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Bell Telephone Laboratories, Inc., New York, N. Y.

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A generalization of Bethe's theory of superlattices so as to take into account the interactions between atoms which are not nearest neighbors in the lattice is considered. This process will not furnish any great improvement in agreement between theory and experiment because it predicts, in disagreement with experiment, that many properties of binary alloys are symmetrical between the two constituents. It is further shown to be in disagreement with certain fundamental features of the interactions of atoms in alloys.

BETHE[1] has given a treatment of the order-disorder transformation in binary alloys of 50 atomic percent composition based upon ideas of the interaction between atoms which are nearest neighbors in the lattice. If the two species of atoms are A and B, then the interaction energy between a pair of nearest neighbors is V_{AA}, V_{BB}, or V_{AB} according to the nature of the pair. It is assumed that these three energy parameters are strictly constants and do not vary with the state of order; and it is further assumed that the configurational free energy, i.e., that due to the arrangement of the A and B atoms upon the lattice sites, can be separated from all other free energies and treated separately.

Several writers[2,3] have generalized Bethe's treatment to arbitrary compositions while restricting themselves to the case in which the lattice type (but not necessarily the spacing) remains the same by assuming that the interaction parameters are independent of composition. The results of these investigations show that the theories are along the right lines but the quantitative agreement with experiment is generally poor. In particular, the theory predicts that the phase diagrams for the order-disorder transformation should be symmetrical about fifty atomic percent, a prediction in disagreement with experiment. A natural extension of the theory consists of introducing three more energy parameters describing interactions between *next* nearest neighbors;[4] indeed even more remote

interactions may be considered. We shall use the phrase "nth neighbor assumption" to describe the case in which interactions are included between all atoms which neighbors of the nth or less degree. One intuitively feels that the contribution of any one atom to the energy of the alloy will be dependent upon the arrangement of the atoms in its immediate vicinity, i.e., those within the neighboring unit cells. For this reason we might expect that an nth neighbor assumption with a reasonably small value of n would mimic quite well the actual situation. It is the purpose of this note to point out that such expectations are not well founded and to mention some other lines of attack.

In the first place, we shall prove that the assumption of interactions between neighbors of any order does not interfere with the symmetry of the phase diagram about fifty atomic percent. Let us denote by V_{1AA}, V_{1BB}, and V_{1AB}, the interactions between nearest neighbors in the lattice and by Z_1 the number of nearest neighbors of each atom (these are the quantities used in Bethe's theory) and by V_{2AA}, V_{2BB}, V_{2AB}, and Z_2 corresponding quantities for next nearest neighbors, etc. In this proof, which is formally identical with that given by the writer for nearest neighbor interactions,[3] it is assumed that the lattice is of a simple type, such as simple cubic, face-centered cubic, or body-centered cubic so that all lattice sites are equivalent as regards their distribution of neighbors (for other lattices, such as the fluorspar structure, interactions between nearest neighbors may give asymmetry). Let us denote by Q_{nAA}, Q_{nBB}, Q_{nAB} the numbers of pairs of atoms which are nth degree neighbors and are formed of AA, BB and AB, respectively. Then

[1] H. A. Bethe, Proc. Roy. Soc. **150A**, 552 (1935).

[2] C. E. Easthope, Proc. Camb. Phil. Soc. **33**, 502 (1937) and **34**, 68 (1938).

[3] W. Shockley, J. Chem. Phys. **6**, 130 (1938).

[4] This case has been treated by T. S. Chang, Proc. Roy. Soc. London **161A**, 546 (1937).

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the contribution of these nth degree interactions to the energy E of alloy is:

$$E_n = V_{nAA}Q_{nAA} + V_{nBB}Q_{nBB} + V_{nAB}Q_{nAB}.$$

If the total number of atoms in the alloy is N and if fractions F_A and F_B of them are A and B, then

$$2Z_n F_A N = 2Q_{nAA} + Q_{nAB},$$
$$2A_n F_B N = 2Q_{nBB} + Q_{nAB}.$$

If we compare the energy of the alloy with that of two crystals of the pure metals, we find that the energy due to the nth degree interactions is

$$E_n' = -V_n Q_{nAB},$$
where $\quad V_n = \frac{1}{2}(V_{nAA} + V_{nBB}) - V_{nAB}.$

This energy term is obviously symmetrical in A and B and so are the terms due to the interactions of all other orders.

Another reason for being skeptical of any of the nth neighbor assumptions is that they represent emasculated central force treatments of the alloy. Let us assume (1) that the atoms interact in pairs, the potential energies being $V_{AA}(r)$, $V_{BB}(r)$ and $V_{AB}(r)$, where r is the distance between atoms and (2) that the lattice of sites is a rigid unalterable framework. Then the distance r_1 between nearest neighbors is a fixed quantity and the same is true of r_2, the distance between next nearest neighbors, etc. These assumptions correspond to the ∞ th neighbor assumption with $V_{nAA} = V_{AA}(r_n)$. The fact that this correspondence arises directly from (2) constitutes a severe criticism of the nth neighbor assumption: for (2) is a quite unreasonable assumption denying the variations of lattice constant with composition which are recognized empirically by Vegard's law and which would otherwise follow from a difference in equilibrium radii of the three V's.

This reasoning suggests that even the nearest neighbor assumption should be modified by allowing the interatomic distances to vary, entailing corresponding changes in the V's; that is, we should use central force potential energies between the nearest neighbors. Hume-Rothery[5] has discussed the formation of a superlattice in Fe$_3$Al on this basis: this alloy is characterized by having no pairs of Al atoms as nearest neighbors

and a minimum number as next nearest neighbors. Although this situation can be readily explained by assuming next-nearest-neighbor interactions, it may equally well be explained, as Hume-Rothery has pointed out, by considering the strains produced by the interactions of nearest neighbors of different atomic diameters; these strains being least when most evenly distributed, that is, when the Al atoms are as far apart as possible. A. H. Wilson[6] has carried out an analytical investigation of the nearest neighbor central force theory for a case corresponding to superstructure formation in CuAu. He predicts a latent heat and a change of lattice constant with order.

The next-nearest-neighbor assumption without allowance for change in atomic spacing has been used by Chang,[4] who finds that as compared with the nearest-neighbor assumption it gives improved agreement with experiment by leading to higher specific heats near the critical temperature of order; and by Bitter,[7] who shows that it can lead to intermetallic compounds. However, the predictions of the nearest neighbor assumption are greatly altered if change in atomic spacing is permitted as has been shown both by the calculations of Wilson[6] and by considerations of the entropy of lattice vibrations;[8] furthermore suitable assumptions about the interatomic forces lead to the expectation of intermetallic compounds. From this we conclude that the introduction of next-nearest-neighbor interactions is not required until the nearest-neighbor central-force picture has been further investigated.

Although improvement may be justifiably expected to follow the introduction of potential energies between nearest-neighbors, it is known that the central force picture is inadequate for metals. This conclusion is drawn from the failure of the Cauchy relations for the elastic constants, and the reason for this failure is well understood from the work of Fuchs[9] using the modern theory of metals. The work of Mott[10] on β-brass has shown that for the superlattice formation in this

[5] W. Hume-Rothery and H. M. Powell, Zeits. f. Krist. 91, 23 (1935). (See also reference 8, p. 40.)

[6] A. H. Wilson, Proc. Camb. Phil. Soc. 34, 81 (1938).
[7] F. Bitter, J. Chem. Phys. 6, 339 (1938).
[8] For a discussion see F. C. Nix and W. Shockley, Rev. Mod. Phys. 10, 1 (1938).
[9] K. Fuchs, Proc. Roy. Soc. 157, 622 (1936).
[10] N. F. Mott, Proc. Phys. Soc. 49, 258 (1937).

alloy the central force picture is untenable. He finds that the atoms do not interact directly in pairs and that the major part of the energy of the superlattice arises from electrostatic interactions between the Cu and Zn atoms, which are unequally charged. This difference in charge depends upon the manner of occupation of the neighboring sites of each of the two atoms; it is greatest when they are occupied as in a super-lattice and least when each atom is surrounded by neighbors of its own species, the atom tending in the latter case to be neutral as in the pure metal. Thus the interaction between any two atoms depends very considerably upon the other atoms which surround them and this is a complete refutation of the central force picture. Mott has suggested an interpretation of the high specific heat of β-brass on this basis.

The Vibrational Spectrum and Thermodynamic Properties of Nickel Carbonyl

BRYCE L. CRAWFORD, JR.,* *Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Massachusetts,*
AND
PAUL C. CROSS,† *Department of Chemistry, Stanford University, California*
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The infra-red absorption spectrum of nickel carbonyl has been measured in the gas phase from 4 to 23μ, and in the liquid phase from 1 to 8μ. Normal coordinate treatments of both the square and tetrahedral models of the AB_4C_4 molecule have been applied to the infra-red and Raman data; the results give further evidence of the tetrahedral structure of nickel carbonyl. An analysis of the vibrational spectrum has been made, based on the tetrahedral model, and has been applied to the statistical calculation of the entropy, heat capacity, and free energy function.

INTRODUCTION

THE theory of directed valence predicts a tetrahedral structure for a nickel carbonyl molecule consisting of four carbonyl groups singly bonded to a neutral nickel atom.[1] Electron diffraction studies[2] appear to confirm this structure. However, the observed nickel-carbon distance indicates strong resonance with a structure involving nickel-carbon double bonds, which may or may not tend to alter the tetrahedral configuration. A square configuration has frequently been proposed, in analogy with the known square configuration of quadricovalent compounds of bivalent nickel.[2] A qualitative analysis of the Raman spectrum of nickel carbonyl was interpreted as favoring the square structure;[3] however, it has been shown that the selection rules were violated in this analysis.[4]

We have therefore undertaken a quantitative analysis of the vibrational spectrum, including infra-red data, considering both the square and tetrahedral models. It was our hope to obtain a new and independent determination of the structure; indications favoring the tetrahedral configuration were found, but the square con-
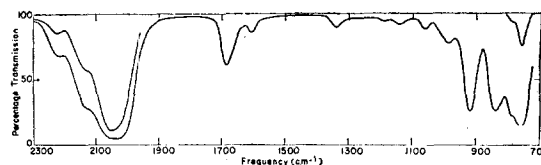

FIG. 1. Absorption spectrum of nickel carbonyl vapor, rocksalt region (20 cm path length, 300 mm pressure).

* National Research Fellow in Chemistry.
† Present address: Brown University, Providence, R. I.
[1] L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).
[2] L. O. Brockway and P. C. Cross, J. Chem. Phys. **3**, 828 (1935).
[3] A. B. F. Duncan and J. W. Murray, J. Chem. Phys. **2**, 636 (1934).
[4] E. B. Wilson, Jr., J. Chem. Phys. **3**, 59 (1935).