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Intermetallic Compounds Produced by Next Nearest Neighbor Interaction in Alloys

A glance through the phase diagrams of binary alloys shows that the formation of intermetallic compounds is an exceedingly common occurrence. Although a general interpretation may be difficult, it is of some interest to show that a simple extension of the Bragg-Williams theory of order-disorder in alloys can give certain types of such compounds in spite of the neglect of such important factors as fluctuations, lattice vibrations, lattice distortions, etc.

A convenient way of describing the long range order in a crystal is by means of the concentration of atoms of types A and B on interpenetrating sublattices, as has been done by Shockley¹ for the system copper-gold. The face-centered lattice of this system may be broken up into four sublattices having the property that any atom of one lattice has four nearest neighbors on each of the other three sublattices. If N_{A1} and N_{B1} represent the number of atoms of types A and B on lattice one, and the variable $y_1 = (N_{A1} - N_{B1}) / (N_{A1} + N_{B1})$ be taken as a measure of the concentration on sublattice 1, Shockley shows that the energy due to the interaction of nearest neighbors may be written, to a first approximation,

$$c(y_1y_2 + y_1y_3 + y_1y_4 + y_2y_3 + y_2y_4 + y_3y_4),$$

c being a constant. The interaction of next nearest neighbors may be taken into account by further breaking up these four sublattices into a larger number and expressing their

interactions as above, but using a new constant for the terms representing the more distant interactions.

The procedure may be illustrated in the simpler case of a body-centered cubic lattice. This may be broken up into two simple cubic lattices which have the property that every atom of one lattice has its eight nearest neighbors on the other lattice. Each of these simple cubic lattices may be further broken up into two lattices which have the property that every atom of one has its six next nearest neighbors on the other. The total energy of interaction may then be written in the form

$$E = N[c(y_1 + y_2)(y_3 + y_4) + c'(y_1y_2 + y_3y_4)],$$

c representing nearest neighbor, and c' next nearest neighbor interaction. Atoms on sublattices 1 or 2 are nearest neighbors of atoms on sublattices 3 and 4. Atoms on sublattices 1 and 3 are next nearest neighbors of atoms on sublattices 2 and 4, respectively. The entropy may be written in the form

$$\Phi = \frac{Nk}{8} \left[8 \ln 2 - \sum_{n=1}^4 \{ (1+y_n) \ln (1+y_n) + (1-y_n) \ln (1-y_n) \} \right]$$

Introducing the long range order variables

$$\begin{aligned} S_{12} &= (y_1 - y_2)/2, \\ S_{34} &= (y_3 - y_4)/2, \\ S &= (y_1 + y_2 - y_3 - y_4)/4 \end{aligned}$$

and the total mean concentration

$$y = (y_1 + y_2 + y_3 + y_4)/4,$$

the energy may be written

$$E = N[2(2c + c')y^2 - 2(2c - c')s^2 - c'(s_{12}^2 + s_{34}^2)]. \quad (1)$$

The variables have the following limits

$$\begin{aligned} 0 &\leq |y| \leq 1 \\ 0 &\leq |s| \leq 1 - |y| \\ 0 &\leq |s_{34}| \leq 1 - |y - s| \\ 0 &\leq |s_{12}| \leq 1 - |y + s|. \end{aligned}$$

With these equations the entire behavior of the system may be worked out. We shall here show only that the intermetallic compound AB may be formed at the absolute zero. To do this we shall find the values of the order parameters which make the energy a minimum for an alloy of arbitrary composition, and for the special case

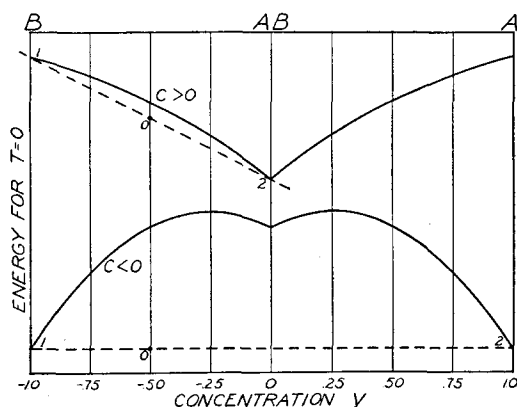


FIG. 1.

$c' < 0$ and $2c - c' > 0$. This is obviously $S_{12} = S_{34} = 0$ and $|S| = 1 - |y|$ and the equilibrium energy at absolute zero has the form

$$E = N[4(2c - c')|y| + 4c'y^2],$$

which is plotted in Fig. 1. A well-known property of these curves is that if a common tangent can be drawn to two points on the curve, and the tangent is everywhere below the curve, then an alloy having a composition represented by a point between the points of tangency, as for instance point 0 on the figure, will break up into two phases having the compositions 1 and 2. For $c > 0$, therefore, we shall have either pure A or pure B in equilibrium with a perfectly ordered compound AB at the absolute zero. For $c < 0$ any alloy will break up into pure A and pure B, but as the temperature is raised it may happen that the intermetallic compound AB will be formed. The precise manner in which the compound and the degree of order will be influenced by the temperature will depend on the relative magnitude of the constants c and c' .

Even after including the next nearest neighbor interaction, the phase diagrams will be symmetrical in A and B, as was pointed out to me by Dr. Shockley. A term in the energy involving y to the first power has consequently been omitted as its inclusion would have no bearing on the results here discussed.

In face-centered cubic alloys compounds of the form A_3B , AB , AB_3 may be described by a similar analysis.

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April 18, 1938.

¹ W. Shockley, J. Chem. Phys. 6, 130 (1938).

Raman Effect in Liquid Acetylene

Faint rotation lines accompanying strong Raman frequencies have been reported in α -pinene¹ and in liquid acetylene.² Because only the P branches of the "rotation bands" were observed there has been continued conjecture as to the origin of these lines. In connection with this problem we have reinvestigated the Raman spectrum of liquid acetylene. And in exposures up to 16 hours with slit widths varying from 0.075 to 0.23 mm no rotation lines were found. These negative results along with the alternative explanation of the α -pinene band proposed in subsequent studies on α - and β -pinene³ militate greatly against the reality of such single-branched rotational effects.

One new line found by us corresponds to a shift of 1259 cm^{-1} . This is extremely diffuse in character and probably is an overtone of the deformation frequency at 630 cm^{-1} . Bhagavantam and Rao⁴ reported a shift of 1233 cm^{-1} excited by Hg 4358A which was not excited by Hg 4047A;

perhaps this is the corresponding shift in gaseous acetylene. Our shift was excited by both of the strong mercury lines.

Accompanying the strong 1961 cm^{-1} shift is a faint companion, 1934 cm^{-1} . These lines can be attributed to identical vibrations in the normal acetylene molecules and in the isotopic molecule $\text{HC}^{13}\equiv\text{C}^{12}\text{H}$. By application of the secular equation for acetylene given by Glockler and Wall⁵ with force constants adjusted to fit our data the position of this isotope lines was calculated to be 1929 cm^{-1} , which is only 5 wave numbers from the observed value. This same calculation indicates that the 3341 cm^{-1} frequency also should be accompanied by an isotope line, 3330 cm^{-1} . No line was observed here.

The 1961 cm^{-1} vibration as excited by Hg lines 4339, 4348, and 4358A ["the triplet"] along with the isotope line excited by 4358A show on the photographic plate in a somewhat regular order. And these lines all fit in the "rotation series" previously reported.² It must be noted, however, that two additional lines not found here were reported in that series.

In gaseous acetylene Bhagavantam and Rao measured a doublet 589 cm^{-1} and 643 cm^{-1} which they attributed to the O , P , R , and S branches (Q branch missing) of the Raman active degenerate deformation frequency. According to them, their interpretation checks with data on infra-red absorption in the gas. In the liquid, however, we do not obtain results strictly analogous. We have found lines at 560 cm^{-1} and 631 cm^{-1} ; the former is very weak as might be expected in view of the low temperature of observation (-75°C), but the greater doublet separation at this temperature would not be predicted. Moreover, another complication lies in the fact that the 631 cm^{-1} shift seems to consist of two distinct components when photographed under high dispersion. These are separated by 10–11 cm^{-1} with a mean value of 631 cm^{-1} . Such a splitting could not be predicted from the curves given by Bhagavantam and Rao on the construction of the doublet. These differences seem to be due to the different environment in the gaseous and liquid states.

The acetylene was prepared from pure calcium carbide, was purified by passing through a sodium plumbite-, chromic acid-, sodium hydroxide-, dehydrite-train; and by distillation.

The experimental data in summary lists the following Raman shifts: 560, 631 (625, 636), 1259, 1934, 1961, and 3341 cm^{-1} .

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May 2, 1938.

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⁴ S. Bhagavantam and A. V. Rao, Proc. Ind. Acad. Sci. 3A, 135 (1936).

⁵ G. Glockler and F. T. Wall, J. Chem. Phys. 5, 813 (1937).

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