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On the Collective Electron Model of Ferromagnetism*

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Synopis

The spontaneous magnetization of the ferromagnetic substance was discussed on the basis of the collectiive electron model, the result of which was applicable to the case of an intrinsic semi-conductor. Sudden disappearance of spontaneous magnetization in some kinds of ferromagnetic semi-conductors was expected form the present theory. This result coinsided with the experimental data on CrS by Haraldsen and Neuber.

I. Introduction

Several researches on the origin of ferromagnetism have been published based on the collective model of metals and semi-conductors. Stoner once developed a formalism of spin reorientation based on the said model and thereupon several writers made some discussions on the ferromagnetism of metals of various electronic structures.(1) At that time the present authors also discussed the ferromagnetism due to this model by applying the Fermi-Dirac statistics to the distribution of electronic spins taking the exchange interaction between each pair of electrons into account. This method of discussion was subsequently extended to several interesting cases of ferromagnetism of metals and semi-conductors and some theoretical conclusions were deduced based on this idea. The said investigation, however, was completed during the unhappy period (1941–1945), during which Japan's diplomatic relations with the Powers were broken off, and contrary to our custom the above mentioned first report was published only in Japanese but not in any Europian language. Since then some questions have been referred to concerning the method of investigation of the subsequent researches already published. So, the summary of the above mentioned first report on the collective electron ferromagnetism will be given below. As seen in the last part of the present report the theory was, at that time, applied also to the discussion of the ferromagnetism of semiconductors. At present, a part of the problem has been solved with success by the localized model of solid. For certain kinds of ferromagnetic semi-conductors, however, the explanation of the phenomena from the side of the collective electron model would be supposed to be closer than that from the localized one and, hence, a discussion developed formerly based on the present theory will also be given on this occasion.

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* The 683 rd report of the Research Institute for Iron, Steel and Other Metals. Published in Japanese in the Nippon Sugaku-Buturigaku-Kai Kaisi, **17** (1943), 92.

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(1) A full bibliographic survey was given by Wohlfarth: Phil. Mag. **42** (1951), 374.

II. Collective electron ferromagnetism

First, let us consider the free energy of the electronic system under the external magnetic field taking into account the interaction among the electrons under consideration. These electrons are supposed to lie in a periodic field of force due to the metallic lattice. Let N be the whole number of electrons under consideration and U (N, H) be the total energy. Then, after dividing the domain of the electronic evergy bands into a number of small ranges ΔE_k $(k=1, 2\cdots\cdots)$, denote the average of energy niveaus in the range ΔE_k by E_k and the number of the energy levels existing in it by Z_k, the spin orientations being taken into consideration, and suppose that N_k electrons are occupying these Z_k levels. The energy levels in the same range are chosen to correspond to the same spin orientation. As to U and N, the following equations are established,

$$U = \sum N_k E_k + f(N_1, N_2 \cdots\cdots), \tag{1}$$

$$N = \sum N_k, \tag{2}$$

where $f(N_1, N_2 \cdots\cdots)$ is the addive energy depending on the distribution of electrons to their respective levels. If we take only exchange energy into account, then f will take the form (8) given in the following paragraph. Now, if W is the number of the state (Z_k, N_k) for a set of the values of N, U, H, it will be

$$W = \prod_k Z_k! / N_k! (Z_k - N_k)!, \tag{3}$$

and, accordingly, the entropy Φ of this system will be expresed as

$$\Phi = k \log W = \sum_k Z_k \left\{ \log Z_k - \frac{N_k}{Z_k} \log N_k - \left(1 - \frac{N_k}{Z_k}\right) \log (Z_k - N_k) \right\}. \tag{4}$$

If both U and N are assumed to be constant for the time being, a remarkable maximum will be obtained at a certain value of (N_k), and in this case W in the above equation may be substituded by W_{max}. Such a set of (N_k) can be given in the following expression by a proper choice of indeterminate multipliers α and β corresponding to Eqs. (1) and (2).

$$N_k / Z_k = 1 / \{1 + \exp(\alpha + \beta E_k + \beta(\partial f / \partial N_k))\}. \tag{5}$$

In putting the value of this (N_k) in the formula (4), we may consider $\sum_k$, for convenience' sake, as follows: Each energy level is enumerated by i $(i=1, 2, \cdots\cdots)$ in order of energy values of levels. $\{\cdots\cdots\}$ under the sign of summation $\sum_k$ in the right hand side of (4) gives the same value for all the energy levels belonging to the energy range ΔE_k; hence, $Z_k\{\cdots\cdots\}_k$ is equal to the sum of the value for each single energy level of that term; thus we may rewrite it as

$$\sum_k Z_k \{\cdots\cdots\}_k = \sum_i \{\cdots\cdots\}_i.$$

Hence

$$\log W = \sum_i \{\log Z_k - (N_k/Z_k) \log N_k - (1 - N_k/Z_k) \log (Z_k - N_k)\}. \tag{6}$$

By rewriting the form of log W by means of (5), we obtain the following expression:

$$\log W = \sum_i \log\{1+\exp(-\alpha-\beta E_i-\beta(\partial f/\partial N_k))\}+\alpha N+\beta E+\beta\sum_i(\partial f/\partial N_k)n_i(k), \quad (7)$$

where $n_i(k)$ denotes N_k/Z_k, and expresses the probability of being occupied by electrons given to the state i belonging to the energy interval ΔE_k.

Here, let us limit our problem only to ferromagnetism. In this case, as explained in the former paragraph, the interaction energy f among the electrons is given by $-JS^2/L$, in which S is the spin quantum number of the system, L the number of atoms and J the exchange integral corresponding to the exchange of a pair of electrons. In order to rewrite the interaction energy in this form by using (N_k) mentioned above, a subsidiary quantity δ_k must be introduced into the calculation; this parameter takes the value either plus or minus unity according as the orientation of the spin associated with Z_k levels lies in a direction either antiparallel or parallel to the spontaneous magnetization of the system under consideration. Since $2S$ is equal to $\sum N_k\delta_k$, the following type of expression will be obtained.

$$f(N_1, N_2 \cdots\cdots) = -(J/4L)(\sum N_k\delta_k)^2 \quad (8)$$

Accordingly, $(\partial f/\partial N_k)$ in the expression of log W is expressed as follows;

$$\frac{\partial f}{\partial N_k} = -(J/2L)(\sum N_k\delta_k)\cdot\delta_k, \quad (9)$$

from which it is clear that the last term $(\sum\partial f/\partial N_k)n_i$ in the left side of Eq. (7), namely, the expression of log W, is easily shown to be twice the interaction energy, namely, $-2JS^2/L$. Hence, log W is given by the following equation:

$$\log W = \sum_i \log\{1+\exp(-\alpha-\beta E_i-\beta\delta_i(JS/L))\}$$
$$+\alpha N+\beta E-\beta\cdot(2JS^2/L). \quad (10)$$

Based on the form of entropy $k\log W$, the relations $\alpha=-\zeta/kT$ and $\beta=1/kT$ are obtained by utilizing the thermodynamic relation, T being the absolute temperature. By putting the respective values of α and β into Eq. (5), the following equation is established:

$$N_k/Z_k = \{1+\exp(E_k+\partial f/\partial N_k)-\zeta)/kT\}^{-1}.$$

This gives the probability for that each state belonging to Z_k will be occupied by an electron, the parameter ζ corresponding to the Fermi energy.

As the total energy U of the system is expressed by $E-(JS^2)/L$, according to the above-mentioned expressions, the free energy F of the system, namely, $U-T\Phi$, takes the following form:

$$F = (JS^2/L) + \zeta N + \Omega, \quad (11)$$

$$\Omega = -kT\sum_i[1+\exp\{(\zeta-E_i+(\delta_i JS)/L)/kT\}]. \quad (12)$$

From the expression of free energy thus obtained the magnetic moment M of the system will be given by

$$M = -\partial F/\partial H. \quad (13)$$

III. Application to intrinsic semi-conductors

Now, these results would be applied to the case of an intrinsic semi-conductor. Neglecting the band width, denote the energy and numbers of the levels of its *full band* by E_1 and $2Lb_1$, respectivelly, and those of the *empty band* by E_2 and Lb_2, respectivelly. It will be inferred that the exchange integral J between any pair of electrons of the full band is exceedingly larger than that of the empty band and that ferromagnetism originates from this band. Then under the action of the external magnetic field H the following equation may be established for the energy levels of the full band:

$$E_i = E_1 + \delta_i \mu H.$$

Here μ is the Bohr magneton.

On the other hand, in the empty band it will be supposed that no change takes place except that E_1 turns out to be E_2 and that the exchange integral of the levels belonging to this band is remarkably small in comparison with that of the full band. Then, the calculation of the summation $\sum$ in the expression Ω can easily be operated, the result being given as follows:

$$\begin{aligned}\Omega = &-kTLb_1 \log\{1+\exp\{\zeta - E_1 - \mu H + (JS/L)/kT)\}\\ &-kTLb_1 \log\{1+\exp\{\zeta - E_1 + \mu H - (LS/L)/kT)\}\\ &-kTLb_2 \log\{1+\exp(\zeta - E_2 - \mu H)/kT\}\\ &-kTLb_2 \log\{1+\exp(\zeta - E_2 + \mu H)/kT\}.\end{aligned}$$

As S is the total spin quantum number, the total magnetic moment M of the system will be expresed by

$$M = -2S\mu. \tag{14}$$

By substituting the expression (12) of Ω into the free energy foumulas (11), (12) together with (14) and calculating the intensity of magnetization by means of (13), we obtain

$$\begin{aligned}M/(L\mu b_1) = &-1/\{1+\exp((E_1 - \zeta + \mu H + \tfrac{1}{2}Jb_1 \cdot M/L\mu b_1)/kT)\}\\ &+1/\{1+\exp\{(E_1 - \mu H - \zeta - \tfrac{1}{2}Jb_1 \cdot M/L\mu b_1)/kT)\}\\ &+1/\{1+\exp\{(E_2 - \zeta - \mu H)/kT\}\\ &-1/\{1+\exp\{(E_2 - \zeta + \mu H)/kT\}.\end{aligned} \tag{15}$$

If the free energy is considered to be a function of M, the values of M given by (15) will give the maximum and minimum points of the free energy. If the expression (15) has several roots at a certain temperature, the value of M corresponding to the absolute minimum of F will give the actual value of magnetization. Furthermore, it is necessary to determine the Fermi energy ζ in the formula before the calculation. From the thermodynamical relation

$$N = -(\partial \Omega / \partial \zeta)_{V,T,M}$$

we obtain

$$N=2Lb_1=Lb_1/[1+\exp\{(E_1+\mu H-\zeta+\frac{1}{2}Jb_1\cdot(M/L\mu b_1))/kT\}]$$
$$+Lb_1/[1+\exp\{(E_1-\mu H-\zeta+\frac{1}{2}Jb_1\cdot(M/L\mu b_1))/kT\}]$$
$$+Lb_2/[1+\exp\{(E_2-\mu H-\zeta)/kT\}]$$
$$+Lb_2/[1+\exp\{E_2+\mu H-\zeta)/kT\}]. \tag{16}$$

Therefore, by solving M and ζ or $M/L\mu b_1$ and ζ, for conuenience' sake, simultaneously from Eqs. (15) and (16), we get the spontaneous magnetization M as a function of temperature.

Now, let us turn to the consideration of the state at the absolute zero before calculating the change of spontaneous magnetization by means of the expressions obtained. At the absolute zero, Lb_1n electrons are excited from the full band to the empty one and then the free energy F of the state which will have the total spin quantum S, is expressed as follows:

$$F=U=Lb_1(E_2-E_1)n-(JS^2/L)+2HS\mu. \tag{17}$$

If n is cconsidered to be fixed, the state of the minimum energy will correspond to the maximum spin quantum number and consequently the following equation will be obtained

$$S=-\frac{1}{2}Lb_1n. \tag{18}$$

Tracing the values of F in the case of $H=0$ for n with these expressions, Fig. 1 is obtained. As shown in the figure, F changes with n in parabolic form and takes the minimum for $n=0$

when $\quad E_2-E_1>Jb_1/4, \quad$ (19)

and when $\quad E_2-E_1<Jb_1/4 \quad$ (20)

$n=1$ corresponds to the minimum. In other words, in the case of (19), the spontaneous magnetization does not appear at the absolute zero, while in the case of (20) the largest spontaneous magnetization appears. Again, in the case of (20) with the gradual increace of the magnetic field up to $H=(E_2-E_1-(b_1J/4))/\mu$, the spontaneous magnetization appears abruptly. Curves in Fig. 1 are of the case of $b_1\leq b_2$.

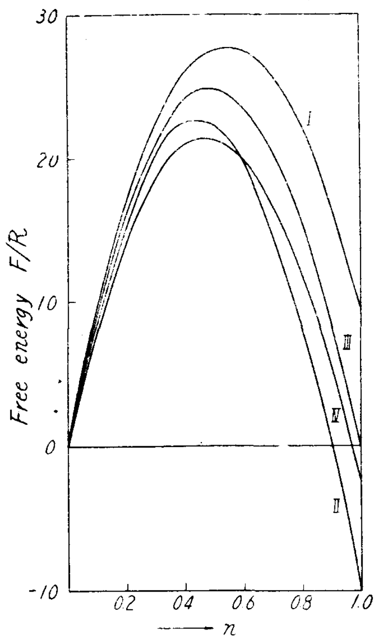

Fig. 1.

Curve I is formed when b_1J is equal to 3.6 (E_2-E_1) and in this case the total energy attains the minimum value at $n=0$, no spontaneous magnetization taking place. Curve II is obtained in the case of b_1J being equal to 4.4 (E_2-E_1). As seen from the figure, $n=1$ corresponds to minimum energy and in this case ferromagnetism appears. Curve III is formed in the case of $b_1J=4(E_2-E_1)$, in which the values of energy for $n=0$ and $n=1$ are equal to each other. This value of exchange is the lowest one for the occurrence of ferromagnetism. Curve IV shows the case in which the magnetic field of the amount of $0.12\times(E_2-E_1)/\mu$ is acting on the case of the curve I. In this case ferromagnetism with the minimum energy appears at $n=1$. For higher temperatures, the relation between the free energy and the magnetic moment is determined by Eqs. (16) and (11). As an example, it is shown in Fig. 2 that in the case of $Jb_1=3(E_2-E_1)$, the curves I, II, III and IV respectively represent the free energies at $T=0.35(E_2-E_1)/k$, $T=0.23(E_2-E_1)/k$, $T=0.15(E_2-E_1)/k$ and $T=0$ as the function of the magnetic moment. The ordinate shows the value of the free energy per mol in the case of $(E_2-E_1)=100\,k$. Curve III′ is given for the enlarged measure of the ordinate III. The arrows in the figure mean the roots given by (16), and with the rise of temperature, the magnetism undergoes a gradual change corresponding to the displacement of to the lowest value of free energy. The changes of magnetic moment with temperature are shown in Fig. 3, in which the numerals mean the ratios of the exchange integral multiplied by b_1 and the difference in the energies of the empty band and the full band, namely, $Jb_1/(E_2-E_1)$. When (E_2-E_1) is fixed, ferromagnetism does not appear so long as Jb_1 is small. In the case of $Jb_1=2.70(E_2-E_1)$, the curve 2.70 in Fig. 3 is formed. In such a case spontaneous magnetization appears in the neighborhood of $T=0.56(E_2-E_1)/k$, but disappears again at a certain lower temperature. If Jb_1 is assumed to increase gradually, the range in which magnetism appears will continuously widen.

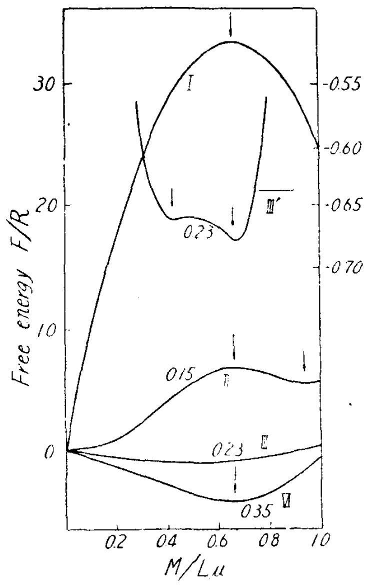

Fig. 2.

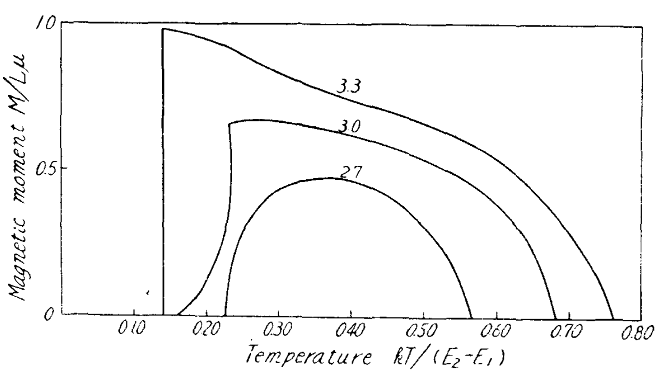

Fig. 3.

In the formula of the magnetic moment, the exchange integral J appears in multiplied form by b_1, the level number (per half an atom) of the lower energy band. Therefore, when both (E_2-E_1) and b_2/b_1 are fixed and the value of Jb_1 is given, the relation between $M/L\mu b_1$ and $kT/(E_2-E_1)$ is determined, which brings forth the relation between the magnetic moment and temperature T. When Jb_1 is fixed and b_1 becomes small, the magnetic moment M becomes small at a certain fixed temperature. Since $M/L\mu b_1$ becomes small when J is fixed and b_1 alone diminishes, M becomes smaller than that when Jb_1 is fixed. If the ratio $Jb_1 : (E_2-E_1)$ takes the value 3.3, a part of the spontaneous magnetization will vanish at a certain temperature. This is because that an abrupt transition of the absolute minimum point of free energy occurs among several relative minimum points. Haraldsen[2] discovered such a jump of magnetism in the case of

(2) H. Haraldsen, ZS. anorg. allgem. Chem. 234 (1937), 337.

CrS (Fig. 4).

Fig. 5 shows the change of spontaneous magnetization caused by the action of magnetic field, in which Jb_1 is equal to $2.90(E_2-E_1)$. The numerals in the figure indicate the strength of the magnetic field by the unit of $\mu/(E_2-E_1)$.

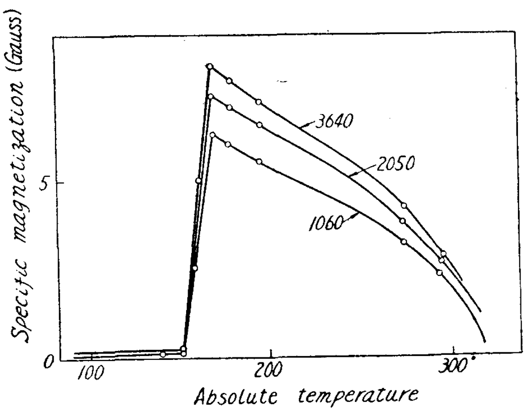

Fig. 4.

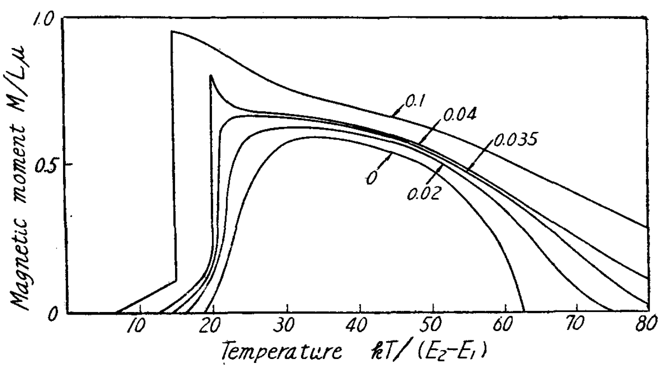

Fig. 5.

Summary

The ferromagnetism due to the collective electron model was discussed by applying the Fermi-Dirac statistics to the orientation of electron spins. A formula for the change of spontaneous magnetization due to temperature was given together with the expressions for various thermodynamic quantities of the system. The results were applied to the cases of the ferromagnetism of semiconductors. The characteristic change of spontaneous magnetization of chromium sulphide was reproduced by the theory.