Spin Fluctuation Theory of Magnetism in $Co(S_xSe_{1-x})_2$ with Pyrite Structure

by Mikio NAKAYAMA 4056

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Spin Fluctuation Theory of Magnetism in $Co(S_xSe_{1-x})_2$ with Pyrite Structure

MiKio NAKAYAMA

Recently the theory of metal magnetism has been developed considerably by using the concept of spin density fluctuations. Though the Hartree-Fock approximation is only reasonable at low temperature, the spin fluctuation theory is a good approximation at high temperature and reduces to the Hartree-Fock approximation in the low temperature limit.

The purpose of this paper is to explain the metamagnetism and the magnetic susceptibility in $Co(S_xSe_{1-x})_2$ by the spin fluctuation theory with the use of the same model density of states. Also, the results of the spin fluctuation theory are compared with those of the Hartree-Fock approximation.

§.1 Introduction

To explain the magnetic prorerties of d-band electrons, both the local moment model and the itinerant model have been used. That is to say, the magnetism of d-band electrons has two opposite properties, local and itinerant. For example the saturation moment per atom at low temperature is not integral in units of Bohr-magnetons. This is the property of the itinerant or band model. But the susceptibility at high temperature obeys the Curie-Weiss law which is considerd to be the property of the local or Heisenberg model.

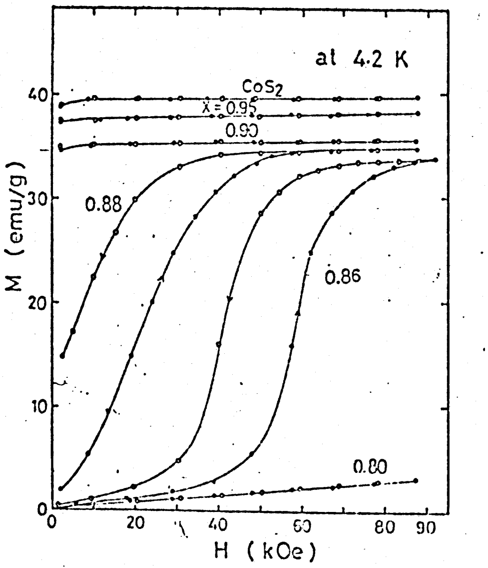
Experiment tells us that the electrons in the d-band are itinerant. The width of the d-band is very narrow, about a few eV, and the exchange energy which is the origin of the electron correlation is the same order as the band width. Then we must start from the itinerant model with the strong correlation, and consider why the itinerant electrons show the local moment like properties at high temperature.

The band theory based on the HF theory gives good results in the ground state, but is not resonable at finite temperature. By recent investigations thermodynamical properties of the magnetism are described in terms of spin density fluctuations. Using the functional integral method for the study of spin density fluctuations, the alloy-analogy can be realized and the spin density fluctuations are treated as static random potentials. For this reason the coherent potential approximation (CPA) can be used.

In this paper we want to explain the magnetic properties of $Co(S_xSe_{1-x})_2$ theoretically with the use of only the model density of states. In §.2 the experimental data of $Co(S_xSe_{1-x})_2$ by Adachi et al. in 1979 is shown. In §.3 the model density of states is determined so as to explain the metamagnetism, and by HF theory the susceptibility at finite temperature is calculated for the comparison with the spin fluctuation theory. In §.4 the theoretical formalism of the spin fluctuation theory is described. In §.5 the susceptibility is calculated from the model density of states by the spin fluctuation theory. In §.6 some discussions are given.

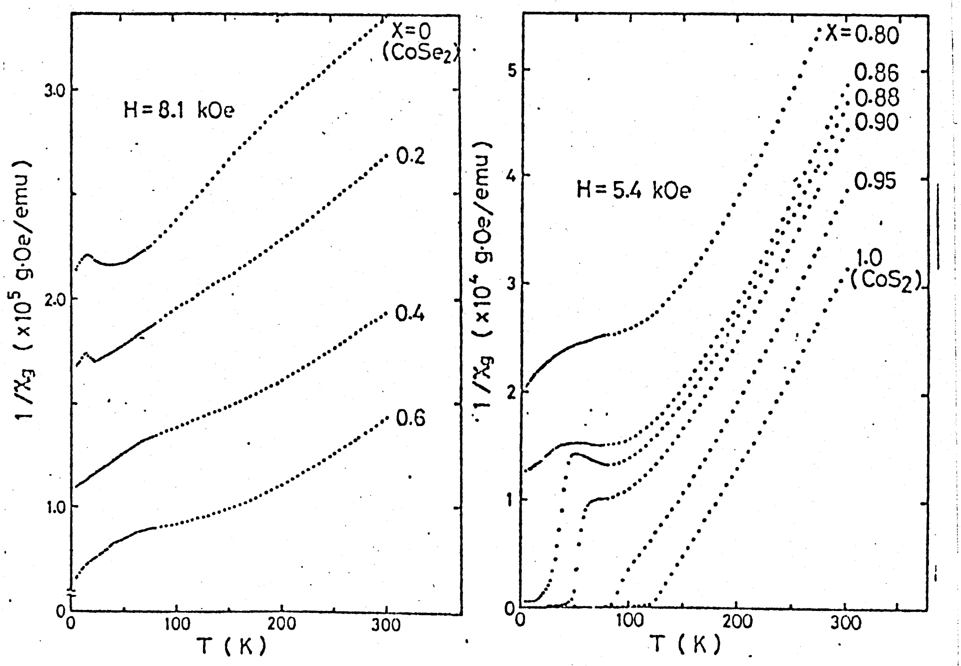
§.2 Experimental data of $Co(S_x\ Se_{1-x})_2$

The magnetic properties of $Co(S_xSe_{1-x})_2$ with the pyrite structure were investigated experimentally by Adachi et al.5),6) in detail. Fig. 2-1 and Fig. 2-2 are copies of J.Phys.Soc. Japan <u>46</u>(1979)1474 by Adachi et al..



Magnetization curves at 4.2 K in high magnetic field up to 93 kOe. The closed and open circles indicate the increasing and decreasing process of the magnetic field, as denoted by arrows, respectively.

Fig. 2-1



(a)

(b)

Fig. 2-2

Inverse susceptibility vs temperature curves from 4.2 K to 300 K. (a) $0\leq x\leq 0.6$ at 8.1 kOe and (b) $0.8\leq x\leq 1.0$ at 5.4 kOe.

In the range of $.89 < x \leq 1.0$ $Co(S_xSe_{1-x})_2$ is ferromagnetic. And the saturation moment per cobalt atom is .855 μ_B for CoS_2 and it decreases gradually with increasing Se content. In the range of $x < .89$ the paramagnetism with large susceptibility occurs. For x=.86 a peculiar so-called metamagnetism is found in paramagnetic state. In this case when the external field is small, the magnetic moment is proportional to the external field, but at a transition field the momet suddenly saturates.

At finite temperature the susceptibility of $Co(S_xSe_{1-x})_2$ with small x has a maximum. For example in $CoSe_2$ the maximum exists at about 40°K. Near the metamagnetism composition the instability of the susceptibility is found at about 30°K, and the susceptibility shows a maximum near 80°K. In the whole system the susceptibility at high temperature obeys the Curie-Weiss law in which the Curie constant takes a value corresponding to 1.5 μ_B local moment per cobalt atom up to 300°K, and 1 μ_B local moment above 300°K.

The electrons contributing to the magnetism are d-band electrons which are seven per cobalt atom. But for the reason of cubic symmetry of pyrite sturucture illustrated in Fig. 2-3, the d-band with five-fold degeneracy splits into two bands, which are the dε-band with three-fold degeracy and the dγ-band with two-fold degeneracy, as illustrated in Fig. 2-4. Thus we may consider only the dγ-band and one electron for the main origin of magnetism. So our band is a quarter filled band.

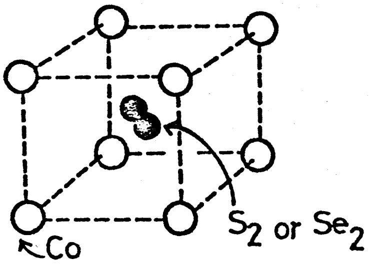


Fig. 2-3

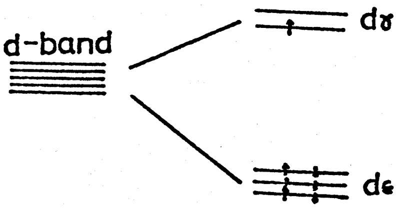


Fig. 2-4

§.3 Metamagnetism and the model density of states

As described in subsequent sections, the spin fluctuation theory reduces to HF thory at low temperature. And the magnetic properties at low temperature are well explained with the use of HF theory. This section is mainly devoted to explain metamagnetism with the use of the model density of states by HF theory. At the same time we determine the parameters in the model density of states

To tell the conclusions at first, the metamagnetism is explained by considering the free energy as a function of the magnetization. We adopt the density of states as shown in Fig. 3-1 and calculate the free energy F as a function of the magnetization M. The results are illustrated in Fig. 3-2 for various values of the external field B_o. As illustrated in Fig. 3-3, when M is small and then the densities of states at the Fermi levels of both up and down spins are low (ρ_2), the curve of F(M) is convex downwards. But when M is large and the densities of states at the Fermi levels of up and down spins are low (ρ_2) and high (ρ_1) respectively, the curve of F(M) is convex upwards. In actual calculations we adopt the model density of states as illustrated in Fig. 3-4 and get better fit with the experimental data of the magnetization curve

The metamagnetism occurs from the following reason. F(M) with a parameter B_o has two local minimum points, M_L and M_H, near B_o=B_t, where B_t is the transition field. When $B_o < B_t$, $F(M_L)$ is smaller than $F(M_H)$, and M_L is proportional to B_o. As B_o increases, the difference between $F(M_L)$ and $F(M_H)$ decreases. And when B_o=B_t the state jumps from M_L to M_H. Thus the metamagnetism is realized.

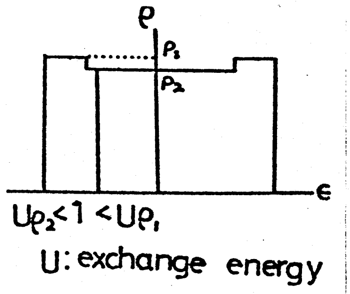


Fig. 3-1

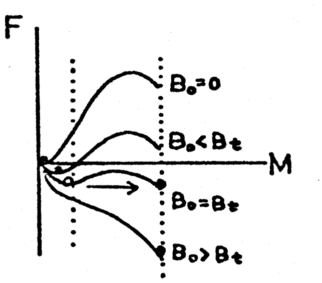
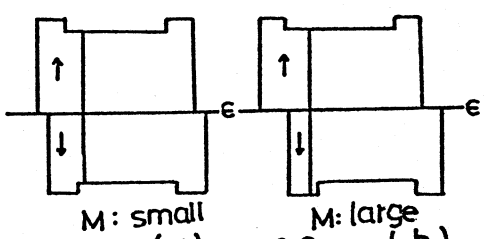


Fig. 3-2



M: small (a)

M: large (b)

Fig. 3-3

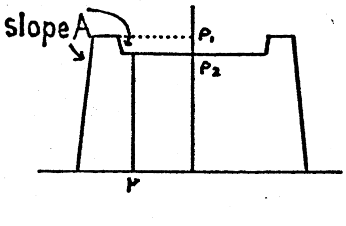


Fig. 3-4

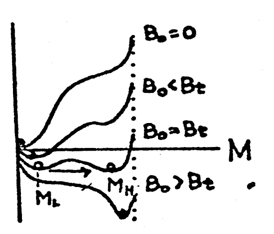


Fig. 3-5

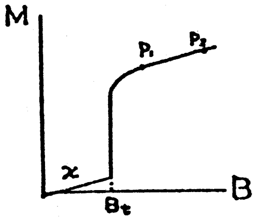


Fig. 3-6

From the definition, the free energy F as a funtion of M is given by

$$e^{-\beta F} = \mathrm{Tr}[\ \delta(\Sigma_{\vec{k}\sigma} n_{\vec{k}\sigma} - N)\delta(\Sigma_{\vec{k}\sigma}\sigma n_{\vec{k}\sigma} - M)\ e^{-\beta H}] \qquad \ldots(3.1)$$

where $n_{\vec{k}\sigma}$ is the number operator of electrons with the Bloch wave number $\vec{k}$ and spin σ, and N is the total number of electrons. In the Hamiltonian we adopt the intra atomic interaction only, namely we use the Hubbard Hamiltonian;[8)]

$$\begin{aligned} &H = H_\circ + H' \\ &H_\circ = \Sigma_{\vec{k}\sigma}(\varepsilon_{\vec{k}\sigma} - \sigma B_\circ) n_{\vec{k}\sigma} \\ &H' = UH_I = U\Sigma_j n_{j\uparrow} n_{j\downarrow} = \frac{U}{4}\Sigma_j n_j{}^2 - U\Sigma_j S_{jz}{}^2, \quad \left(\begin{array}{l} S_{jz} \equiv \frac{1}{2}\Sigma_\sigma \sigma n_{j\sigma} \\ n_j \equiv \Sigma_\sigma n_{j\sigma} \end{array} \right. \end{aligned} \qquad \ldots(3.2)$$

For simplicity, non-degenerate band is considered. $B_\circ$ is the external field, and $n_{j\sigma}$ is the number operator for the Wannier state electrons in j-site with spin σ.

Splitting F into two parts, we obtain

$$\begin{aligned} &F = F_\circ + \Delta F \\ &e^{-\beta F_\circ} = \mathrm{Tr}[\ \delta(\Sigma_{\vec{k}\sigma} n_{\vec{k}\sigma} - N)\delta(\Sigma_{\vec{k}\sigma}\sigma n_{\vec{k}\sigma} - M)\ e^{-\beta H_\circ}] \\ &\Delta F = \int_0^U < H_I >_U dU \end{aligned} \qquad \ldots(3.3)$$

, where $< \cdots >_U$ means the statistical average:

$$< \cdots >_U = \mathrm{Tr}[\ \cdots\ e^{-\beta(H_\circ + UH_I)}\ \delta(\Sigma_{\vec{k}\sigma} n_{\vec{k}\sigma} - N)\delta(\Sigma_{\vec{k}\sigma}\sigma n_{\vec{k}\sigma} - M)]\ /\ e^{-\beta F}.$$

In HF approximation, ΔF becomes

$$\Delta F \simeq \int_0^U < H_I >_{U=0} dU = U < H_I >_{U=0} \simeq \frac{I}{4}(N^2 - M^2), \qquad I \equiv \frac{U}{N_\circ} \qquad \ldots(3.4)$$

where $N_\circ$ is the number of sites. $e^{-\beta F_\circ}$ can be calculated easily with the use of simple identities;

$$\begin{aligned} &\delta(\Sigma_{\vec{k}\sigma} n_{\vec{k}\sigma} - N) = \frac{1}{2\pi\beta i}\int_{\mu_\circ - i\infty}^{\mu_\circ + i\infty} d\mu\ e^{-\beta\mu(N - \Sigma_{\vec{k}\sigma} n_{\vec{k}\sigma})} \\ &\delta(\Sigma_{\vec{k}\sigma}\sigma n_{\vec{k}\sigma} - M) = \frac{1}{2\pi\beta i}\int_{\xi_\circ - i\infty}^{\xi_\circ + i\infty} d\xi\ e^{-\beta\xi(M - \Sigma_{\vec{k}\sigma}\sigma n_{\vec{k}\sigma})} \end{aligned} \qquad \ldots(3.5)$$

and the following approximation which is adequate when t of eq. (3.6) is macroscopic or thermodynamical variable.

$$\begin{aligned} &e^{-\beta F} = \int_{t_\circ - i\infty}^{t_\circ + i\infty} dt\ e^{-\beta f(t)} \simeq e^{-\beta f(t_\circ)}, \\ &\text{with condition;}\quad \frac{\partial f}{\partial t}\Big|_{t = t_\circ} = 0\ . \end{aligned} \qquad \ldots(3.6)$$

In eq. (3.5) μ and ξ can be interpreted as the chemical potential and the inner field, respectively. Because in the following section we will use these techniques presented in eq. (3.5) and eq. (3.6), we dared to use such methods in this section. The methods of eq. (3.5) and eq. (3.6) are called the Lagrange multipliers and the saddle point approximation respectively.

After the calculations of the previous page, we have the following result.

$$F(M)= \mu N+\xi M- \beta^{-1}\Sigma_{\sigma}\int d\varepsilon\ \rho(\varepsilon)\ln(1+e^{-\beta(\varepsilon-\mu-\sigma(B_{\circ}+\xi))})+ \frac{I}{4}\ (N^2-M^2)$$

with conditions;

$$N= \Sigma_{\sigma}\int d\varepsilon\ \rho(\varepsilon)(1+e^{\beta(\varepsilon-\mu-\sigma(B_{\circ}+\xi))})^{-1}$$

$$M= \Sigma_{\sigma}\int d\varepsilon\sigma\rho(\varepsilon)(1+e^{\beta(\varepsilon-\mu-\sigma(B_{\circ}+\xi))})^{-1}. \qquad ...(3.7)$$

If we want the susceptibility χ within HF theory, χ is derived from

$$\chi^{-1}= \frac{\partial}{\partial M}\frac{\partial F}{\partial M}\Big|_{M=0} \ .$$

And with taking note of μ and ξ as functions of N and M, we have the well known HF- susceptibility;

$$\chi^{-1}= \frac{2\bar{\chi}}{1- I\bar{\chi}}$$

$$\bar{\chi} = \int d\varepsilon\ \rho(\varepsilon)\beta e^{\beta(\varepsilon-\mu)}(1+e^{\beta(\varepsilon-\mu)})^{-2}$$

with condition;

$$N= 2\int d\varepsilon\ \rho(\varepsilon)(1+e^{\beta(\varepsilon-\mu)})^{-1} \ . \qquad ...(3.8)$$

Up to the present, we have considered the formulations at finite temperature. But HF theory is not a good approximation at high temperature, so we can't expect that this theory will explain the properties of $Co(S_xSe_{1-x})_2$ at high temperature. Thus we use these formulations only in low temperature limit, and explain the metamagnetic properties at low temperature. Within this limit HF theory is the same as the spin fluctuation theory. From eq. (3.7) and eq. (3.8) we have the following equations with a step of $\beta \to \infty$.

$$F(M)= -MB_{\circ}+ \Sigma_{\sigma}\int^{\mu+\sigma B} d\varepsilon\ \rho(\varepsilon)\varepsilon+ \frac{I}{4}\ (N^2-M^2)$$

$$N= \Sigma_{\sigma}\int^{\mu+\sigma B} d\varepsilon\ \rho(\varepsilon)$$

$$M= \Sigma_{\sigma}\int^{\mu+\sigma B} d\varepsilon\ \sigma\rho(\varepsilon)\ , \qquad B\equiv B_{\circ}+\xi$$

$$\bar{\chi}= \rho(\mu)\ . \qquad ...(3.9)$$

In numerical calculations we use the density of states per site, then we must interpret F, N, and M as per site and replace I with U. The effects of two- fold degeneracy are only the replacement of $U \to \frac{U}{2}$ and $\rho(\varepsilon) \to 2\rho(\varepsilon)$. With the use of the local density of states as illustrated in Fig. 3-4 the best value of independet parameters, namely, ρ_1, ρ_2, U, and A were determined so as to fit in the experimental data of the magnetization curve of metamagnetism at low temperature. As the experimental data we selected the susceptibility χ, the transition field B_t, and two points (P_1 and P_2 on linear pert) as Fig. 3-6. The decided model density of states is presented in Fig. 3-7. Fig. 3-8 is the comparison between the experimental magnetization curve and the theoretical one from the model density of states. Using this model density of states we calculated F(M) concretely. It is presented in Fig. 3-9. In our calculations, for simplicity the band width is normalized to 1 eV.

This model density of states is obtained from only the data of $Co(S_xSe_{1-x})_2$ with x = .86 . For other mixing ratio the shape and the width of the density of states must be changed. However, to make calculations simple, we make here the following simple but reasonable assumption:

> The shapes and widths of the model density of states are the same for all mixing ratio x, instead of this, we change the exchange interaction energy U effectively.

For the later comparison with the spin fluctuation theory, the susceptibility at finite temperature with HF theory was calculated and given by Fig. 3-10. The maximum of susceptibility exists at about 350°K. And the curves don't obey the Curie -Weiss law at high temperature. Here the effective interaction U are determined by the low temperature susceptibility of the experimental data.

mixing ratio x	effective interaction U
.0	.78784
.2	.80524
.4	.83660
.6	.86186
.86	.90198

§.4 Spin fuluctuation theory with the aid of the coherent potential approximation

4-1 Formulation of functional integral method

In many-body problems of solid states physics, one simple identity;16)

$$\sqrt{\frac{\varepsilon}{\beta}} \int_{-\infty}^{+\infty} d\xi \; e^{-\frac{\pi}{\beta}\xi^2\varepsilon - 2\sqrt{\pi}\,\hat{a}\xi\varepsilon} = e^{\beta\hat{a}^2\varepsilon} \sqrt{\frac{\varepsilon}{\beta}} \int_{-\infty}^{+\infty} d\xi \; e^{-(\sqrt{\frac{\pi}{\beta}}\,\xi+\sqrt{\beta}\,\hat{a})^2\varepsilon} = e^{\beta\hat{a}^2\varepsilon} \qquad \ldots(4.1.1)$$

made the posibilities of new approximations. This identity can transform the square term in operater $\hat{a}$ in the exponent into a linear term in it.

In general the grand potential Ω is important in order to investigate the thermodynamical quantities. From the definition

$$e^{-\beta\Omega} = \mathrm{Tr}\; e^{-\beta(H-\mu\hat{N})} , \qquad \ldots(4.1.2)$$

where H is the Hamiltonian and $\hat{N}$ is the total number operater of electrons. Let the Hamiltonian of a system be divided into the one of a non-interacting part and the one of a interacting part. Then we can write Ω as

$$H = H_o + H'$$

$$\Omega = \Omega_o + \Delta\Omega$$

$$\Omega_o = \mathrm{Tr}\; e^{-\beta(H_o-\mu\hat{N})}$$

$$e^{-\beta\Delta\Omega} = < T\tau\; e^{-\int_0^\beta H'(\tau)d\tau} >$$

$$H'(\tau) = e^{\tau\hat{H}_o}\, H'\, e^{-\tau\hat{H}_o} , \qquad \hat{H}_o \equiv H_o - \mu\hat{N}$$

$$< \cdots > \equiv \mathrm{Tr}(\cdots e^{-\beta\hat{H}_o}) \,/\, \mathrm{Tr}\; e^{-\beta\hat{H}_o} , \qquad \ldots(4.1.3)$$

where $T\tau$ is the imaginary-time ordering operater, $H'(\tau)$ is the interaction representation of H', and < ⋯ > means the average about $\hat{H}_o$.

If H' is small compared with H_o, H' is considered as a perturbation to H_o. But in our problem H_o and H' are of the same order. For example in §.3, the value of band width corresponding to H_o is 1 eV, and the interaction energy U corresponding to H' is about .9eV. So we can't use the perturbation theory, and we need the other approximation.

To use the identity in eq. (4.1.1) , we express H' in the form of

$$H' = -\beta\hat{a}^2 \ . \qquad \ldots(4.1.4)$$

Substituting eq. (4.1.4) into eq.(4.1.3) and dividing the integrated resion into infinitesimal intervals, we have

$$e^{-\beta\Delta\Omega} = \lim_{n\to\infty} < T\tau \, e^{\Sigma_{i=1}^{n} \beta\hat{a}(\tau_i)^2\varepsilon} > , \qquad \varepsilon \equiv \frac{\beta}{n} \ , \ \tau_i \equiv \frac{\beta}{n} i \ . \qquad \ldots(4.1.5)$$

Here we use the identity descrived in eq. (4.1.1), and get

$$e^{-\beta\Delta\Omega} = \lim_{n\to\infty} < T\tau \, [\Pi_{i=1}^{n} \sqrt{\frac{\varepsilon}{\beta}} \int d\xi(\tau_i)] \, e^{-\Sigma_i[\frac{\pi}{\beta}\xi(\tau_i)^2 + 2\sqrt{\pi} \, \hat{a}(\tau_i)\xi(\tau_i)]\varepsilon} >$$

$$= \int \delta\xi(\tau) \, e^{-\int_0^\beta \frac{\pi}{\beta}\xi(\tau)^2 d\tau} < T\tau \, e^{-\int_0^\beta 2\sqrt{\pi} \, \hat{a}(\tau)\xi(\tau)d\tau} >$$

$$\int \delta\xi(\tau) \equiv \lim_{n\to\infty} \Pi_{i=1}^{n} \sqrt{\frac{\varepsilon}{\beta}} \int d\xi(\tau_i), \ldots(4.1.6)$$

where the Feynmann's path integral formulation 14) is used. The eq. (4.1.6) is the exact form and the starting point of approximations.

4-2 Application of functional integral method

With the use of the formulation mentioned above, we can transform the Hubbard Hamiltonian ;

$$H = H_\circ + H'$$

$$H_\circ = \Sigma_{\vec{k}\gamma\sigma} \varepsilon_{\vec{k}} n_{\vec{k}\gamma\sigma}$$

$$H' = \frac{U}{4}\Sigma_{j\gamma} n_{j\gamma}^2 - J\Sigma_{j\gamma}(\vec{S}_{j\gamma} \cdot \hat{\xi}_{j\gamma})^2 \ , \qquad \vec{S}_{j\gamma} \equiv \frac{1}{2}Sp \, \vec{\sigma} n_{j\gamma\sigma} \ , \qquad \ldots(4.2.1)$$

where almost all the notations are the same as eq. (3.2). H is generalized to take account of the degeneracy of orbitals. The subscript γ is added for the w-fold degeneracy of orbitals, so γ takes the values $\gamma = 1,2,\cdots,w$. For simplicity all orbitals in dγ-band are considered to be equivalent , and we introduce U and J which are the effective Coulomb and the effective exchange energies, respectively. To satisfy the rotational invariance of the theory, we used $\hat{\xi}_{j\gamma}$ which is a unit vector in arbitrary direction for each site. And Sp means the trace in the spin space, and $\vec{\sigma}$ is Pauli's spin vector.

Comparing eq. (4.2.1) with eq. (4.1.4), $-\frac{U}{4\beta}n_{j\gamma}^2$ and $\frac{J}{\beta}(\vec{S}_{j\gamma}\cdot\hat{\xi}_{j\gamma})^2$ are corresponding to $\hat{a}^2$. Since there are two kinds of square terms in the Hamiltonian, we must introduce two kinds of field, namely, charge fields $\eta_{j\gamma}(\tau)$ and exchange fields $\xi_{j\gamma}(\tau)$. Then with the use of the fomulation in §.4-1 we can write off the following equations.

$$e^{-\beta\Delta\Omega} = \int \delta\vec{\xi}(\tau)\delta\eta(\tau)\ e^{-\beta\Psi(\xi,\eta)}$$

$$-\beta\Psi(\xi,\eta) = -\frac{\pi}{\beta}\Sigma_{j\gamma}\int_0^\beta[\vec{\xi}_{j\gamma}(\tau)^2+\eta_{j\gamma}(\tau)^2]d\tau - \beta\Psi_1(\xi,\eta)$$

$$e^{-\beta\Psi_1(\xi,\eta)} = \langle T\tau\ e^{-\Sigma_{j\gamma}\int_0^\beta[2\bar{c}_1\vec{S}_{j\gamma}(\tau)\cdot\vec{\xi}_{j\gamma}(\tau)+2\bar{c}_2 n_{j\gamma}(\tau)\eta_{j\gamma}(\tau)]d\tau}\rangle$$

$$\vec{\xi}_{j\gamma}(\tau) \equiv \hat{\xi}_{j\gamma}\xi_{j\gamma}(\tau)$$

$$\delta\xi(\tau) \equiv \Pi_{j\gamma}\delta\xi_{j\gamma}(\tau) \qquad \bar{c}_1 \equiv \sqrt{\frac{\pi J}{\beta}}$$

$$\delta\eta(\tau) \equiv \Pi_{j\gamma}\delta\eta_{j\gamma}(\tau) \qquad \bar{c}_2 \equiv \sqrt{-\frac{\pi U}{4\beta}}\ , \qquad \ldots(4.2.2)$$

where we averaged in the direction of $\hat{\xi}_{j\gamma}$ to restore the rotational invaliance of the theory.

For simplicity, we excute for $\eta_{j\gamma}(\tau)$ the so-called saddle point approximation which was stated in eq. (3.6) of §.3. Here we note that the saddle point approximation about microscopic quantities, for example $\eta_{j\gamma}(\tau)$ and $\xi_{j\gamma}(\tau)$, is a poor approximation at high temperature. But we adopt this approximation about η assuming that the charge fields scarcely fluctuate compared with the exchange fields owing to the charge neutrality. Then we have

$$e^{-\beta\Delta\Omega} = \int \delta\vec{\xi}(\tau)\ e^{-\beta\Psi(\xi,\eta)}$$

$$\text{with condition;}\ \frac{\delta\Psi}{\delta\eta_{j\gamma}(\tau)} = 0 \longrightarrow \eta_{j\gamma}(\tau) = -\frac{\beta}{\pi}\bar{c}_2 \ll n_{j\gamma}(\tau)\gg$$

$$\ll \cdots \gg \equiv \langle T\tau \cdots e^{-\Sigma_{j\gamma}\int_0^\beta[2\bar{c}_1\vec{S}_{j\gamma}(\tau)\cdot\vec{\xi}_{j\gamma}(\tau)+2\bar{c}_2 n_{j\gamma}(\tau)\eta_{j\gamma}(\tau)]d\tau}\rangle / e^{-\beta\Psi_1}\ . \qquad \ldots(4.2.3)$$

The charge fields $\eta_{j\gamma}(\tau)$ are decided from the self consistent equation mentioned above. But if the neutrarity of charge is maintained, we have

$$<< n_{j\gamma}(\tau) >>= \frac{N}{N_o w} \qquad N_o\text{: number of sites}$$
$$\eta_{j\gamma}(\tau)= -\frac{\beta}{\pi}\bar{c}_2 \frac{N}{N_o w} \qquad \text{for all } j \text{ and } \gamma \quad .$$

In this simple case, the charge fields only increases the energy with a constant $\frac{N^2 U}{4N_o w}$. Consequently after omitting this constant energy, the following simplified equations are obtained.

$$e^{-\beta\Delta\Omega}= \int \delta\vec{\xi}(\tau)\ e^{-\beta\Psi(\xi)}$$
$$-\beta\Psi(\xi)= -\ \frac{\pi}{\beta}\Sigma_{j\gamma}\int_0^\beta \vec{\xi}(\tau)^2 d\tau- \beta\Psi_1(\xi)$$

$$e^{-\beta\Psi_1} = < T\tau\ e^{-\Sigma_{j\gamma}\int_0^\beta 2\bar{c}_1 \vec{S}_{j\gamma}(\tau)\cdot\vec{\xi}_{j\gamma}(\tau)\ d\tau} > \quad . \qquad \ldots(4.2.4)$$

From eq. (4.2.4), statistical averages, correlation functions, and the dynamical susceptibility are exactly given (Appendix) by

$$< \vec{S}_{j\gamma}(\tau) >= -\sqrt{\frac{\pi}{J\beta}} < \vec{\xi}_{j\gamma}(\tau) >$$
$$< T\tau\vec{S}_{j\gamma}(\tau)\vec{S}_{i\delta}(\tau') >= \frac{\pi}{J\beta}\left[< \vec{\xi}_{j\gamma}(\tau)\vec{\xi}_{i\delta}(\tau') >- \frac{\beta}{2\pi}\delta_{ji}\delta_{\gamma\delta}\delta(\tau-\tau')\right]$$

$$\chi(q,i\omega_m)= \Sigma_{\gamma\delta}\frac{\pi N_o}{J}\left[< \vec{\xi}_{q\gamma m}\vec{\xi}_{-q\delta m} >- < \vec{\xi}_{q\gamma m} >< \vec{\xi}_{-q\delta m} >- \frac{\delta_{\gamma\delta}}{2\ \pi}\right]$$

$$\left(\begin{array}{l} \vec{\xi}_{q\gamma m}= \frac{1}{\sqrt{N_o}}\Sigma_j\vec{\xi}_{j\gamma m}\ e^{-iqR_j} \\ \vec{\xi}_{j\gamma m}= \frac{1}{\beta}\int_0^\beta \vec{\xi}_{j\gamma}(\tau)\ e^{i\omega_m\tau}\ d\tau \end{array}\right. , \qquad \ldots(4.2.5)$$

where the average of any functions of ξ are defined by

$$< f(\xi) >\equiv \int\delta\vec{\xi}(\tau)f(\xi)\ e^{-\beta\Psi(\xi)} / e^{-\beta\Delta\Omega} . \qquad \ldots(4.2.6)$$

4-3 Model and approximations

At first we adopt the static approximation, with which τ-dependence of $\vec{\xi}$ is neglected. In this sense our theory is classical. And for simplicity $\vec{\xi}$'s are considered to be independent of orbitals. Then we have

$$e^{-\beta\Delta\Omega}=\int \Pi_j d\vec{\xi}_j \; e^{-\pi w\Sigma_j\xi_j^2-\beta\Psi_1}$$

$$e^{-\beta\Psi_1} = < e^{-2\beta\bar{c}_1 w\Sigma_j\vec{S}_j\cdot\vec{\xi}_j} >$$

After the Fourier transformation, these equations become

$$e^{-\beta\Delta\Omega}= \int d\vec{\xi}_\circ\Pi'_q d\vec{\xi}_q \; e^{-\pi w\vec{\xi}_\circ{}^2-\pi w\Sigma_j\delta\vec{\xi}_j{}^2} < e^{-2\beta c_1 w\vec{S}_\circ\cdot\vec{\xi}_\circ-2\beta\bar{c}_1 w\Sigma_j\vec{S}_j\cdot\delta\vec{\xi}_j} >$$
$$\vec{S}_\circ\equiv\Sigma_j\vec{S}_j \; , \quad c_1\equiv \bar{c}_1 \,/\, \sqrt{N_\circ} \; ,$$

where the prime means to omit the terms with q=0 . The macroscopic quantities $\vec{\xi}_\circ$ can be approximated by the saddle point approximation with the condition of $\vec{\xi}_\circ=-\frac{\beta}{\pi}c_1 << \vec{S}_\circ >>$. Here we consider only paramagnetic phase. Then we may put $<< \vec{S}_\circ >>=0$. So the following equations are obtained.

$$e^{-\beta\Delta\Omega}= \int\Pi'_q d\vec{\xi}_q \; e^{-\pi w\Sigma_j\delta\vec{\xi}_j^2 -\beta\Psi_1}$$

$$e^{-\beta\Psi_1} = < e^{-2\beta\bar{c}_1 w\Sigma_j\vec{S}_j\cdot\delta\vec{\xi}_j} > \qquad \ldots(4.3.1)$$

As mentioned in §.4-2 , we must not use the saddle point approximation about the exchange field $\delta\vec{\xi}_j$ directly. In the spin fluctuation theory , the most important macroscopic variable is x , defined by

$$x\equiv \frac{1}{N_\circ\beta}\Sigma_j\delta\vec{\xi}_j\cdot\delta\vec{\xi}_j \; . \qquad \ldots(4.3.2)$$

From eq. (4.2.5) this valiable is related with the squared local spin density as

$$< \vec{S}_j^{\,2} >= \frac{1}{2J}(2\pi x w^2-\frac{3w}{\beta}) \; , \qquad \ldots(4.3.3)$$

where we considerd < x > = x , and the system to be isotropic.

The macroscopic variable x can be approximated by the saddle point approximation. To carry out this calculations, we must express Ψ_1 as a function of x. Then we expand Ψ_1 in terms of $\delta\xi$, and assume that the coupling among the spin fluctuation modes is mainly local and the higher order terms can be expressed in terms of x. We adopt the following model functional for Ψ_1 of the isotropic system.

$$\begin{aligned}\Psi_1 &= -\frac{2\pi J}{\beta}\Sigma_{ji}X_{ji}(x)\delta\vec{\xi}_j\cdot\delta\vec{\xi}_i+\pi N_\circ L(x)\\ &= -\frac{2\pi J}{\beta}\,\Sigma'_q\,X_q(x)\vec{\xi}_q\cdot\vec{\xi}_{-q}\,+\pi N_\circ L(x)\end{aligned} \qquad \text{...(4.3.4)}$$

with

$$\Sigma'_q X_q(x)=0 \quad .$$

The methods of calculating $X_q(x)$ and L(x) with CPA will be discussed in §.4-4 and §.4-5. Here with the use of the model functional in eq. (4.3.4) , we express $e^{-\beta\Delta\Omega}$ as

$$e^{-\beta\Delta\Omega}= \int dx\int\Pi'_q d\vec{\xi}_q\delta(x-\frac{1}{N_\circ\beta}\Sigma'_q\vec{\xi}_q\cdot\vec{\xi}_{-q})\ e^{-\pi N_\circ\beta wx+2\pi J\Sigma'_q X_q(x)\vec{\xi}_q\cdot\vec{\xi}_{-q}-\pi N_\circ\beta L(x)} ,$$

$$\delta(x-\frac{1}{N_\circ\beta}\Sigma'_q\vec{\xi}_q\cdot\vec{\xi}_{-q})\ \rightarrow\ \int d\lambda\ e^{2\pi JN_\circ\beta\lambda(x-\frac{1}{N_\circ\beta}\Sigma'_q\vec{\xi}_q\cdot\vec{\xi}_{-q})} , \qquad \text{...(4.3.5)}$$

and the delta function could be rewritten with the Lagrange multipliers stated in §.3 . Then the integrations of $d\vec{\xi}_q$ can be carried out exactly, and because other parameters , x and λ, are the macroscopic variables from the definition and the conjugate variable of x respectively, the saddle point approximation in x and λ may be a reasonable method. So we have

$$-\beta\Delta\Omega= 2\pi N_\circ\beta J\lambda x\ -\pi N_\circ\beta wx\ -\pi N_\circ\beta L(x)\ -\frac{3}{2}\Sigma'_q\ln[2J(\lambda-X_q(x)]$$

with conditions; $x= \frac{3}{4\ N_\circ\beta J}\Sigma'_q\ \frac{1}{\lambda-X_q}$

$$\lambda= \frac{1}{2J}(w+\frac{\partial L}{\partial x})-\frac{3}{4\pi N_\circ\beta J}\Sigma'_q\ \frac{1}{\lambda-X_q}\ \frac{\partial X_q}{\partial x}\quad . \qquad \text{...(4.3.6)}$$

With the use of $\overline{\chi}_L$ defined by $\overline{\chi}_L \equiv \frac{w}{2J} - \lambda$, the useful forms of the conditions are given by

$$\overline{\chi}_L = -\frac{1}{2J}\frac{\partial L}{\partial x} + \frac{3}{2\pi N_\circ \beta w}\Sigma'_q \frac{1}{1-2\frac{J}{w}\overline{\chi}_q}\frac{\partial X_q}{\partial x}$$

$$\overline{\chi}_q = X_q(x) + \overline{\chi}_L$$

$$x = \frac{3}{2\pi N_\circ \beta w}\Sigma'_q \frac{1}{1-2\frac{J}{w}\overline{\chi}_q} = \frac{3}{2\pi\beta w}\int P(\sigma)\frac{\delta+1}{\delta+\sigma}\,d\sigma\ , \qquad \ldots(4.3.7)$$

$$\delta \equiv \frac{1}{2\frac{J}{w}\overline{\chi}_\circ} - 1\ ,\ \sigma_q \equiv 1 - \frac{\overline{\chi}_q}{\overline{\chi}_\circ}\ ,\ P(\sigma) \equiv \frac{1}{N_\circ}\Sigma'_q \delta(\sigma - \sigma_q)\ .$$

Since x is a macroscopic valiable we may safely replace x with the average value, then $x = \langle x \rangle = \frac{1}{N_\circ \beta}\Sigma'_q \langle \vec{\xi}_q \cdot \vec{\xi}_{-q} \rangle$. As compared with eq. (4.3.7), we get

$$\langle \xi^\alpha_q \xi^\alpha_{-q} \rangle = \frac{1}{2\pi w}\frac{1}{1-2\frac{J}{w}\overline{\chi}_q}\ , \quad \alpha = x, y, z \qquad \ldots(4.3.8)$$

Substituting eq.(4.3.8) into eq.(4.2.5) , we can get the following formula for the dynamical susceptibility χ_q per site as a function of x.

$$\chi_q = \frac{\chi^{\alpha\alpha}(q)}{N_\circ} = \frac{\pi}{J}\left[w^2\langle \xi^\alpha_q \xi^\alpha_{-q} \rangle - w^2 \langle \xi^\alpha_q \rangle \langle \xi^\alpha_{-q} \rangle - \frac{w}{2\pi}\right] = \frac{\overline{\chi}_q}{1-2\frac{J}{w}\overline{\chi}_q}\ , \qquad \ldots(4.3.9)$$

where we used $\langle \xi^\alpha_q \rangle = 0$ in paramagnetic phase.

To obtain the temperature dependence of x , we need a distribution function P(σ). Here supposing a simple distribution function;

$$P(\sigma) = \frac{1}{\pi\langle\sigma\rangle^2}\sqrt{\sigma(2\langle\sigma\rangle - \sigma)}\ , \quad \langle \cdots \rangle = \int \cdots P(\sigma)\,d\sigma$$

$$\langle\sigma\rangle = \langle 1 - \overline{\chi}_q / \overline{\chi}_\circ \rangle = 1 - \frac{\overline{\chi}_L}{\overline{\chi}_\circ}\ , \qquad \ldots(4.3.10)$$

we have

$$\beta^{-1} = \frac{\pi w x}{3(\delta+1)}\left(|\langle\sigma\rangle| + \delta + \sqrt{\delta^2 + 2\delta|\langle\sigma\rangle|}\right)\ . \qquad \ldots(4.3.11)$$

If $X_q(x)$ and $L(x)$ are provided as functions of x concretely, the susceptibility as a function of temperature is derived self-consistently with the use of previous equations. The uniform susceptibility is considered as the limit of $q \to 0$.

4-4 The coherent potential approximation condition of Ψ_1

In this section, we calculate Ψ_1 as a function of x directly within the single-site approximation. If we simplify the exchange fields to have the same magnitude for all sites;

$$\delta\vec{\xi}_j = \beta x \qquad \text{for all } j \; , \qquad \ldots(4.4.1)$$

then our problem becomes the problem of electrons in the randomly directed fields. This situation becomes obvious from eq. (4.3.1). For our purpose eq. (4.3.1) may be rewritten as

$$\Psi_1 = w\Psi_1'$$

$$Z' \equiv e^{-\beta\Psi_1'} = \mathrm{Tr}\, e^{-\beta H_V} / \mathrm{Tr}\, e^{-\beta\hat{H}_\circ}$$

$$H_V = \Sigma_{\vec{k}\sigma}(\varepsilon_{\vec{k}}-\mu)n_{\vec{k}\sigma} + \mathrm{tr}\,\nu V_j n_j$$

$$\hat{H}_\circ = \Sigma_{\vec{k}\sigma}(\varepsilon_{\vec{k}}-\mu)n_{\vec{k}\sigma}$$

$$V_j = \bar{c}_1\vec{\sigma}\cdot\delta\vec{\xi}_j = \bar{c}_1\begin{pmatrix} \delta\xi_j^z & \delta\xi_j^- \\ \delta\xi_j^+ & -\delta\xi_j^z \end{pmatrix} , \quad \delta\xi_j^\pm = \delta\xi_j^x \pm \delta\xi_j^y \; , \qquad \ldots(4.4.2)$$

where the prime denotes the quantities per orbital, and ν is a parameter which becomes 1 afterward. And tr means the trace on the site and spin spaces. Interestingly V_j plays a role of a local random potential in the Hamiltonian.

In order to calculate Ψ_1' , we differentiate Ψ_1' with respect to ν,13)

$$\frac{\partial}{\partial\nu}\Psi_1' = -\beta\frac{\partial}{\partial\nu}\ln Z' = \mathrm{tr}\, V_j\langle n_{j\sigma}\rangle_V \quad ; \; \langle\cdots\rangle_V = \mathrm{Tr}[\cdots e^{-\beta H_V}]/\,\mathrm{Tr}\, e^{-\beta H_V} \; ,$$

where $\langle n_{j\sigma}\rangle_V$ may be expressed by the temperature Green function of H_V. Then with the use of well known properties of the Green function, the Green function of H_V may be expressed by the Green function of $\hat{H}_\circ$ in the following ways.

$$\langle n_{j\sigma}\rangle_V = -\beta^{-1}\, G_{jj\sigma}(\tau=0^-) \qquad ; \; G_{ji\sigma}(\tau) \equiv -\beta\langle T\tau a_{j\sigma}(\tau)a_{i\sigma}^+(0)\rangle_V$$

$$\begin{aligned} \mathrm{tr}\, G(\tau=0^-)V &= \Sigma_m \mathrm{tr}\, G(i\omega_m)V\, e^{-i\omega_m 0^-} \qquad : \omega_m = \frac{\pi}{\beta}(2m+1) \\ &= \Sigma_m \mathrm{tr}\, (1-g(i\omega_m)\nu V)^{-1} g(i\omega_m) V\, e^{-i\omega_m 0^-} \\ &= \frac{\partial}{\partial\nu}\Sigma_m \mathrm{tr}\, \ln(1-g\nu V)\, e^{-i\omega_m 0^-} \qquad \ldots(4.4.3) \\ &\qquad : g_{ji\sigma}(i\omega_m) = \frac{1}{N_o}\Sigma_{\vec{k}} \frac{e^{i\vec{k}(\vec{R}_j-\vec{R}_i)}}{i\omega_m-\varepsilon_{\vec{k}}+\mu} \end{aligned}$$

where a^+ and a are the creation and the annihilation operater respectively, and g is the Green function of $\hat{H}_o$. Then Ψ_1' is given by the folloing equation after the integration with ν.

$$\Psi_1' = -\beta^{-1}\, \Sigma_m \mathrm{tr}\, \ln(1-gV)\, e^{-i\omega_m 0^-} \qquad \ldots(4.4.4)$$

The coherent potential approximation can be obtained from eq. (4.4.4) with replacing the random potential in Green function by the medium coherent potential Σ. such as

$$G^{-1}(z) = g^{-1}(z) - \Sigma(z)\ , \qquad \ldots(4.4.5)$$

and we split G into the site-diagonal part F and the non site-diagonal part $\tilde{G}$. Then 1-gV can be rewritten as

$$1-gV = gG^{-1}(1-\tilde{G}t)[1-F(V-\Sigma)]^{-1} \qquad : t \equiv (V-\Sigma)[1-F(V-\Sigma)]$$

and Ψ_1' becomes

$$\begin{aligned} \Psi_1' &= \Psi_1'^{(1)} + [\ \Psi_1'^{(2)} + \Psi_1'^{(3)} + \cdots\ ] \\ \Psi_1'^{(1)} &= -\beta^{-1}\Sigma_m \mathrm{tr}[\ln g - \ln G + \ln(1-F(V-\Sigma))]\, e^{-i\omega_m 0^-} \\ \Psi_1' - \Psi_1'^{(1)} &= -\beta^{-1}\Sigma_m \mathrm{tr}\, \ln(1-\tilde{G}t)\, e^{-i\omega_m 0^-}\ , \qquad \ldots(4.4.6) \end{aligned}$$

where t is a so-called t-matrix, and $\Psi_1'^{(n)}$ includes all terms which are related with n sites. Compering eq. (4.4.6) with our model functional, the site-diagonal term $\Psi_1'(1)$ corresponds to L(x) , and $\Psi_1'^{(2)}$ corresponds to $X_q(x)$. To decide the coherent potential Σ within the limits of the single-site approximation, we minimize the site-diagonal term $\Psi_1'^{(1)}$ with respect to Σ. Then we have

$$\frac{\delta\Psi_1{}'^{(1)}}{\delta\Sigma} = -\beta^{-1}\Sigma_m \mathrm{tr}(F^2 - \frac{\partial F}{\partial\Sigma})t\ e^{-i\omega_m 0^-} = 0\ , \qquad \ldots(4.4.7)$$

and note that only t depends on sites, we get the well known CPA condition;

$$\sum_j t_j(z) = 0 \qquad z\text{:complex}\ , \qquad \ldots(4.4.8)$$

as a sufficient condition. When we substitute F, Σ, and V_j into eq.(4.4.8), consider only $\delta\vec{\xi}_j^2 = \beta x$ as an important parameter, and neglect all other combinations, that is to say, $\sum_j(\delta\xi_j^z\ \delta\xi_j^\pm)$, $\sum_j \delta\xi_j^z$, $\sum_j \delta\xi_j^\pm$, and so on, then we have the following self consistent eqation of Σ within the limits of the paramagnetic phase.

$$\Sigma = -F(\Sigma^2 - \pi J x)$$

$$F(z) = \int \frac{\rho(\varepsilon)}{z-\varepsilon+\mu-\Sigma(z)}\, d\varepsilon\ . \qquad \ldots(4.4.9)$$

With the use of eq. (4.4.9) , t_j has the form of

$$t_j = (1+F\Sigma)^{-1}\ \bar{c}_1 \begin{pmatrix} \delta\xi_j^z & \delta\xi_j^- \\ \delta\xi_j^+ & -\delta\xi_j^z \end{pmatrix}\ . \qquad \ldots(4.4.10)$$

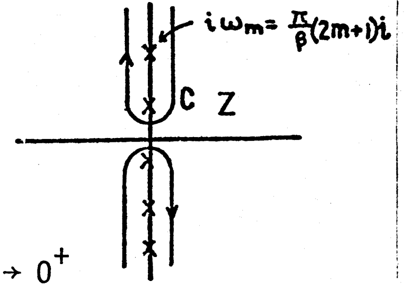
4-5 Calculation of $\overline{\chi}_L(x)$ and $X_q(x)$ with CPA condition

As mentioned in §.4-4, L(x) and $X_q(x)$ are obtained from $\Psi_1{}'^{(1)}$ and $\Psi_1{}'^{(2)}$ respectively such as

$$\pi N_\circ L(x) = w\Psi_1{}'^{(1)} = -w\beta^{-1}\Sigma_m \mathrm{tr}[\ln g - \ln G + \ln(1-F(V-\Sigma)]\ e^{-i\omega_m 0^-}$$

$$-\frac{2\pi J}{\beta}\Sigma_{ji} X_{ji}(x)\delta\vec{\xi}_j\cdot\delta\vec{\xi}_i = w\Psi_1{}'^{(2)} = -w\beta^{-1}\Sigma_m \mathrm{tr}\ \ln(1-\tilde{G}t)\ e^{-i\omega_m 0^-}\Big|_{\text{terms related with 2-sites}}\ . \qquad \ldots(4.5.1)$$

In eq.(4.5.1), the sum of m can be transformed by the well known formula about the Fermi Green function $f(z)$ as



$$\Sigma_m f(i\omega_m)\ e^{-i\omega_m 0^-} = \frac{\beta}{2\pi i}\int_C dz \frac{1}{1+e^{\beta z}}\ f(z)\ e^{-iz0^-}$$

$$= \frac{\beta}{\pi}\int_{-\infty}^{+\infty} d\omega \frac{1}{1+e^{\beta\omega}}\ \mathrm{Im}\ f(\omega - i\delta)\ , \quad \delta \to 0^+ \qquad \ldots(4.5.2)$$

In this paper we approximate $\bar{\chi}_L$ as

$$\bar{\chi}_L = -\frac{1}{2J}\frac{\partial L}{\partial x} \cdot \qquad \ldots(4.5.3)$$

And substituting eq. (4.5.1) into eq. (4.5.3) , we have

$$\bar{\chi}_L = \frac{W}{2\pi^2 JN_\circ}\int_{-\infty}^{+\infty} d\omega \frac{1}{1+e^{\beta\omega}}\frac{\partial}{\partial x}\mathrm{Im}\ \mathrm{tr}[\ln g - \ln G + \ln(1-F(V-\Sigma))] \ .$$

With the use of CPA condition, we have the final result of $\bar{\chi}_L$ as

$$\bar{\chi}_L = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega \frac{1}{1+e^{\beta\omega}}\ \mathrm{Im}\ F^2(1+F\Sigma)^{-1}$$

$$\cong \frac{1}{2\pi}\int^{0} d\omega\ \mathrm{Im}\ F^2(1+F\Sigma)^{-1}. \qquad \ldots(4.5.4)$$

Next we calculate $\chi_{ji}(x)$. To calculate $\chi_{ji}(x)$ we expand the second equation of eq.(4.5.1) and collect the terms related with 2-sites

$$\begin{aligned}\Sigma_{ji}\chi_{ji}(x)\delta\vec{\xi}_j\cdot\delta\vec{\xi}_i &= -\frac{W}{2\pi J}\Sigma_m \mathrm{tr}\Sigma_{\kappa=1}^{\infty}\kappa^{-1}(\tilde{G}t)^{\kappa}\ e^{-i\omega_m 0^-}\Big|_{\text{2-sites terms}} \\ &= -\frac{W}{2\pi J}\Sigma_m\Sigma_{\substack{ji\\ j\neq i}}\ \mathrm{Sp}\Sigma_{\kappa=1}^{\infty}\ \frac{1}{2\kappa}\ (\tilde{G}_{ji}t_i\tilde{G}_{ij}t_j)^{\kappa}\ e^{-i\omega_m 0^-} \\ &= -\frac{W}{2\pi J}\Sigma_m\Sigma_{j>i}\mathrm{Sp}\ \ln(1-\tilde{G}_{ji}t_i\tilde{G}_{ij}t_j)\ e^{-i\omega_m 0^-} \\ &= -\frac{W}{2\pi J}\Sigma_m\Sigma_{j>i}\ln[1-\mathrm{Sp}(\tilde{G}_{ji}t_i\tilde{G}_{ij}t_j)+\det(\tilde{G}_{ji}t_i\tilde{G}_{ij}t_j)]\ e^{-i\omega_m 0^-}\ ,\end{aligned} \qquad \ldots(4.5.6)$$

Where we used Sp[ln A]= ln[det A], and the properties of 2×2 matrix, det(1-A) =1-Sp A +det A . After expantions of the logarithmic function, we retain only the bilinear terms in t-matrix, and with the use of eq. (4.4.10), we have

$$\chi_{ji}(x) = \frac{W}{2\beta}\Sigma_m\tilde{G}_{ji}\tilde{G}_{ij}(1+F\Sigma)^{-2}\ e^{-i\omega_m 0^-} \qquad \ldots(4.5.7)$$

After the Fourier transformation, using eq. (4.5.2), we transform the sum about m into the integration about ω. We have

$$\chi_q(x) = \frac{W}{2\pi}\int d\omega \frac{1}{1+e^{\beta\omega}}\mathrm{Im}\ \tilde{G}_{k+q}\tilde{G}_k(1+F\Sigma)^{-2}. \qquad \ldots(4.5.8)$$

To calculate $\chi_q(x)$ we need the band structure of the materials. But $\chi_0(x)$ can be obtained from only the density of states. The definition of $\tilde{G}_k(\omega)$ is

$$\tilde{G}_k(\omega) = G_k - F = \frac{1}{\omega - \varepsilon_k + \mu - \Sigma(\omega)} - \int d\omega \frac{\rho(\omega)}{\omega - \varepsilon_k + \mu - \Sigma(\omega)} \quad . \qquad \ldots(4.5.9)$$

Then the following equation is obtained.

$$X_0(x) = \frac{W}{2\pi} \int d\omega \frac{1}{1+e^{\beta\omega}} \mathrm{Im}\left(\frac{\partial F}{\partial \Sigma} - F^2\right)(1+F\Sigma)^{-2}$$

$$\cong \frac{W}{2\pi} \int d\omega \; \mathrm{Im}\left(\frac{\partial F}{\partial \Sigma} - F^2\right)(1+F\Sigma)^{-2} \qquad \ldots(4.5.10)$$

In the low temperature limit the coherent potential is small compared with 1, then we have

$$\bar{\chi}_\circ = X_0 + \bar{\chi}_L \cong \frac{1}{2\pi}\int^0 d\omega \; \mathrm{Im}\frac{\partial F}{\partial \Sigma} = \frac{1}{2}\rho(\mu) \quad , \quad \text{:when } w=1 \quad . \qquad \ldots(4.5.11)$$

This result is the same as HF theory at 0°K . The difference of the coefficient comes from the unit of M and $B_\circ$, $M \equiv \frac{1}{2}\Sigma_{\vec{k}\sigma} \sigma n_{\vec{k}\sigma}$ and $M \equiv \Sigma_{\vec{k}\sigma} \sigma n_{\vec{k}\sigma}$ are the definitions in the spin fluctuation theory and HF theory respectively in our case.

§.5 Numerical calculations

Numerical calculations have been carried out with the use of the same density of states as was given in §.3 to explain the metamagnetism, and the results are shown in Fig. 5.1 — 5.9.

We show in Fig. 5.1 a graph of $<\sigma>$ vs. B, where $B \equiv 4\pi Jx$. At low temperature $<\sigma>$ is negative, and with increasing amplitude of the spin fluctuations, $<\sigma>$ becomes positive. This is consistent with the observation that $Co(S_xSe_{1-x})_2$ with small x are paramagnetic, having negative Weiss constant, while those with $x \cong 1$ show ferromagnetism. $X_\circ$ and $\overline{X}_L$ as a functions of B are shown in Fig. 5.2 and Fig. 5.3, respectively.

We first discuss the paramagnetic compounds with $x \leqq 0.86$. The calculated inverse susceptibilities are shown in Fig. 5.5. The susceptibilities at high temperature evidently obey the Curie-Weiss law. The dashed line indicates the slope correspond to Curie constant of 1 μ_B classical local moment at each site. The effective moment is 1.5 μ_B in $CoSe_2$ and reduces with increasing x, for 1.34 μ_B at x= 0.86. These are larger than the observed values. The reason will be discussed later.

The maximum of the suseptibility of $CoSe_2$ appears at about 30°K. This is near the maximum of the experimental data. The observed maximum of $Co(S_xSe_{1-x})_2$ with x= 0.86 at 80°K is not explained by this calculation. The instability occurs near the metamagnetic region x= 0.86 at 10°K, and the detailed situations near the metamagnetic region are shown in Fig. 5-7. This type of instability seems to exist in actuality as is seen in the experimental results in Fig. 2-2. We need to make more detailed study of this point in order to clarify the mechanism of the instability.

Next we consider the systems which become ferromagnetic at low temperatures. When Curie temperature is small, the inverse susceptibility curves are straight from the starting point or Tc. But with increasing with Tc, $1/\chi$ becomes concave upward near Tc. For J= 1.6 we calculate $1/\chi$ up to 500°K as shown in Fig. 5-8, and the inverse susceptibility curve break off a little at about 250°K. For the reason of the simple model density of states, the magnetization tends to saturate easily with increasing effective interaction J at 0°K, as shown in Fig 5-9. It was not possible to give a quantitative explanation of the saturation moment at 0°K and the Curie temperature in a consistent way.

§.6 Discussions

The purpose of this paper was to explain the metamagnetism and the temperature dependence of the susceptibility at the same time with the use of the simple density of states. Although various specific charactristics of the magnetic susceptibility of $Co(S_xSe_{1-x})_2$ system have been reproduced qualitatively well, quantitative comparison was not quite satisfactory. We will remark here just two points which suggest the posibility of improvements

In our calculations the effective moment derived from the Curie constant is larger than 1 μ_B even over 300°K. The reason of this can be understood from Fig. 5-4. In Fig. 5-4 the root mean square of the local spin density approaches 1 μ_B as temperature goes up and exceeds 1 μ_B at high temperatures. Such a situation occurs because of our simple neglect of the effective charge fluctuations which allows the amplitude of the local spin fluctuation to increase beyound 1 μ_B. This situation may be improved by taking account of the effect of charge fluctuations.2)

Next our model density of states may be too simple to apply to a real system. As a matter of fact Asano has recently made a band calculation of transition metal di-chalcogenides with pyrite type crystal structure. The calculated density of states differs significantly from the one adopted here, although there is the same qualitative similarity. It should be worth while to repeat the same calculation as given here with the use of Asano's density of states. Such a calculation is now under way.

Acknowledgments

The author wishes to thank Prof.T.Moriya, Dr.Y.Takahashi, and Dr.K.Usami for a number of instructive disccusions.

Appendix

Here we derive the eq.(4.2.5). The first equation comes from

$$
\begin{aligned}
<\vec{S}_{i\delta}(\tau')> &= \mathrm{Tr}[\vec{S}_{i\delta}(\tau')\ e^{-\beta(H-\mu\hat{N})}]\ /\ e^{-\beta\Omega} \\
&= e^{\beta\Delta\Omega}\int\delta\xi(\tau)[\ e^{-\frac{\pi}{\beta}\Sigma_{j\gamma}\int_0^\beta\vec{\xi}_{j\gamma}(\tau)^2 d\tau} < T\tau\ \vec{S}_{i\delta}(\tau')\ e^{-\Sigma_{j\gamma}\int_0^\beta 2\bar{c}_1\vec{S}_{j\delta}(\tau)\cdot\vec{\xi}_{j\gamma}(\tau)d\tau} >]
\end{aligned}
$$

with replacing $\vec{S}_{i\delta}(\tau')$ by a differential operator $\frac{-1}{2\bar{c}_1}\frac{\delta}{\delta\xi_{i\delta}(\tau')}$, and after differentiate by parts, we get the first equation.

The second equation is given by the same way ,too. The last equation is derived with the use of the Kubo linear response theory$^{15)}$. By this theory the susceptibility can be expressed with the retarded Green function as

$$
\begin{aligned}
\chi_{ji}(\omega)=G^R_{ji}(\omega) \qquad &: G^R_{ji}(\omega)=\int_{-\infty}^{+\infty} G^R_{ji}(t)\ e^{i\omega t}\ dt \\
&\ G^R_{ji}(t)=-\frac{1}{i\hbar}\,\Theta(t) < [\Sigma_\gamma\delta\vec{S}_{j\gamma}(t),\Sigma_\delta\delta\vec{S}_{i\delta}(0)] > \\
&\ \delta\vec{S}_{j\gamma}(t)=e^{i\hat{H}_\circ t/\hbar}\ \delta\vec{S}_{j\gamma}\ e^{-i\hat{H}_\circ t/\hbar}\ .
\end{aligned}
$$

And the retarded Green function $G^R_{ji}(\omega)$ can be expressed by the thermal Green function with analytic continuation as

$$
\begin{aligned}
G^R_{ji}(\omega)=G_{ji}(\omega_m) \qquad &: i\omega_m=\omega \quad , \qquad \omega_m=\frac{\pi}{\beta}(2m+1) \\
&\ G_{ji}(\omega_m)=\int_0^\beta < T\tau\Sigma_\gamma\delta\vec{S}_{j\gamma}(\tau)\Sigma_\delta\delta\vec{S}_{i\delta}(\tau)>\ ^{i\omega_m\tau}\ d\tau \\
&\ \delta S_{j\gamma}(\tau)=e^{\tau\hat{H}_\circ}\ \delta\vec{S}_{j\gamma}\ e^{-\tau\hat{H}_\circ}\ .
\end{aligned}
$$

With the use of $\delta\vec{S}_{j\gamma}(\tau)=\vec{S}_{j\gamma}(\tau)-<\vec{S}_{j\gamma}(\tau)>$, we have

$$
\chi_{ji}(i\omega_m)=\Sigma_{\gamma\delta}\,\frac{1}{\beta}\int_0^\beta < T\tau\vec{S}_{j\gamma}(\tau)\vec{S}_{i\delta}(\tau')> - <\vec{S}_{j\gamma}(\tau)> <S_{i\delta}(\tau')>\ e^{i\omega_m(\tau-\tau')}d\tau d\tau'\ .
$$

After the substitution of the first and the second equations and the Furier transformation, we have the final result.

Refernces

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Figure Captions

Fig. 3-7 The model density of states with the parameters determined by the experimental data of the magnetization curve of metamagnetism at low temperature.

Fig. 3-8 The comparison between the experimental magnetization curve of $\mathrm{Co}(S_x Se_{1-x})_2$ with x= 0.86 and the theoretical one from the model density of states in Fig. 3-7.

Fig. 3-9 The magnetization dependence of the free energy F as a function of the external field B_o, where B_t is the transition field as the same as the one in Fig. 3-8.

Fig. 3-10 The inverse susceptibilities as functions of temperature for each mixing ratio x in $\mathrm{Co}(S_x Se_{1-x})_2$ by the Hartree-Fock approximation.

Fig. 5-1 The random field dependence of $<\sigma>$.

Fig. 5-2 The random field dependence of χ_o.

Fig. 5-3 The random field dependence of $\overline{\chi}_L$

Fig. 5-4 The root mean square of the local spin density as a fuction of the temperature.

Fig. 5-5 The inverse susceptibilities as functions of temperature for each mixing ratio x in $\mathrm{Co}(S_x Se_{1-x})_2$ by the spin fluctuation theory. The dashed line indicates the slope corresponding to Curie constant of 1 μ_B classical local moment at each site.

Fig. 5-6 The inverse susceptibilities as fucntions of temperature for the systems which become ferromagnetic at low temperature.

Fig. 5-7 The inverse susceptibilities as functions of temperature near the metamagnetic region.

Fig. 5-8 The inverse susceptibility as a function of temperature for the exchange interaction J= 1.6 up to 500°K.

Fig. 5-9 The exchange interaction dependence of the saturation moment at 0°K.

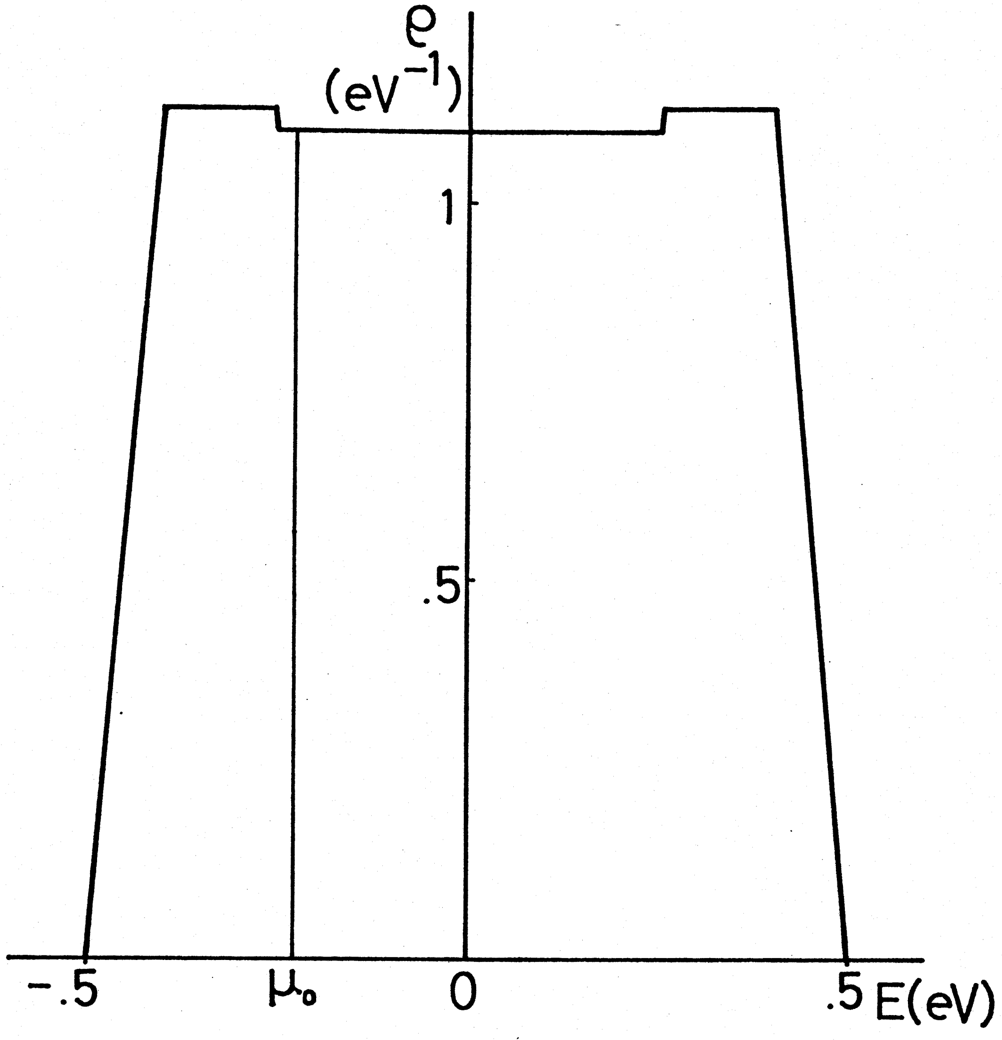
ρ
(eV^{-1})
1
.5
-.5
μ_o
0
.5
E(eV)

Fig. 3-7

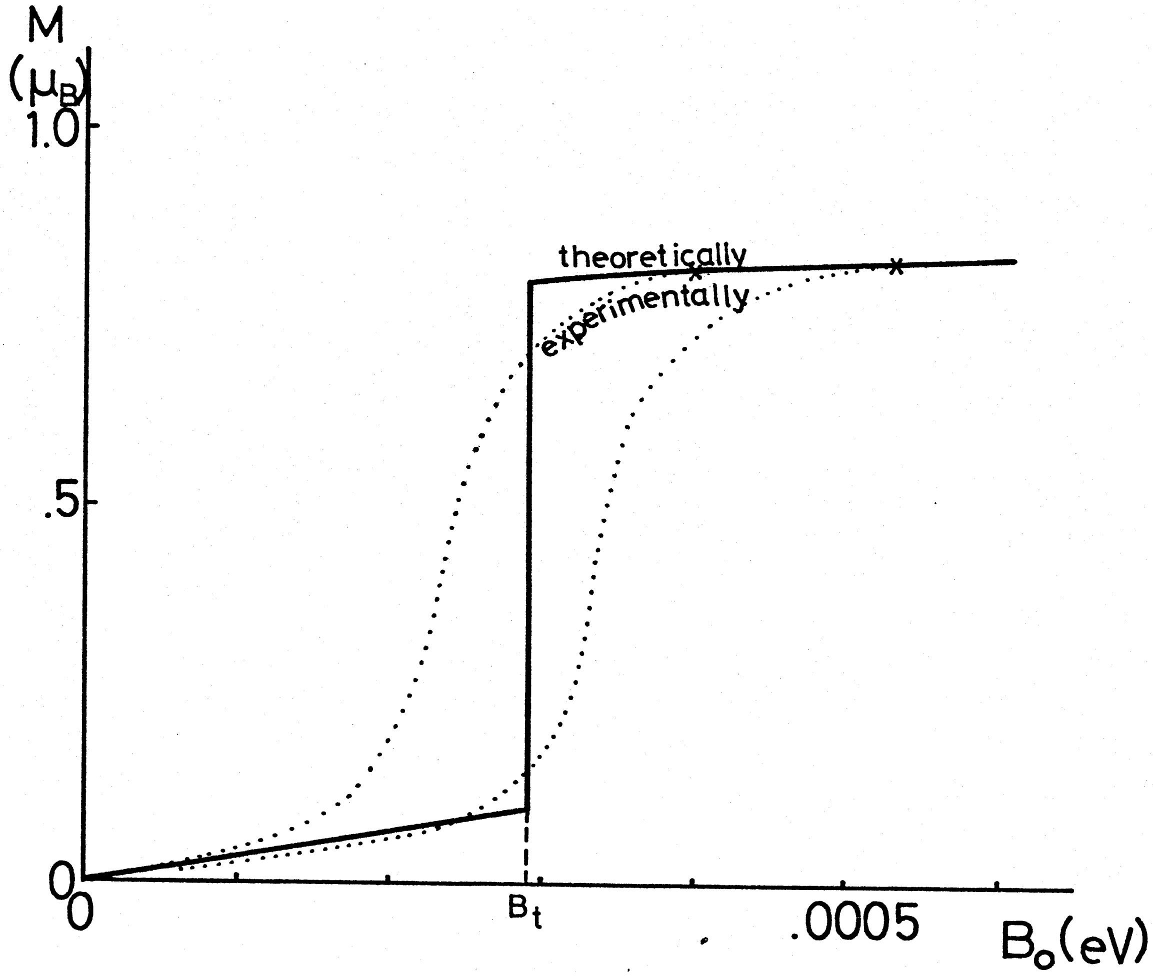
M
(μ_B)
1.0
.5
0
0
B_t
.0005
B_o(eV)
theoretically
experimentally

Fig. 3-8

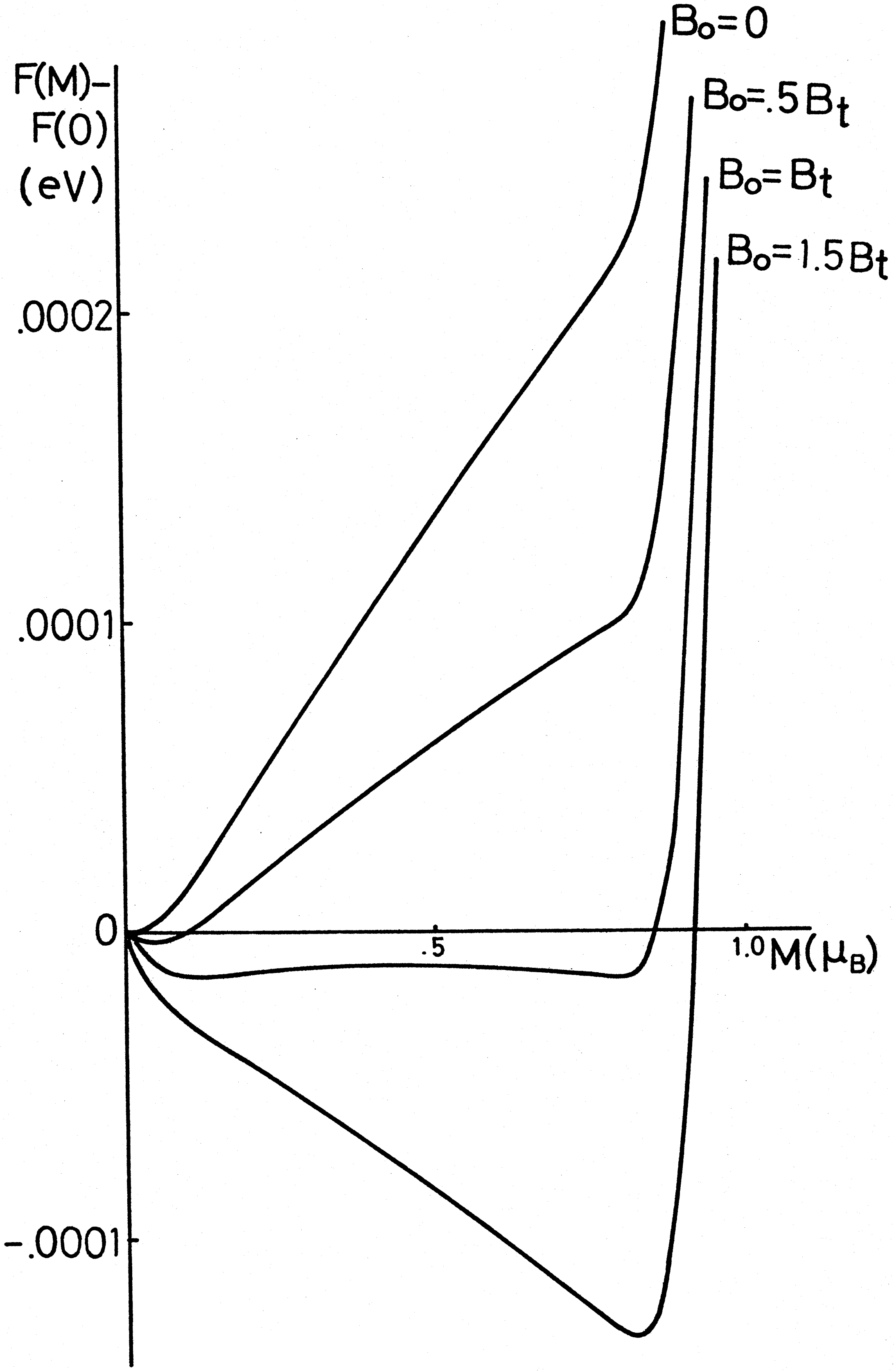

Fig. 3-9

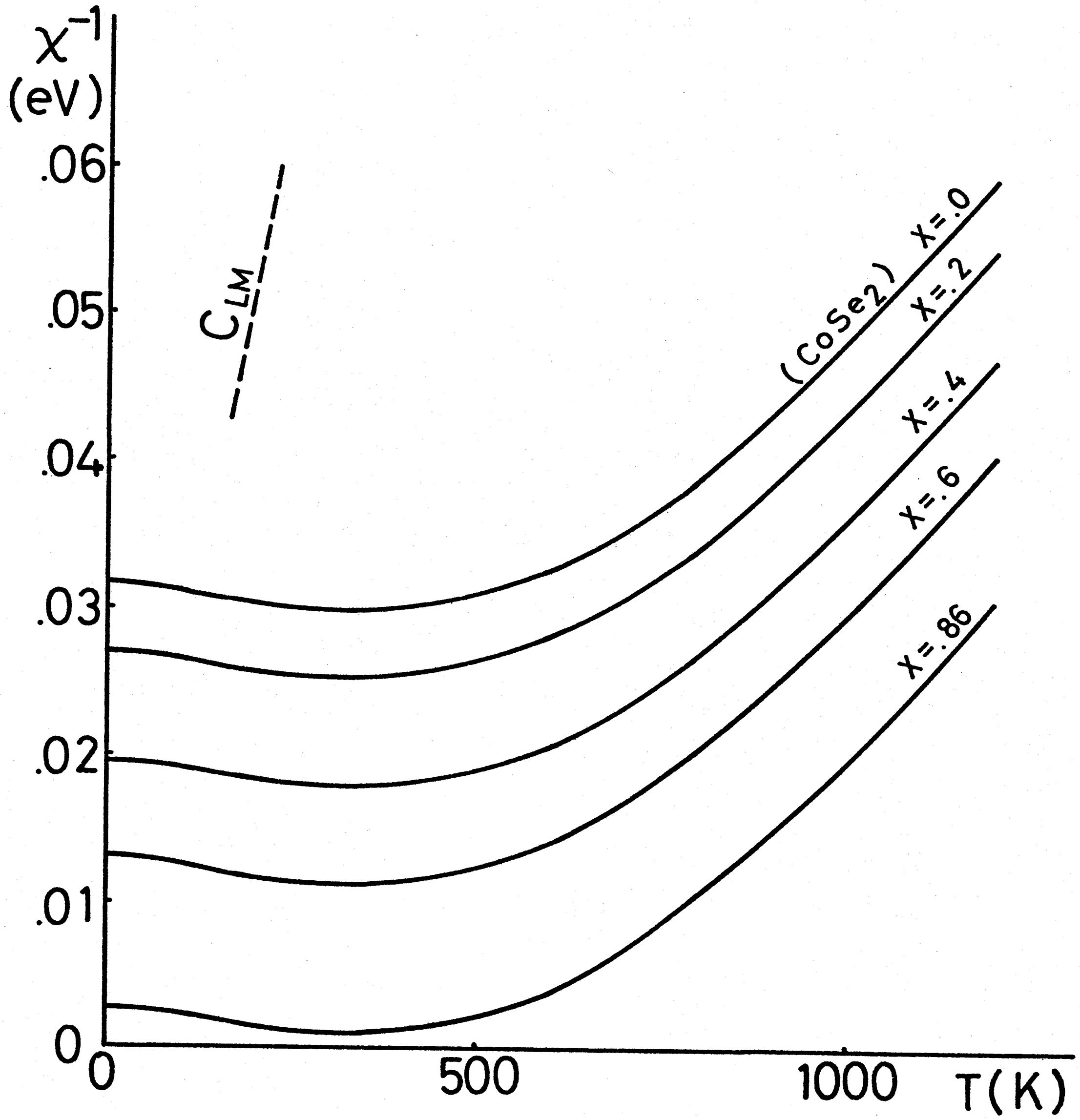

Fig. 3-10

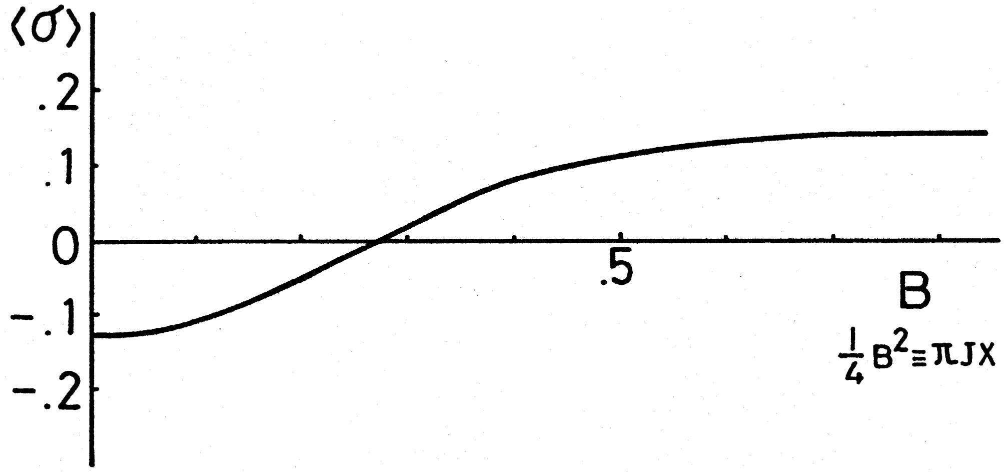

Fig. 5-1

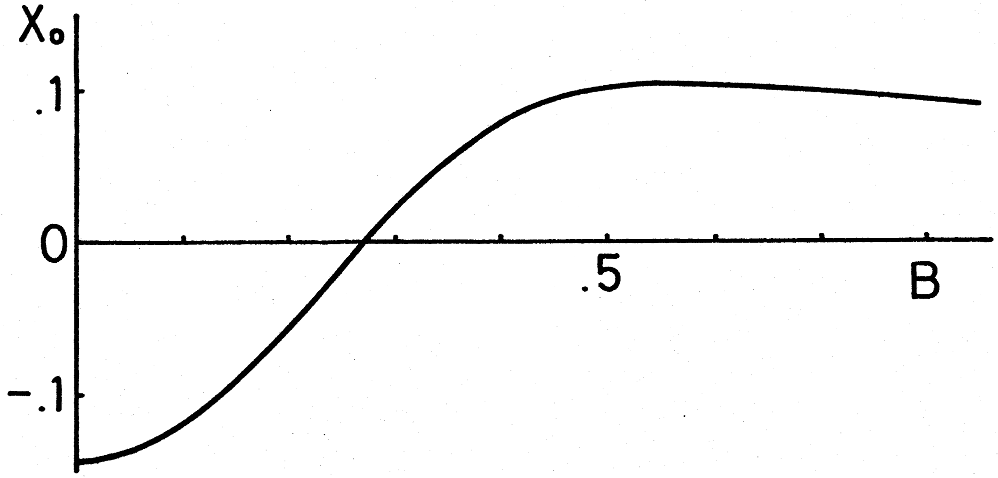

Fig. 5-2

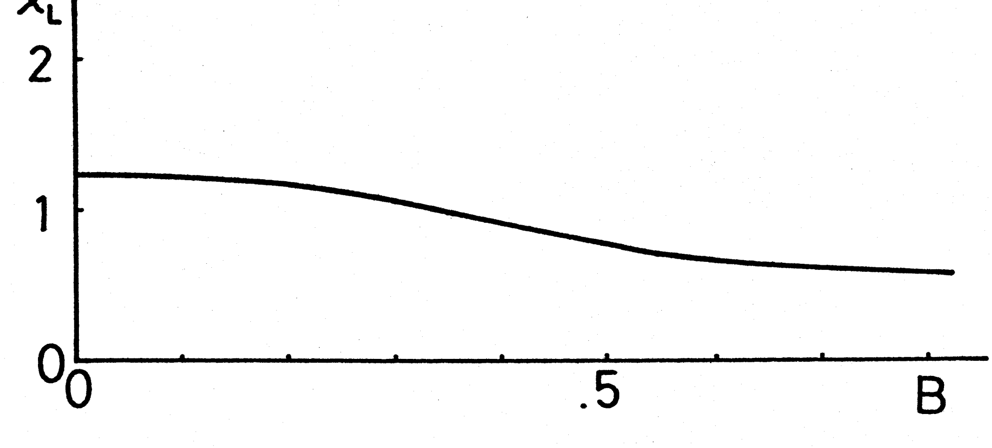

Fig. 5-3

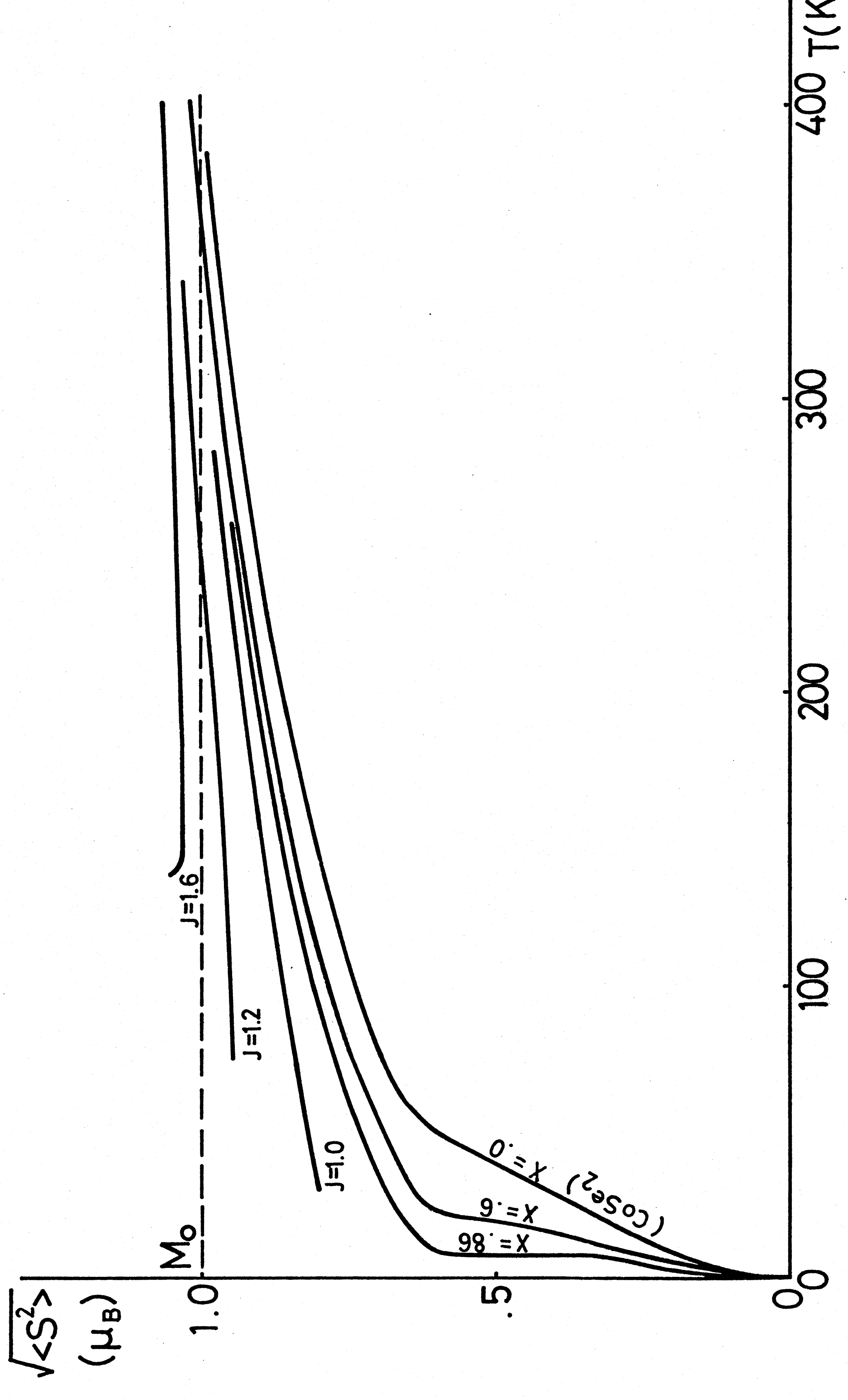

Fig.5-4

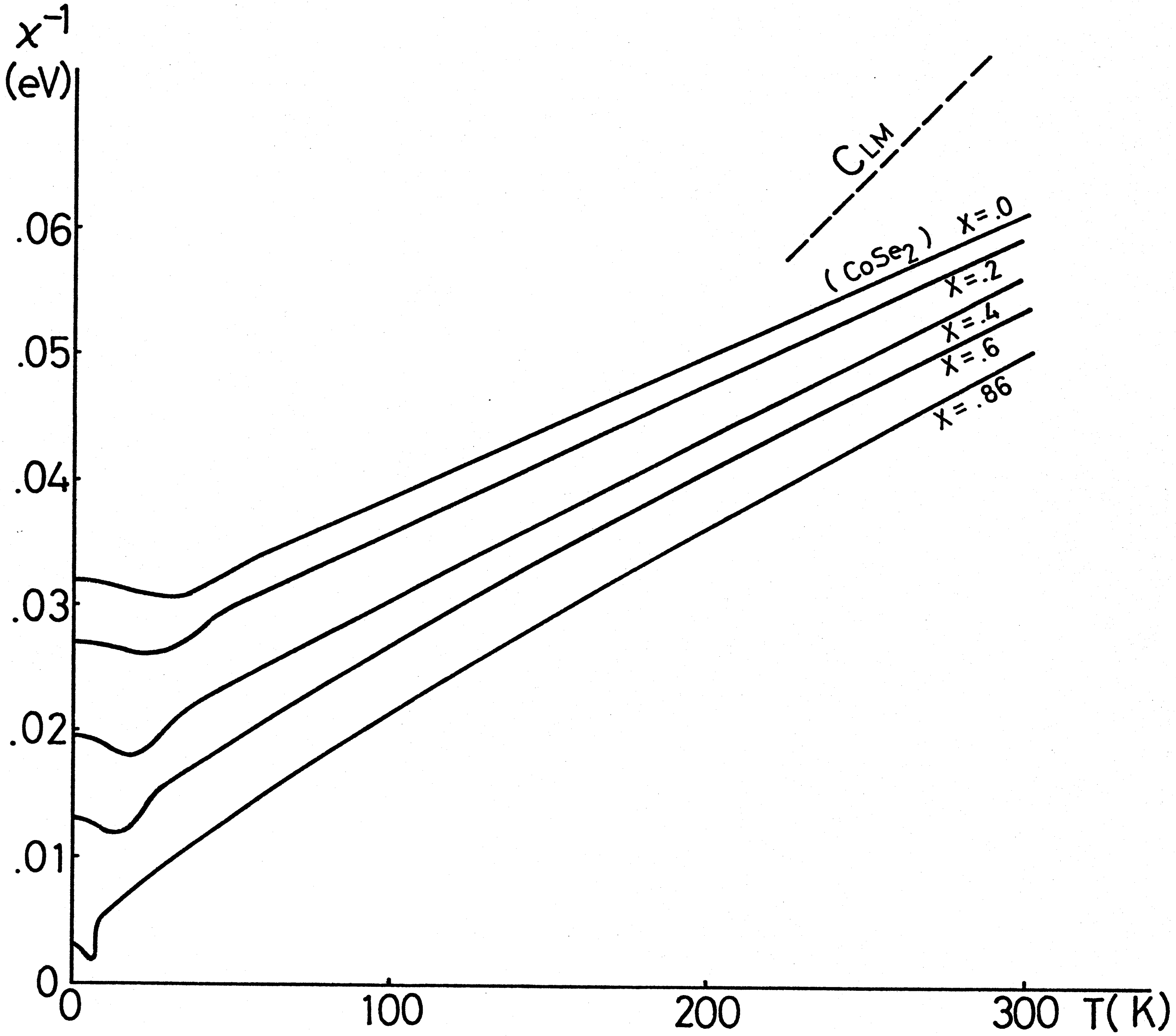
χ^{-1}
(eV)
.06
.05
.04
.03
.02
.01
0
0
100
200
300
T(K)
C_{LM}
(CoSe$_2$)
X=.0
X=.2
X=.4
X=.6
X=.86

Fig. 5-5

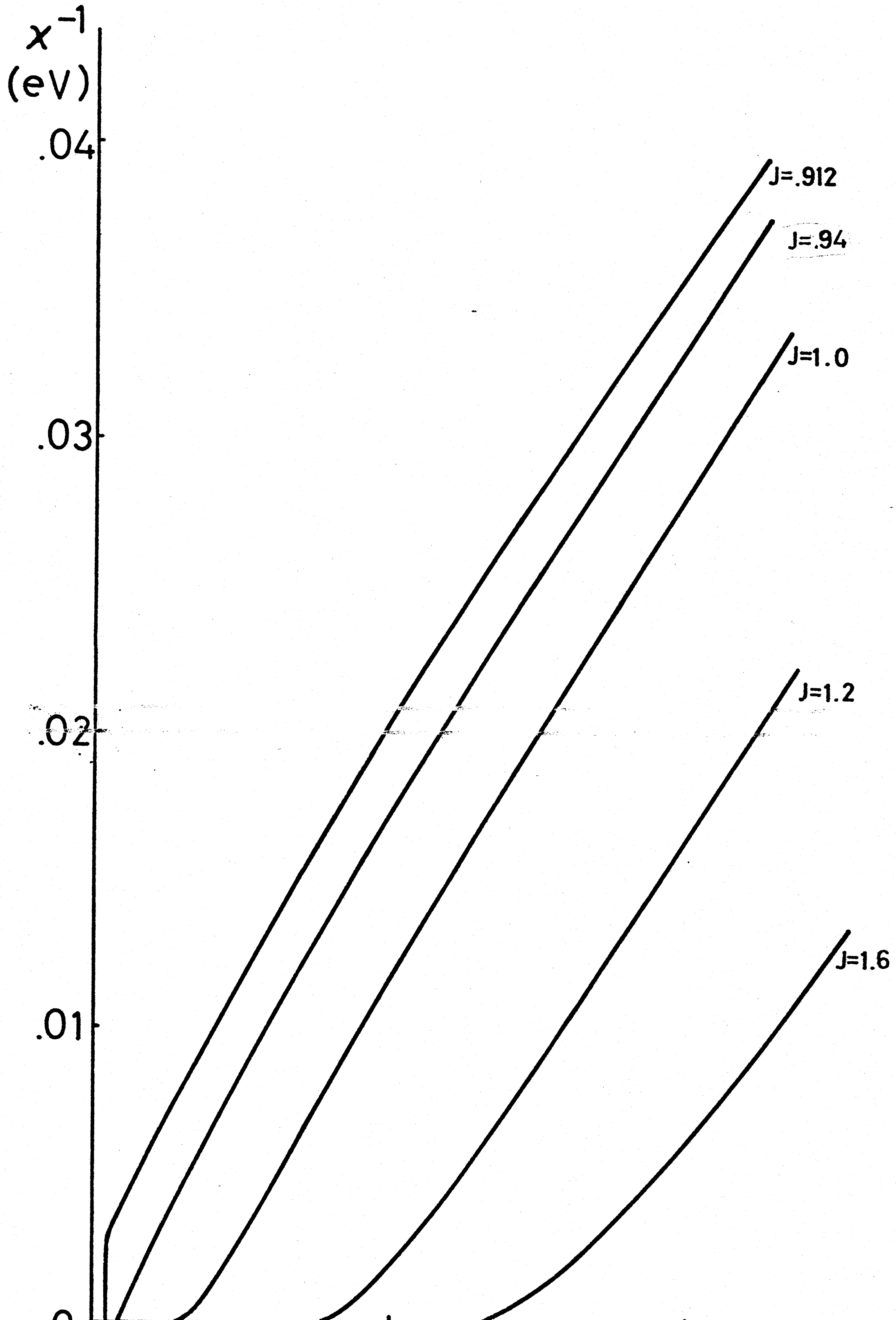

Fig. 5-6

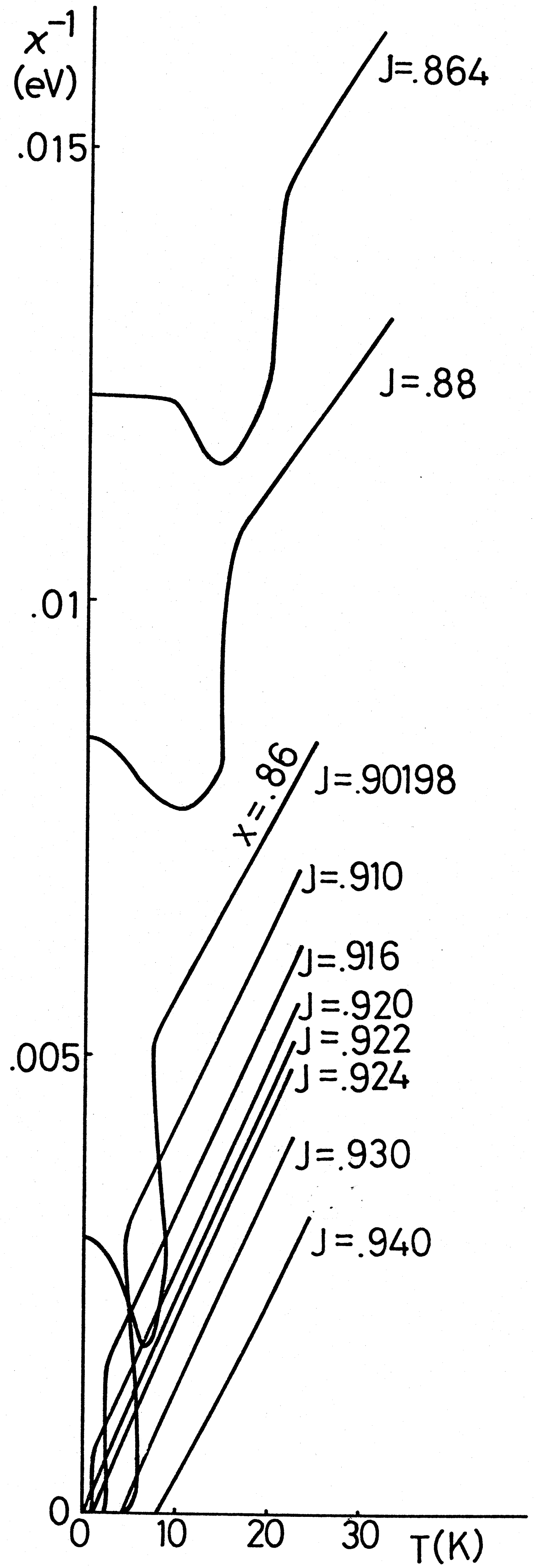
χ^{-1}
(eV)
.015
.01
.005
0
0
10
20
30
T(K)
J=.864
J=.88
x=.86
J=.90198
J=.910
J=.916
J=.920
J=.922
J=.924
J=.930
J=.940

Fig.5-7

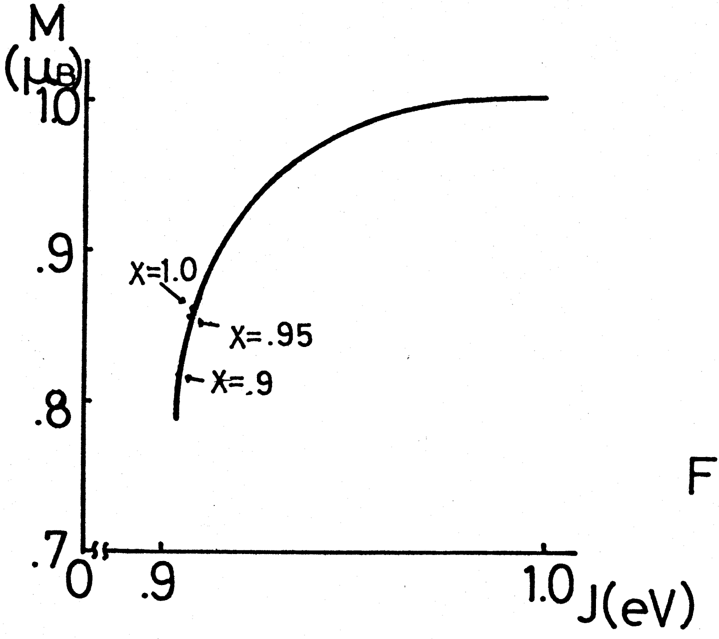
M
(μB)
1.0
.9
.8
.7
X=1.0
X=.95
X=.9
0
.9
1.0
J(eV)

Fig. 5-9

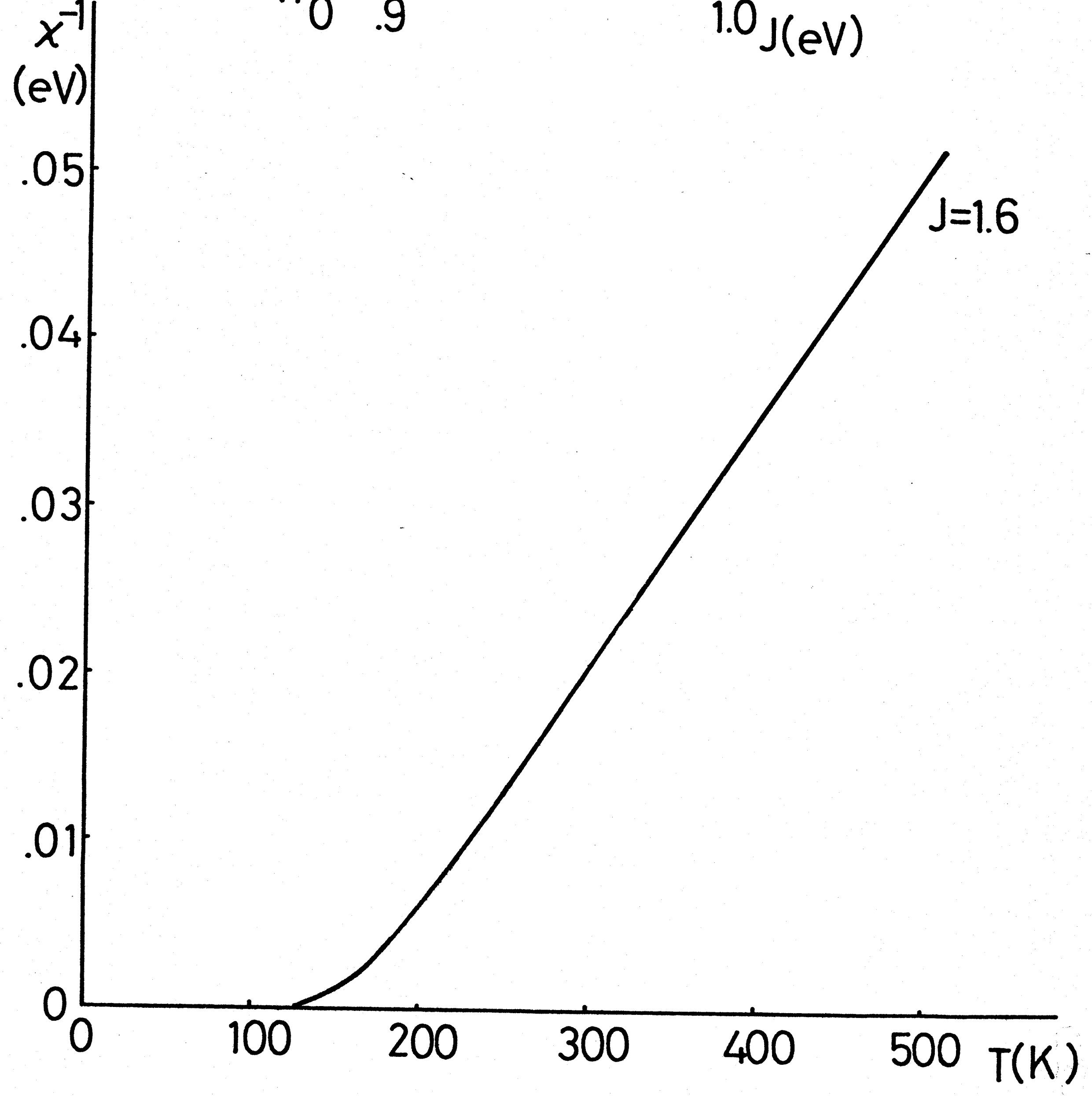
χ⁻¹
(eV)
.05
.04
.03
.02
.01
0
J=1.6
0
100
200
300
400
500
T(K)

Fig. 5-8