## Theory of Cooperative Phenomena

GÉRARD FOURNET Office National d'Etudes de Recherches Aéronautiques, Châtillon s/Bagneux, Seine, France (Received December 31, 1951)

 $\mathbf{I}^{N}$  a recent paper Kikuchi<sup>1</sup> has given a new theory of co-operative phenomena. We would like to call attention to the theory of order disorder transformations in binary alloys  $A_n B_m$ developed by Yvon<sup>2</sup> in France and in particular to compare his results with those of Kikuchi. The simplifying hypotheses are the same as those of the other theories. The only energy function that is necessary to consider is

$$W(r) = W_{AA}(r) + W_{BB}(r) - 2W_{AB}(r), \qquad (1)$$

where  $W_{AA}(r)$  refers to the mutual potential energy of two A atoms separated by a distance r. Yvon assumes that  $W(r_p)$ (hereafter designated by  $W_p$ ) decreases rapidly with  $r_p$ , where  $r_p$ refers to the distance between pth neighbors. The probability  $n_{1,A}(\mathbf{x}_i)$  of finding one A atom at the site defined by  $\mathbf{x}_i$  and the probability  $n_{2,AA}(\mathbf{x}_i, \mathbf{x}_j)$  of finding simultaneously one A atom at  $\mathbf{x}_i$  and one A atom at  $\mathbf{x}_i$  are expressed in the form of a series. By considering several terms, results as precise as are desired can be obtained. When we assume only  $W_1$  nonzero and consider only two terms in the expansion for  $n_1$  and one term for  $n_2$ , we obtain the classical approximation<sup>2,3</sup> of Bethe, Fowler, and Guggenheim and Takagi. We will show with an example that three of four terms suffice to reproduce exactly the results of the best approximations. In addition to its theoretical rigor the theory of Yvon has also the advantage of utilizing terms  $A_{\alpha}$  (in calculating  $n_1$ ) and  $B_q$  (in calculating  $n_2$ ) which are independent of the lattice. The calculation of a limited number of terms (work now in progress) will permit treating nearly every case. One can also take into account further energies  $W_2, W_3 \cdots$  which can play important roles, as witness the case of  $\beta$ -brass.<sup>4</sup>

For comparison of the theories of Yvon and Kikuchi we have calculated the configurational energy above the critical temperature for a simple cubic lattice where there are 50 percent A atoms (or spin +) and 50 percent B atoms (or spin -). The configurational energy (only  $W_1$  nonzero) is given by

$$E = \frac{1}{2} \cdot M \cdot 6 \cdot n_{2,AA}(r_1) \cdot W_1,$$

where M refers to the total number of sites and  $n_{2,AA}(r_1)$ , the value of  $n_{2,AA}(\mathbf{x}_i, \mathbf{x}_j)$  for  $(\mathbf{x}_i - \mathbf{x}_j) = r_1$ . The theory of Yvon gives for  $n_2$ 

$$\log n_2 = \log B_2 + \Sigma \log B_3 + \Sigma \log B_4 + \cdots, \tag{2}$$

where  $B_4$ , for example, refers to the terms using groups of 4 sites. We must consider only groups where closure is obtained with only nearest neighbor interactions. In the simple cubic lattice the first terms are given in Fig. 1.



FIG. 1. 1°: Number of terms for simple cubic lattice. 2°: Number of terms for two-dimensional square lattice.

In order to conform with the notation of Kikuchi we must write [see Eq. (1)]

 $W_1 = -\epsilon + (-\epsilon) - 2(+\epsilon) = -4\epsilon$  and  $K = \epsilon/kT$ .

$$n_{2,AA}(r_1) = B_2 B_4^4 B_{6,1}^{12} B_{6,2}^{24} B_{7,1}^8,$$

one obtains

we find

$$-E/(M\epsilon) = 3K + 11K^3 + (542/5)K^5 + \cdots$$

identical to the result (D7.6) that Kikuchi reported from more complicated calculations than those given in his paper. We point out that if we make the approximation

$$n_{2,AA}(r_1) = B_2 B_4^4 B_{6,1}^{12} B_{6,2}^{24},$$

$$-E/(M\epsilon) = 3K + 11K^{3} + (422/5)K^{5} + \cdots,$$

the expression (D7.3) obtained by Kikuchi from the calculations in his paper.

Since the  $B_q$  do not depend on the lattice under consideration, we can use the values already calculated to obtain immediate results for the two-dimensional square lattice. We have, in fact, for this lattice on the one hand,

 $E = \frac{1}{2} \cdot M \cdot 4 \cdot n_{2,AA}(r_1) \cdot W_1,$ 

and on the other,

$$n_{2,AA}(r_1) = B_2 B_4^2 B_{6,1}^2 B_{6,2}^4 B_{7,1}^0$$

from which

$$-E/(2M\epsilon) = K + (5/3)K^3 + (32/15)K^5 + \cdots$$
 (3)

In the treatment of Kikuchi<sup>1</sup> for the same lattice the configurational energy in the disordered state is

$$E = 2M\epsilon(4y_2 - 1) = 2M\epsilon(H^{-2} - H^2)/(6 - H^2 - H^{-2}),$$

an expression that furnishes a development that is identical to (3). We know also that the result of the variational method<sup>5</sup> (identical with that of Kikuchi) contains only three exact terms in the development of the free energy for high temperatures [see (97), reference 5].

I thank Professor Guinier for some discussions and Dr. Walker for the translation of the manuscript.

R. Kikuchi, Phys. Rev. 81, 988 (1951).
J. Yvon, Cahiers phys. 28, 1 (1945).
G. Fournet (to be published).
G. Fournet, Compt. rend. 232, 155 (1951).
H. A. Kramers and G. H. Wannier, Phys. Rev. 60, 252, 263 (1941).

## Color Centers and Thermoluminescence in Alkali Halides

J. SHARMA

Khaira Laboratory of Physics, University College of Science, Calcutta, India (Received December 31, 1951)

N our study of thermoluminescence of alkali halides excited I N our study of thermonumnescence of the transition  $-184^{\circ}$ C, we and colored by cathode-ray bombardment at  $-184^{\circ}$ C, we have found that the coloration is closely associated with trapping centers. Some of the thermoluminescent traps give out peak emissions at temperatures exactly corresponding with those at which the color centers disappear. Thus, it appears that when F-centers are thermally destroyed they also directly or indirectly give out emissions. In the present work the rate of heating has been maintained fairly high, about 10-12°C/sec. However, no measurement of the absorption spectrum has yet been made here, and the production of color centers has been judged from visual coloration of the samples taken in finely powdered form. The failure of earlier workers to notice the effect may be a result of their working with single crystals where the rate of heating was low.

Potassium iodide powder (E. Merck, reagent type, melted and recrystallized in vacuum) is found to give four thermoluminescence peaks at 110-120, 158, 176, and 235°K. Of these the relative heights of the first three peaks depend slightly on the thermal history of the powder, but the trap at 235°K remains undisturbed (see Fig. 1). Under cathode-ray bombardment the sample becomes



FIG. 1. Thermoluminescence curve of potassium iodide starting from liquid oxygen temperature, after excitation by cathode-rays at 10 kv for five minutes. The temperature record No. I corresponds to the thermoluminescence curve. The dotted part of temperature record No. II gives the temperature range at which coloration disappears on heating from 91°K after bendradure. after bombardment.

bluish green in color, presumably as a result of strong F-center absorption in the red region. It has been found that if the sample after bombardment is heated from liquid oxygen temperature, the coloration suddenly disappears at about 235°K, which is also the maximum glow temperature of the last luminescent trap. The present case is similar to that observed by Pringsheim<sup>1</sup> in the case of LiF, at  $-135^{\circ}$ C, where an absorption band at 3200A disappears with strong emission in the blue region. Further, it has been seen here that the most favorable temperature for the bluish green coloration of potassium iodide is about 200°K, and this is also the temperature at which bombardment and subsequent thermoluminescence gives large amount of stored energy from the trap released at 235°K. If the heating is begun from 200°K after bleaching the coloration with visible light, the output of the peak decreases. On the other hand, if irradiation with visible light is done at liquid oxygen temperature, then the shallow traps are reduced in relative intensity while the trap with maximum glow at 235°K is enhanced (see Fig. 2). This suggests the destruction of shallow traps while the one at 235°K increases in population.

In accordance with the observation of Pringsheim,<sup>2</sup> it has been found that the weak coloration produced at room temperature is more stable than that produced at liquid oxygen temperature. When colored by bombardment at room temperature, it dis-



FIG. 2. The lower curves give the thermoluminescence records in which the sample (KI) after bombardment was irradiated with (a) total light and (b) red light from an Fe-arc. Obviously it shows quenching of shallow traps and enhancement of the last  $235^{\circ}$ K trap. The upper curves are simultaneous records for comparison from the portion of the sample which was protected from the arc light.

appears at about 160°C, and here too it is associated with a faint luminescence.

Similar phenomena have been observed in potassium chloride. On bombardment at liquid oxygen temperature it gets colored pink.3 On heating, the color disappears in two stages, at about 200°K and 520°K. At first the pink color disappears, leaving a magenta coloration which dies out at the higher temperature. Both colors are destroyed with strong luminescence peaks. When cathode-ray bombardment is done at about room temperature, only the latter coloration is produced.

In sodium chloride considerable bombardment at liquid oxygen temperature produced a greenish yellow color. On heating, at about 165°K it became dark brown and this color disappeared at about 500°K. Both the colors give strong emissions when they are thermally destroyed. The emission in NaCl in the latter case is so strong that even in a normally illuminated room its blue light could be easily seen. In another experiment, the sample was bombarded at room temperature and left for eighteen hours. On heating the color again disappeared, with strong emission in the blue region.

Since F-centers are most easily and copiously produced, it appears that their destruction is intimately connected with a high temperature strong emission peak.

The author is thankful to Professor S. N. Bose, Khaira Professor of Physics, University College of Science, Calcutta, for his guidance and helpful interest in the work.

P. Pringsheim and P. Yuster, Phys. Rev. 77, 90 (1950).
Delbeco, Pringsheim, and Yuster, J. Chem. Phys. 19, 574 (1951).
H. N. Bose, Proc. Phys. Soc. (London) (to be published).

## Temperature Dependence of the Line Half-Width of Ferromagnetic Resonance in Single Crystals of Zinc-Manganese Ferrite

Tosihiko Okamura, Yūzō Kojima, and Yosiharu Torizuka Research Institute for Scientific Measurements, Sendai, Japan (Received October 29, 1951)

SINGLE crystals of nickel ferrite<sup>1</sup> and zinc manganese ferrite<sup>2</sup> were prepared by Calt Vaccount of the second se were prepared by Galt, Yager, and others, and the g-factor, line half-width, anisotropy constant, and other physical properties were determined precisely at room temperature. According to their experimental results on the width of the resonance line at the



FIG. 1. Temperature dependence of the line half-width for a single crystal of  $MnOZnO2Fe_{2}O_{3}$ .