 5

and (40) becomes

$$\int_0^\infty E(T) d(1/kT) = S_{T=\infty} - S_{T=0} = N \log 2$$

which gives with (1) and (3)

$$\int_0^1 \frac{dx}{x} (1 - \sigma) = \frac{4}{z} \log 2. \tag{42}$$

In our case, $z = 6$, so that the right-hand side of equation (42) is 0.462. The left-hand side is 0.465 if the final results of § 8 are inserted, whereas

the approximation of § 5 gives a result 50% too high. The small difference between the "first approximation," considering long-distance order, and the second also seems to show that the final approximation is rather good.

I wish to thank Professor W. L. Bragg very much for suggesting this problem and for many discussions. My special thanks are due to my friend Dr. Peierls, who gave innumerable valuable suggestions. In fact, the method of approximation outlined in § 5 is entirely due to him, and all improvements of the calculation were done on similar lines.

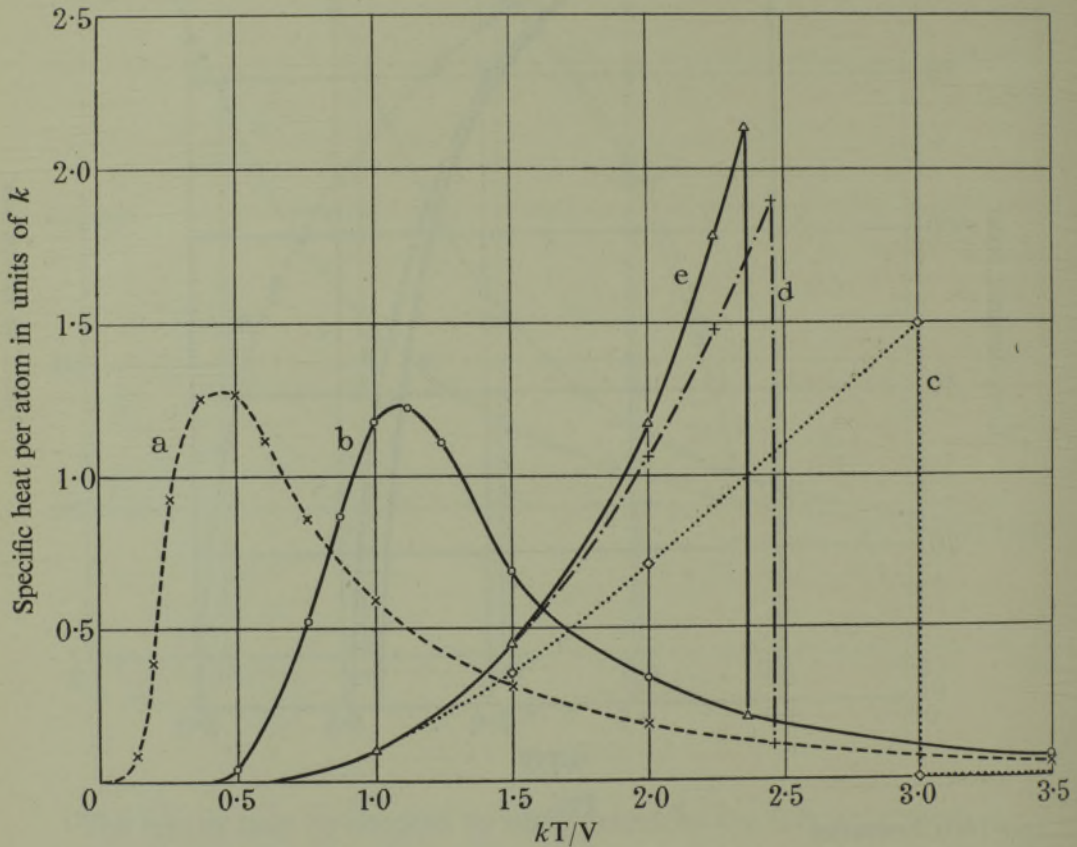


FIG. 6

SUMMARY

The order in an alloy containing two sorts of atoms in equal proportion is calculated statistically, assuming interaction only between nearest neighbours. At high temperatures, there is only a correlation between near atoms, the state of the crystal as regards order is similar to a liquid.

At low temperatures, the crystal as a whole is ordered, the structure is "solid-like." This order at long distances is restricted to two or more dimensions.*

The long-distance order and the energy as functions of temperature are both discussed qualitatively (§ 4) and calculated (§§ 6 to 9). It is shown that the theory of Bragg and Williams gives a fair first approximation. The long-distance order vanishes (with vertical tangent) at a certain critical temperature Θ . All the physical quantities plotted as functions of T have a kink at $T = \Theta$ but no jump. This is due to the fact that two "symmetrical" states exist, having the same energy (§ 4). The derivatives of physical quantities, such as the specific heat, have jumps at the critical temperature. The extra specific heat due to the destruction of order is rather large on the low-temperature side of the critical temperature; it is 70% of the ordinary specific heat due to thermal motion of the atoms (provided all atoms of the crystal take part in the transition). On the high-temperature side of Θ , it falls to about 10% of this value. Higher above the critical temperature, the specific heat decreases, but not very rapidly.

* This should be noted in connection with ferromagnetism which is restricted to *three* dimensions, due to a quantum mechanical effect.
