Bull. Shimane Univ. (Natural Sci.) No. 15, pp. 12—18. December, 1965.

Second Order Phase Transition in Certain Antiferromagnetic Crystals

Toshio TAKEHARA

Weiss molecular field theory is applied to the calculation of the susceptibility and the specific heat in an alternant spin system of the crystal of the copper sulphate pentahydrate type. The system has two species of antiferromagnetic linear chains of ions. The four sublattice model are introduced and the derived susceptibility curve like in ferriamagnetic explain the temperature dependent behaviour in spite of the rough approximation. The theory predicts the specific heat anomalies corresponding to the transition point of the two independent systems. Such result can not be found in the measurements.

§ 1. Introduction

In certain types of peramagnets there are sometimes different kinds of environment of spins of the same species which are mixed and correlated with each other through the existence of spin-spin interaction. Paramagnetic resonance studies in such cases were first observed in $CuSO_4 \cdot 5H_2O$ by Bagguley and Griffith,[1] then in $K_2CuCl_4 \cdot 2H_2O$ and Mn$(HCOO)_2 \cdot 2H_2O$ by Abe et al.[2] Results of the susceptibility and the specific heat measurements of $CuSO_4 \cdot 5H_2O$ and $CuSeO_4 \cdot 5H_2O$ by Haseda et al.[3] convinced us the situation that two kinds of dissimilar copper ion present.

In this paper the theoretical calculation of the susceptibility and the specific heat anomaly is performed for the four sublattice model in the crystal of $CuSO_4 \cdot 5H_2O$ type.

§ 2. Molecular Field Theory Applied to Antiferromagnetic $CuSO_4 \cdot 5H_2O$ Type Crystal

X-ray analysis of copper sulphate pentahydrate, $CuSO_4 \cdot 5H_2O$, was made by Beevers and Lipson.[4] The unit cell is triclinic with axes $a_0 = 6.12$, $b_0 = 10.7$, $c_0 = 5.97$Å and interaxial angles $\alpha=82°16'$, $\beta=107°26'$, $\gamma=102°40'$.

The crystal structure is shown in Fig. 1. They report the following facts : Unit cell has two inequivalent copper ions at (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, 0). Each type of ions is surrounded by four water molecules and two oxygen ions in a similar but not the same way. The atomic configurations betwieen copper ions of the same type are quite different for the two types of ions. Each copper ion has two copper neighbours of the same sort at a distance $a_0=6.12$Å, two more at a distance of $c_0=5.97$Å, whereas there are two pairs of near neighbours of another sort at distance 5.65Å and 6.8Å. Other copper ions are more than 8Å apart.

The two systems of copper ions with different environment are distinguished by I and II. In one of the system I the magnetic interaction energy is of the order of 1°K, whereas

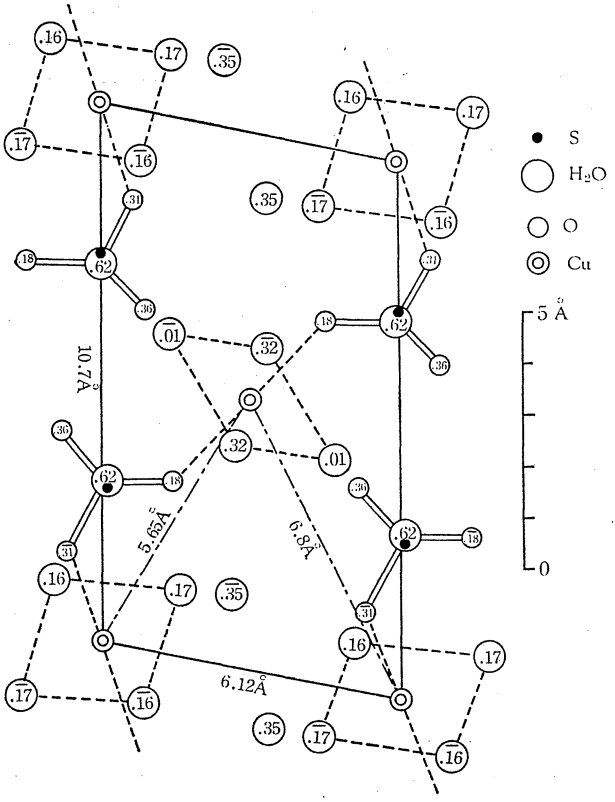

Fig. 1. Projection of the crystal structure of copper sulphate pentanydrate on a plane normal to the c axis (after Beevers and Lipson). The distances to the plane of the drawing are given in percentages of $c_0=5.97$ A. The dashed lines between the various oxygen atoms are drawn to show the tetragonal environments of the Cu^{2+}ions ; the dashed line connecting two oxygens belonging to sulphate groups correspond to the crystal field axes.

the interionic interactions between I and II are much smaller and the interactions in the system II will not exist appreciably. The ions of system I can be identified with the ion at ($\frac{1}{2}$, $\frac{1}{2}$, 0). They are linked in a direction parallel to the c axis to ions through the indirect exchange or superexchange interaction containing two hydrogen molecules between the exchange path, and linked parallel to a axis and also linked in the a b plane along the two diagonal directions. Their interaction between magnetic ions arise via the two or more intermediary negative ions. The superexchange mechanism is complicated and the magnitude might not be estimated easily.

The exchange interactions of the Heisenberg type are equivalent to an interatomic potential (Hamiltonian), apart from an additive constant :

$$\mathcal{H}=-2Jz\boldsymbol{S}_i\cdot\boldsymbol{S}_j\,, \tag{1}$$

$\boldsymbol{S}_i$ and $\boldsymbol{S}_j$ are, respectively, the spin angular momentum vector of atoms i and j measured in units of $\hbar$ and J is the exchange integral. In antiferromagnetism, J is negative and denote coefficient of the superexchange coupling. In our problem J and J_1 denote the antiferromagnetic interaction between the ions of system I along c and a axis respectively ; J_2 and J_3 denote the coupling between the ions of I and II in the two diagonal directions. The existence of antiferromagnetic ordering has not yet been proved from first principles, except for the special model of a two dimensional Ising system, as Onsager[5] showed for the one dimensional Ising system, but all experimental evidence shows that it does exist.

When the temperature is raised from absolute zero, J_2 or J_3 is destroyed, then the system II can not sustain ordered state.

Then the system I is isolated from the system II, it can still be in ordering state through the interaction J and J_1. If the temperature is further raised, interaction J_1 is destroyed and then the whole spin systems become paramagnetic.

We assume that the whole spin system in the ordering state is divided into four sublattices, that is, the system I and II are divided into alternant up and dowm spin lattice. The spin on each sublattice is denoted by $\boldsymbol{S}_{\mathrm{I}}^{\pm}$ and $\boldsymbol{S}_{\mathrm{II}}^{\pm}$ respectively.

Hamiltonian of an i-th atom of system I is

$$\mathscr{H}_{\mathrm{I},i} = -2\,(J+J_1)\, z\boldsymbol{S}_i\,\langle \boldsymbol{S}_{\mathrm{I}}^{\mp}\rangle - 2(J_2+J_3)\, z\boldsymbol{S}_i\,\langle \boldsymbol{S}_{\mathrm{II}}^{\mp}\rangle. \qquad (2)$$

z is the number of nearest neighbour spins around a spin $\boldsymbol{S}_i$, and $z=2$ always is in our case. The $\mp$ sign depends on whether the spin $\boldsymbol{S}_i$ is on the sublattice of up or down spin.

The total magnetic moment of each sublattice $\boldsymbol{M}_{\mathrm{I}}^{\pm}$ and $\boldsymbol{M}_{\mathrm{II}}^{\pm}$ are then

$$\boldsymbol{M}_{\mathrm{I}}^{\pm} = \frac{1}{4} Ng\mu_B \langle \boldsymbol{S}_{\mathrm{I}}^{\pm} \rangle, \qquad \boldsymbol{M}_{\mathrm{II}}^{\pm} = \frac{1}{4} Ng\mu_B \langle \boldsymbol{S}_{\mathrm{II}}^{\pm} \rangle, \qquad (3)$$

where g is the Landé g-factor, which is assumed isotropic, that is, it does not depend on the direction of the spin, with respect to the crystal orientation. N is the total number of magnetic ions. Then (2) become

$$\mathscr{H}_{\mathrm{I},i} = -g\mu_B \boldsymbol{S}_i \cdot \boldsymbol{H}_{\mathrm{I},i}^{\pm}, \qquad (4)$$

where

$$\boldsymbol{H}_{\mathrm{I},i}^{\pm} = -A\boldsymbol{M}_{\mathrm{I}}^{\mp} - \Gamma \boldsymbol{M}_{\mathrm{II}}^{\mp} \qquad (5)$$

is the exchange field acting on each spin of the system I, and

$$A = -\frac{8(J+J_1)z}{Ng^2\mu_B^2}, \qquad \Gamma = -\frac{8(J_2+J_3)z}{Ng^2\mu_B^2}, \qquad (6)$$

and similarly

$$\boldsymbol{H}_{\mathrm{II},i}^{\pm} = -\Gamma \boldsymbol{M}_{\mathrm{I}}^{\mp}. \qquad (7)$$

In the applied magnetic field H, the magnitude of the magnetization vector $\boldsymbol{M}_{\mathrm{I}}^{\pm}$ and $\boldsymbol{M}_{\mathrm{II}}^{\pm}$ are given by the standard theory of the molecular field approximation, and are

$$M_{\mathrm{I}}^{\pm} = \frac{1}{4} Ng\mu_B SB_S\,(y_{\mathrm{I}}^{\pm}), \quad \text{with} \quad y_{\mathrm{I}}^{\pm} = (H+H_{\mathrm{I}}^{\mp})g\mu_B S/kT, \qquad (8)$$

and

$$M_{\mathrm{II}}^{\pm} = \frac{1}{4} Ng\mu_B\, SB_S\,(y_{\mathrm{II}}^{\pm}), \quad \text{with} \quad y_{\mathrm{II}}^{\pm} = (H+H_{\mathrm{II}}^{\mp})g\mu_B S/kT. \qquad (9)$$

Here

$$B_S\,(y) = \frac{2S+1}{2S}\coth\frac{2S+1}{2S}\,y - \frac{1}{2S}\coth\frac{y}{2S} \qquad (10)$$

is the Brillouin function, which reduces to tanh y for $S=\frac{1}{2}$ (for the ion Cu^{++}) and to the Langevin function $\coth y - 1/y$ for $S=\infty$. When there is no external field $M_{\mathrm{I}}^{\pm}$ and $M_{\mathrm{II}}^{\pm}$ are antiparallel to each other :

$$M_{\mathrm{I}}^{+} = -M_{\mathrm{I}}^{-}, \qquad M_{\mathrm{II}}^{+} = -M_{\mathrm{II}}^{-}, \tag{11}$$

and (8) and (9) gives the magnitude of the saturation magnetization M_{I} and M_{II}, which can be obtained from

$$M_{\mathrm{I}} = \frac{1}{4} Ng\mu_B S\ B_S\{g\mu_B S\ (AM_{\mathrm{I}} + \Gamma M_{\mathrm{II}})/kT\}, \tag{12}$$

and

$$M_{\mathrm{II}} = \frac{1}{4} Ng\mu_B S\ B_S\{g\mu_B S\Gamma M_{\mathrm{II}}/kT\}. \tag{13}$$

Here (5) and (7) have been used. M_{I} and M_{II} are decreasing functions of temperatures as in the case of ferromagnetism and vanishes at the critical point, or the Nėel point, T_N. Nėel point can be found by expanding the Brillouin functions in (12) and (13) for small argument. For $|y| \ll 1$,

$$B_S(y) \doteqdot \frac{S+1}{3S} y - \frac{1}{45} \frac{(S+1)\{(S+1)^2+S^2\}}{2S^3} y^3 + \dots, \tag{14}$$

and therefore (12) and (13) results in the equations :

$$T_N M_{\mathrm{I}} - \frac{C}{4} (AM_{\mathrm{I}} + \Gamma M_{\mathrm{II}}) = 0, \tag{15}$$

$$T_N M_{\mathrm{II}} - \frac{C}{4}\, 4\Gamma M_{\mathrm{I}} = 0, \tag{16}$$

where T has been replaced by the Nėel temperature T_N, since the equation applies to that only, and

$$C = \frac{Ng^2\mu_B^2\ S(S+1)}{3k}. \tag{17}$$

These two linear uniform equations in the magnetizations M_{I} and M_{II} of the sublattices cannot all be independent and they only give a solution differing from zero for the sublattice magnetizations if the determinant of the coefficients of M_{I} and M_{II} is zero. This gives an equation of the second degree in T_N with two roots :

$$\begin{vmatrix} A - \dfrac{T_N}{4C} & \Gamma \\ \Gamma & -\dfrac{T_N}{4C} \end{vmatrix} = 0. \tag{18}$$

It seems to us that there are two Nėel temperature. It means only that there are two different M_{I} andM_{II} versus T curves for the resultant magnetization with two Nėel points. Two roots of the determinant equation are one positive and one negative, so that in negative case there will be no spontaneous magnetization. Only for the positive root of T_N the state will occur. We find according to (18)

$$T_N = \frac{1}{8} C\,[A + A\sqrt{1+4\Gamma^2/A^2}\ ]. \tag{19}$$

To derive the susceptibility above the Nėel temperature, we expand the Brillouin function in (12) and (13) and write down, like in the equations (15) and (16) in the applied field, as

$$M_{\mathrm{I}}^{\pm} = \frac{C}{4T}\,(H - AM_{\mathrm{I}}^{\mp} - \Gamma M_{\mathrm{II}}^{\mp}), \tag{20}$$

and

$$M_{\mathrm{II}}^{\pm} = \frac{C}{4T}\,(H - \Gamma M_{\mathrm{I}}^{\mp}). \tag{21}$$

since $\boldsymbol{M}_{\mathrm{I}}^{\mp}$ and $\boldsymbol{M}_{\mathrm{II}}^{\pm}$ are all parallel to H in paramagnetic region, Solving these equations, we obtain $M_{\mathrm{I}}^{+} = M_{\mathrm{I}}^{-}$, Summing up these equations we obtain the total magnetization $M_{\mathrm{I}}^{+} + M_{\mathrm{I}}^{-} + M_{\mathrm{II}}^{+} + M_{\mathrm{II}}^{-}$. Then dividing it by H we obtain the susceptibility above the Néel temperature

$$\chi = \frac{CT + \frac{1}{8}C^2\,(A+\Gamma)}{T^2 + \frac{C\Gamma}{4}\,T + \frac{C^2 A\Gamma}{16}}\,. \tag{22}$$

We derive from (22) the relation

$$\frac{1}{\chi} = \frac{T}{C} - \frac{1}{\chi_0} - \frac{\sigma}{T+\Theta}\,, \tag{23}$$

with the constants :

$$\frac{1}{\chi_0} = \frac{A-\Gamma}{8}\,, \tag{24}$$

$$\sigma = \frac{1}{64}\,C\,(A^2 - \Gamma^2) + \frac{CA\Gamma}{4}\,, \tag{25}$$

$$\Theta = \frac{1}{8}\,C\,(A+\Gamma)\,. \tag{26}$$

Equation (23) shows that $1/\chi$ versus T curve is nearly straight lines above the Néel temperature. Below the Néel temperature the susceptibility of the system I will have negative slope or zero if the system I is ordered, but the system II is in disorder and contribution to the paramagnetic susceptibility exists with C/2 instead of C in (23), the slope below the Néel temperature is doubled that above. The curve is bent in the Néel point and has the discontinuous slope.

Next, the specific heat discontinuity must be derived in the Néel point. The magnetic interaction energy is

$$\begin{aligned} E_M &= -\frac{1}{2}\,(\boldsymbol{M}_{\mathrm{I}}^{+}\boldsymbol{H}_{\mathrm{I}}^{+} + \boldsymbol{M}_{\mathrm{I}}^{-}\boldsymbol{H}_{\mathrm{I}}^{-} + \boldsymbol{M}_{\mathrm{II}}^{+}\boldsymbol{H}_{\mathrm{II}}^{+} + \boldsymbol{M}_{\mathrm{II}}^{-}\boldsymbol{H}_{\mathrm{II}}^{-}) \\ &= A\boldsymbol{M}_{\mathrm{I}}^{+}\boldsymbol{M}_{\mathrm{I}}^{-} + \Gamma\boldsymbol{M}_{\mathrm{I}}^{+}\boldsymbol{M}_{\mathrm{II}}^{-} + \Gamma\boldsymbol{M}_{\mathrm{I}}^{-}\boldsymbol{M}_{\mathrm{II}}^{+} \\ &= -AM_{\mathrm{I}}^{2} - \Gamma M_{\mathrm{I}}M_{\mathrm{II}}, \end{aligned} \tag{27}$$

where the equation (5) and (7) are used.

Owing to the decrease of M_{I} and M_{II}, the change of the total magnetic interaction energy with the temperature is accompanied by an extra contribution to the specific heat which in the absence of external fields, is given by

$$C_M = \frac{dE_M}{dT} = -A\frac{dM_{\mathrm{I}}^2}{dT} - \Gamma M_{\mathrm{I}}\frac{dM_{\mathrm{II}}}{dT} - \Gamma M_{\mathrm{II}}\frac{dM_{\mathrm{I}}}{dT}\,. \tag{28}$$

Just below the Néel point, $M_{\mathrm{II}} = 0$ and $dM_{\mathrm{II}}/dT = 0$, and only the first term contributes the specific heat C_M and has a maximum and above it C_M is zero, i. e. there occurs a jump equal to

$$\varDelta C_M = \frac{5}{4}\ \frac{S(S+1)}{S^2+(S+1)^2}\ Nk, \tag{29}$$

which is given by using the equation

$$\left(\frac{M_{\mathrm{I}}}{M_{\mathrm{I}\infty}}\right)^2 = \frac{10}{3}\ \frac{(S+1)^2}{(S+1)^2+S^2}\ \left(\frac{T}{T_N}\right)^3 \left(\frac{T_N}{T}-1\right). \tag{30}$$

A finite jump of this kind in specific heat is characteristic of what is called a second order transition.

§ 3. Comparison with Experiment and Discussion

Experimental studies of the susceptibility and the specific heat of $CuSO_4{\cdot}5H_2O$ and $CuSeO_4{\cdot}5H_2O$ were performed by Haseda et al[3] below 1°K. A part of their results are shown in Figs. 2 and 3. $1/\chi$ versus temperature curve composed of two straight lines, one of which (low temperature side) is extrapolated to pass through very near the origin.

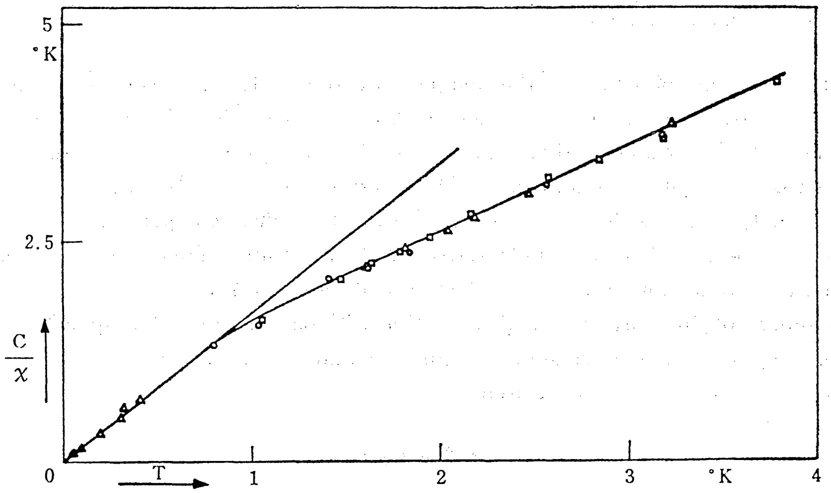

Fig. 2. The ratio of the Curie constant C and the adiabatic susceptibility χ of $CuSO_4{\cdot}5H_2O$ plotted as a function of temperature below 4°K. (after Haseda et al.)
○α axis □β axis △γ axis

and bent down towards the T axis with less slope of about half of the lower temperature part. The discontinuous point of slope will correspond to the Néel point. It is about 1°K. The above analysis explains this curve and equation (19) of T_N is of the order of 1°K. $1/\chi$ behavior found in $CuSeO_4{\cdot}5H_2O$ below 0.1°K is characteristic of antiferromagnetism. In the Néel point the discontinuity of the specific heat might be expected. But the measurements of the specific heat shows anomaly below 0.05°K, which corresponds not to T_N but to the point below 0.1°K of the susceptibility.

In the ordinary antiferromagnetic and ferrimagnetic one sublattice magnetization exists solely by virtue of the other. In our case the sublattice magnetization of the system I remaines isolated after the sublattice magnetization have vanished. We can imagine here

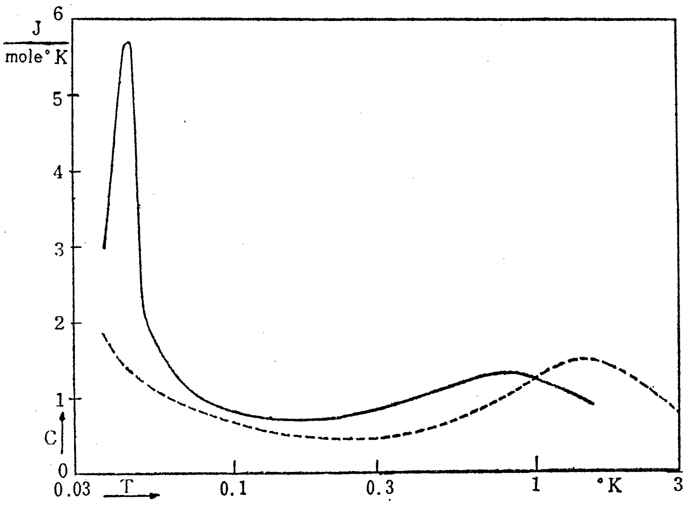

Fig. 3. Comparison of the specific heat versus temperature curves of $CuSO_4$. $5H_2O$ (dashed line) and $CuSeO_4.5H_2O$ (solid line). The temperatures are plotted on a logarithmic scale. (after Haseda et al.)

two Néel points, one of which is the temperature that only the system II vanishes, and the other the temperature of the system I also vanishes. Specific heat anomaly may correspond to the lower one. In this point the specific heat jump can be computed likewise. Experiment shows only one anomaly. The reason can not understand to me. If this difficulty is solved, the tails of the specific heat curve must be explained. The molecular field theory cannot explain such tails sbove the Curie point. This will be a measure of the short range order and the statistical treatments are needed.

The numbers of this sort of crystals ever find will be very few. The specific heat data I know is only that of copper sulphate and selenate only. A number of measurement about such sort of crystals are desired.

References

1) D. H. S. Bagguley and J. H. E. Griffith, Proc. Roy. Soc. **A201** (1950) 366.
2) K. Ono, H. Abe and J. Shimada, Phys. Rev. **92** (1953) 551.
H. Abe, K. Ono, I. Hayashi, J. Shimada andk. Iwanaga, J. Phys. Soc. Japan **9** (1954) 813.
H. Abe, (unpublished) — Mn $(HCOO)_2 \cdot 2H_2O$
3) A. R. Miedema, H. van Kempen, T. Haseda and W. J. Huiskamp, Physica **28** (1962) 119.
4) C. H. Beevers and H. Lipson, Proc. Roy. Soc. **A146** (1934) 570.
5) L. Onsager, Phys. Rev. **65** (1944) 117.