On the Properties of Chromium Sulphides and Iron Sulphides. II

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Synopsis

The experimental data on the electrical and magnetic properties of chromium sulphides and iron sulphides are discussed on the basis of itinerant electron model of semiconductors. As for the electronic structures of the said substances it is concluded that there is a conduction band which overlaps the electronic energy bands responsible for the occurrence of ferromagnetism.

I. Introduction

In the previous paper(1), the authors reported the measurements on the electrical and magnetic properties of chromium sulphides and iron sulphides. These substances have considerably low electrical resistivity, the temperature coefficients of which are in most cases positive. But their magnetic behavior is somewhat different from metals since all of the ferromagnetic chromium sulphides and some of the iron sulphides have a magnetic transition temperature below which they are paramagnetic. It was suggested that this peculiar property of these substances might be considered in the light of the itinerant electron model as proposed previously by Hirone and Miyahara(2) (henthforth to be denoted H. M.) with some modifications. In this paper the results of the numerical calculation on this basis are given. Furthermore measurements on the electrical conductivity were extended to the paramagnetic region of the sulphur content in the chromium sulphides. The general results obtained confirm the validity of the consideration taken up here.

II. Possible simple models

It was a great achievement of H. M. statistics to explain the temperature dependency of the magnetism of the chromium sulphides. According to it, the magnetic transition of ferromagnetic semiconductors is considered to be a change in the distribution of electrons in the electronic energy bands of the substance. However, the band model taken in H. M. for chromium sulphides is disagreeable for the reason that the theory predicts a sharp jump in electrical conductivity at the magnetic transition temperature: the electrons excited from the lower band should change the conductivity considerably at that temperature. Those theoretical

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(1) H. Watanabe and N. Tsuya, Sci. Rep. RITU, A 2 (1950), 503.

(2) T. Hirone and S. Miyahara, Nippon Sûgaku Butsuri Gakkai-shi 17 (1943), 92 (in Japanese).

results, however, contradict with the experience: the measured electrical resistance does not show any marked discontinuity at the magnetic transition point of the substances. To avoid this difficulty, it seems necessary that the band which is responsible for conductivity should have little connection with ferromagnetism. Therefore, the model should be so modified that the conduction band will overlap the bands responsible for ferromagnetism. At first we tried to simplify further the model by omitting one of the latter bands. Two modifications of the theory are given below; one of them (a) was, however, not satisfactory for our purpose, while the other (b) gave a complete explanation of the above phenomena.

(a) The first model is shown schematically in Fig. 1. The conduction band or the s-band overlaps the relatively narrow d-band with Z_0 electronic energy levels. The state density of the s-band is assumed constant and denoted by ν_s and the Fermi level is taken at the position lower than the d-band by ε_0. E_1 denotes the energy ot the d-band measured from the bottom of the s-band. The temperature will have an effect in raising the electrons to the d-band, at which ferromagnetism occurs.

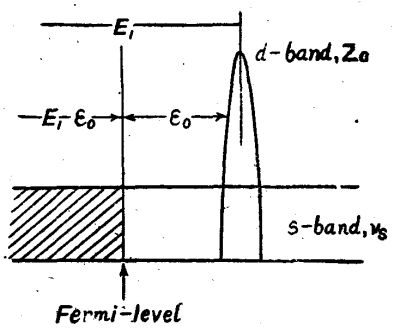

Fig. 1. Model (a)

The free energy of the electronic system can be represented by

$$F=-\nu_s E_1^2-\frac{\nu_s}{2}\pi^2(RT)^2+J\sigma^2L-2\nu_s\varepsilon_0\zeta-\nu_s\zeta^2-Z_0RT \log\left[\left(1+\exp\left(\frac{\zeta+J\sigma}{kT}\right)\right)\left(1+\exp\left(\frac{\zeta-J\sigma}{kT}\right)\right)\right]$$

where J is the exchange integral between electrons in the d-band, σ the spin quantum number per unit molecule, L the number of molecules per unit volume and ζ the electrochemical potential. F takes the stationary value when the independent variables σ and ζ satisfy the following conditions.

$$\frac{2L\sigma}{Z_0}=\frac{\exp\left(\frac{\zeta+J\sigma}{RT}\right)}{1+\exp\left(\frac{\zeta+J\sigma}{kT}\right)}-\frac{\exp\left(\frac{\zeta-J\sigma}{kT}\right)}{1+\exp\left(\frac{\zeta-J\sigma}{kT}\right)} \tag{1}$$

$$-\frac{2\nu_s(\varepsilon_0+\zeta)}{Z_0}=\frac{\exp\left(\frac{\zeta+J\sigma}{kT}\right)}{1+\exp\left(\frac{\zeta+J\sigma}{kT}\right)}+\frac{\exp\left(\frac{\zeta-J\sigma}{kT}\right)}{1+\exp\left(\frac{\zeta-J\sigma}{kT}\right)} \tag{2}$$

Differentiating the both sides of equation (1) with respect to σ and then putting $\sigma=0$ in the resulting relation, the Curie point T_c of the resulting ferromagnetism is determined.

$$\frac{L}{JZ_0}kT_c=\frac{\lambda}{(1+\lambda)^2},\quad \text{where}\quad \lambda=\exp\left(\frac{\zeta}{kT}\right) \tag{1'}$$

Combining (1') with (2) in which σ is put equal to zero, we can eliminate T_c and

obtain,

$$-\frac{\nu_s\varepsilon_0}{Z_0}\left(1+\frac{JZ_0}{L\varepsilon_0}\ \frac{\lambda}{(1+\lambda)^2}\log\lambda\right)=\frac{\lambda}{1+\lambda} \qquad (3)$$

The expressions of the both side of (3) as functions of λ are shown in Fig. 2. The value of λ at the intersection points of these two curves give the solution of equation (3). In the case shown in the figure there are two λ values λ_1 and λ_2. The critical temperatures T_{c1} and T_{c2} corresponding to those values of λ

$$kT_{c_2}^1=\frac{JZ_0}{L}\ \frac{\lambda_2^1}{(1+\lambda_2^1)}$$

are the two Curie temperatures for this system. The results of calculation are shown in Fig. 3. It is found by numerical calculations that for certain conditions the ferromagnetism occurs in a certain temperature range. For the occurrence of the ferromagnetism of this type, it is required that the exchange integral J should at least reach the value which makes the two Curie points equal, namely, $\lambda_1=\lambda_2$. This condition may roughly be described as the value of λ being the one which makes the function

$$\frac{\lambda}{(1+\lambda)^2}\log\lambda$$

maximum. This value of λ is

$$\log\lambda_m=-\frac{1+\lambda_m}{1-\lambda_m},$$

or $\lambda_m=0.2136$.

Substituting this value in the formula (3) the condition for the occurrence of ferromagnetism is found to be approximately

$$-\frac{\nu_s\varepsilon_0}{Z_0}\left\{1+\frac{JZ_0}{L\varepsilon_0}\ \frac{\lambda_m}{(1+\lambda_m)}\log\lambda_m\right\}\geqq\frac{\lambda_m}{1+\lambda_m}$$

In Fig. 3 we have adopted for the abscissa the reduced temperature defined by

$$\theta=\frac{2L}{JZ_0}T,$$

and for the ordinate the reduced magnetization

$$x=\frac{2L}{Z_0}\sigma$$

The numbers named for the curves indicate the parameter values of $JZ_0/2L\varepsilon_0$. For all the curves $L/J\nu_s$ is kept constant at 0.85. As is seen from the figure, the temperature dependence of the calculated ferromagnetism is indeed peculiar, but the sharp drop of ferromagnetism at low temperatures is not so accentuated as

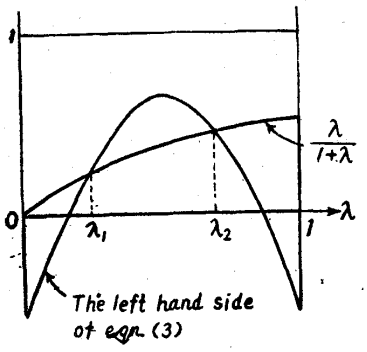

Fig. 2.

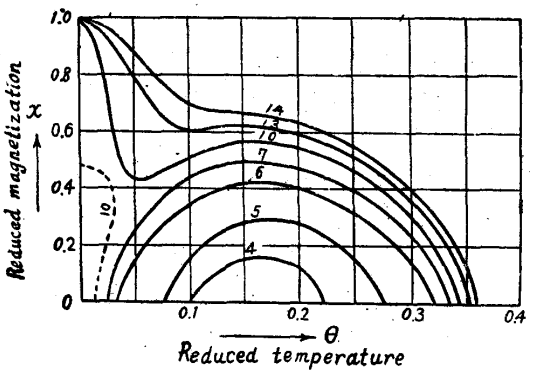

Fig. 3. Magnetization-temperature curves calculated with the model (a) for $L/J\nu_s=0.85$. The numbers on the curves are the values of $JZ_0/2L\varepsilon_0$. The dotted curve is that for unstable solution.

in Hirone-Miyahara's[3] and for this reason we have returned to the original picture with another empty band of high density of energy levels Z_1.

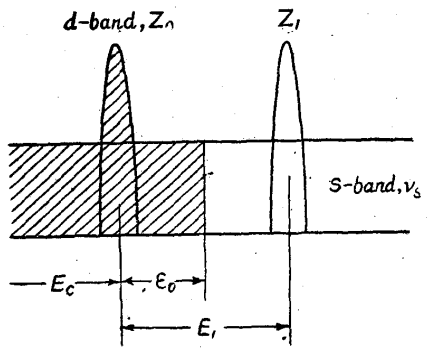

Fig. 4. Model (b)

(b) This model is illustrated in Fig. 4. In this case the Fermi level is assumed above the d-band by ε_0. Z_1 band is higher than the d-band by E_1. The free energy of the system then takes the following type of expressions;

$$F=-\nu_s E_0^2-\frac{\nu_s}{2}\pi^2(RT)^2+J\sigma^2L+2\nu_s\varepsilon_0\zeta+2Z_0\zeta-\nu_s\zeta^2$$
$$-Z_0RT\log\left[\left(1+\exp\left(\frac{\zeta+J\sigma}{kT}\right)\right)\left(1+\exp\left(\frac{\zeta-J\sigma}{kT}\right)\right)\right]-2Z_1RT\log\left(1+\exp\frac{\zeta-E_1}{kT}\right).$$

The simultaneous equations which determine σ and ζ for a given value of T are now

$$\frac{2L\sigma}{Z_0}=\frac{\exp\left(\frac{\zeta+J\sigma}{kT}\right)}{1+\exp\left(\frac{\zeta+J\sigma}{kT}\right)}-\frac{\exp\left(\frac{\zeta-J\sigma}{kT}\right)}{1+\exp\left(\frac{\zeta-J\sigma}{RT}\right)} \tag{4}$$

and

$$2Z_0+2\nu_s\varepsilon_0=2\nu_s\zeta+Z_0\left\{\frac{\exp\left(\frac{\zeta+J\sigma}{kT}\right)}{1+\exp\left(\frac{\zeta+J\sigma}{kT}\right)}+\frac{\exp\left(\frac{\zeta-J\sigma}{kT}\right)}{1+\exp\left(\frac{\zeta-J\sigma}{kT}\right)}\right\}+2Z_1\frac{\exp\left(\frac{\zeta-E_1}{kT}\right)}{1+\exp\left(\frac{\zeta-E_1}{kT}\right)} \tag{5}$$

By using the substitutions

$$x=\frac{2L}{Z_0}\sigma \qquad \alpha=\frac{2\nu_s\varepsilon_0}{Z_0} \qquad \varepsilon_1=\frac{2LE_1}{JZ_0}$$

$$\theta=\frac{kT}{J} \qquad \frac{x}{\sigma}=\frac{2LkT}{JZ_0} \qquad \gamma=\frac{J\nu_s}{L} \qquad \lambda=\exp\left(-\frac{\zeta}{kT}\right)$$

these equations are transformed into

$$x=\frac{\exp\left(\frac{x}{\theta}\right)}{\lambda+\exp\left(\frac{x}{\theta}\right)}-\frac{\exp\left(-\frac{x}{\theta}\right)}{\lambda+\exp\left(-\frac{x}{\theta}\right)} \tag{4'}$$

and

$$2+\alpha+\gamma\theta\log\lambda=\frac{\exp\left(\frac{x}{\theta}\right)}{\lambda+\exp\left(\frac{x}{\theta}\right)}+\frac{\exp\left(-\frac{x}{\theta}\right)}{\lambda+\exp\left(-\frac{x}{\theta}\right)}+\frac{2Z_1}{Z_0}\frac{\exp\left(-\frac{\varepsilon_1}{\theta}\right)}{\lambda+\exp\left(-\frac{\varepsilon_1}{\theta}\right)} \tag{5'}$$

respectively. Our project is to find x of these equations which becomes a discontinuous function of θ at certain value of θ satisfing the condition that this solution corresponds to the lowest value of the free energy. In order to have such a

(3) As far as the results are concerned our calculation is rather similar to the older calculations of S. Miyahara: Z. Phys. **113** (1939) 247.

solution, there must be certain relations between the parameters α_1, γ and $2Z_1/Z_0$ in the equations. These are found as follows.

The desirable solution must satisfy two important conditions : 1) it must be taken from the solutions of (4′) and (5′) which are continuous functions of θ from absolute zero of temperature to the Curie point. 2) this solution, however, must be a nonrealizable one near absolute zero when the minimum condition for the free energy is taken into account. So the said requirements for the parameters were sought so that these two conditions should be satisfied; we have analysed the solutions at absolute zero and determined the conditions for the occurrence of the solution $x=1$ and its instability. Subsequently two cases were found:

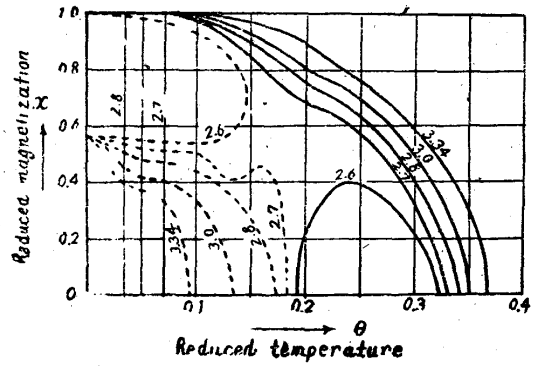

Fig. 5. Magnetization-temperature curves calculated with the model (b) for $2\nu_s\varepsilon_0/Z_0=1$, $2Z_1/Z_0=0.6$. The numbers on the curves are the values of $J\nu_s/L$. The dotted curves are those for unstable solutions.

Case 1. $\varepsilon_1<1$, $\gamma\varepsilon_1>\alpha+1$

$$2\alpha-\frac{4Z_1}{Z_0}<\gamma-1<2\alpha$$

Case 2. $\varepsilon_1<1$, $\gamma\varepsilon_1<\alpha+1$

$$\frac{2Z_1}{Z_0}>\frac{1}{\varepsilon_1}-1-\alpha$$

$$\gamma<-\frac{2(1+\alpha)\varepsilon_1-1}{\varepsilon_1}$$

Some of the results of the numerical calculations are shown in Fig. 5. These correspond to case 1. The general feature of these curves are essentially the same as those of original H. M., again reproducing the experimental curve for CrS satisfactorily. (e.g. for the case $J\nu_s/L=2.7$)

III. Electrical conductivity of CrS containing less sulphur than ferromagnetic CrS

The above theory reproduces the metallic character of the ferromagnetic CrS. This is also valid for paramagnetic region of the sulphur content between stoichiometric and ferromagnetic CrS. These data are shown in Fig. 6. In general, the temperature coefficient of resistance is positive, but, for the specimen corresponding to the stoichiometric composition Cr_1S_1, it becomes negative at higher temperatures, making a maximum in resistance near the ordinary temperature. The absolute value of the resistance of these sintered specimens, of course, varied widely from specimen to specimen, and we could not make definite statements about specific resistance. If the conduction band assumed

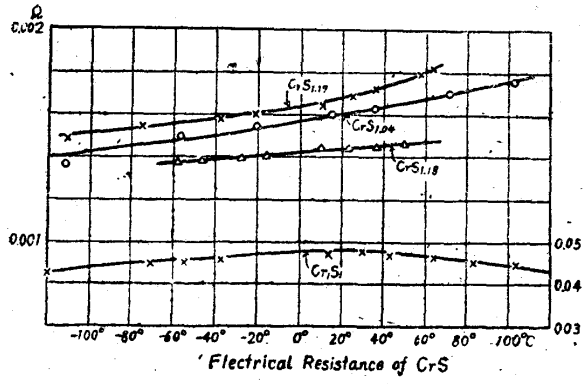

Fig. 6. Electrical Resistance of CrS.

in our model is caused by the deviation from the stoichiometric composition of the substance of sulphur content, it is expected that the specimen corresponding to Cr_1S_1 will exhibit large resistivity. It is not undeniable from the data given here that pure CrS without lattice defects might be highly resistive. We observed that when CrS_n whose values of n was greater than unity was heated and its resistance was measured in vacuo, the resistance always increased, which seemed to indicate that the resistivity would increase with decreasing sulphur content.

IV. Conclusion

The band model modified from the Hirone-Miyahara's is suitable for discussing the magnetism of the CrS and FeS with variable content of sulphur. It is not clear if the conduction band assumed in this model is caused by the deviation from the stoichiometric composition of the substance. It is desired to obtain pure CrS or FeS with perfect lattice which corresponds to the stoichiometric composition and its resistivity measured(4).

In conclusion the authors wish to express their sincere thanks to Dr. K. Honda and to Prof. T. Hirone for their supervision and guidance in the course of the present investigation. A part of the fund for this investigation was defrayed from the Scientific Research Funds of the Ministry of Education.

(4) According to J. Königsberger and coworkers, the resistance of a sample of pyrrhotite, whose composition is nearly expressed by the formula FeS, decreases as the temperature is increased from −189° to 300°. However, there is a minimum in resistance near 200°C above which the resistance begins to increase to approach a sharp anomaly at 360°, where the transition from α-pyrrhotite to β-pyrrhotite takes place. The minimum value of resistivity amounts to 3×10^{-4} Ω cm ca. See J. Königsberger and K. Schilling, Phys. Zeit. **9** (1908) 349 ; J. Königsberger, the same journal **13** (1912) 281 ; J. Königsbeger, O. Reichenheim and K. Schilling, the same journal **12** (1911) 1139.