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Susceptibilities and Specific Heats of Linear Antiferromagnetic Lattices

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Recent experimental studies concerning the specific heat, the susceptibility and the paramagnetic resonance of single crystals of $CuSO_4 \cdot 5H_2O$ and $CuSeO_4 \cdot 5H_2O$ in the temperature range below 1°K revealed that there are two kinds of copper ion present in a unit cell. It is supposed that each species of ions are arranged antiferromagnetically in a linear chain and there are weak interactions between them. For these substances a four sublattice model is presented, and applying the molecular field theory The Néel point and the susceptibility versus temperature curves are explained. The speecific heat jump is also expected.

1. Introduction

In recent years the specific heat and the susceptibility of $Cu(NH_3)_4SO_4 \cdot H_2O$ has been measured by several authors 1) 2) 3) in the liquid helium temperature range. The results of such measurements are entirely different from the behaviour of common antiferromagnetic substances. The specific heat versus temperature curve shows a broad maximum, the general shape showing some resemblance to a Schottky anomaly. However, in this case the broad maximum cannot be expected since the Cu^{++} ion is in a ^2S state and has no excited levels below about 10^4 degrees.

From crystallographic investigations of $Cu(NH_3)_4SO_4 \cdot H_2O$, it can be concluded that the copper ions are arranged in linear chains, The strength of the magnetic interaction among copper ions in a chain can be expected much larger than the interaction between ions of different chain. The crystal may magnetically be considered as a bundle of practically non-interacting linear chains.

The specific heat of $CuSO_4 \cdot 5H_2O$ was measured previously by Geballe and Giauque 4) and by Duijckaerts 5) in the liquid helium temperature range. The specific heat versus temperature curve shows a maximum at 1.4°K, a minor maximum near 0.75°K and a minimum at 0.4°K, the general shape resembling to a Schottky type anomaly. However, the height of the specific heat maximum was found to be one half of that of a Schottky type anomaly for two levels and consequently the amount of entropy lost above 0.4°K by the magnetic system is $\frac{1}{2}R\ln2$ per mole. This result is rather surprising. In Fig. 1 the results of the latest measurements of specific heat by Haseda *et al* 6) are compared with those of Geballe and Giauque and of Duijckaerts. The specific heat maximum occurs at $T=1.5$°K.

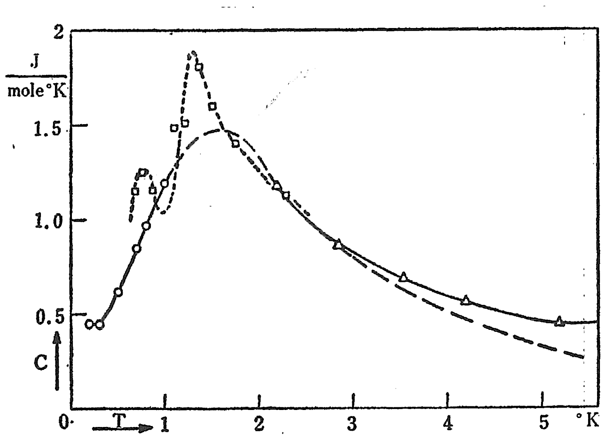

Fig. 1 The specific heat of $CuSO_4$. $5H_2O$ between 0.2 and 6°K. The dashed linc at revatively high temperatures is obtained by subtracting the lattice specific heat.
□ Geballe and Giauque ○ Haseda *et al* △ Duijckaerts

The specific heat decreases below 1°K and has a minimum at T=0.25°K. Below 0.25°K, the specific heat increases to the lowest temperature reached (0.035°K). Fig. 2 shows the curve.

The specific heat of $CuSeO_4\cdot 5H_2O$ has been measured by Hsseda *et al* too The results are given in Figs 3 and 4. The specific heat curve is similar to that obtained on the sulphate, a broad maximum being present at 0.8°K and a minimum near 0.2°K. Below 0.2°K the specific heat rises steeply and reaches another sharp maximum at 0.045°K. The eyperimental results on both sulphate and selenate salts show a broad maximum in their specific curve (Fig. 5). The specific heat curve for the selenates shows a typical lambda type anomaly at T=0.045°K. The specific heat curve of the sulphate crystal isomorphous with the selenate crystal will show, at the lower temperature side, the sharp maximum.

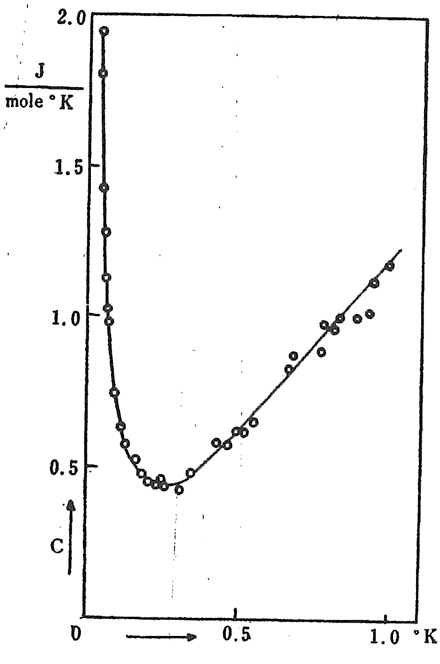

Fig. 2 The specific heat, C, of $CuSO\cdot_4 5H_2O$ versus the temperature T.

For both copper salts the estimated entropy removed from the magnetic system at the temperature of specific heat minimum equals nearly half the entropy which is available (½ Rln2).

It is well known that the usual types of exchange interaction do not lead to long range order in an isolated linear chain. Only short range order can exist and according to the

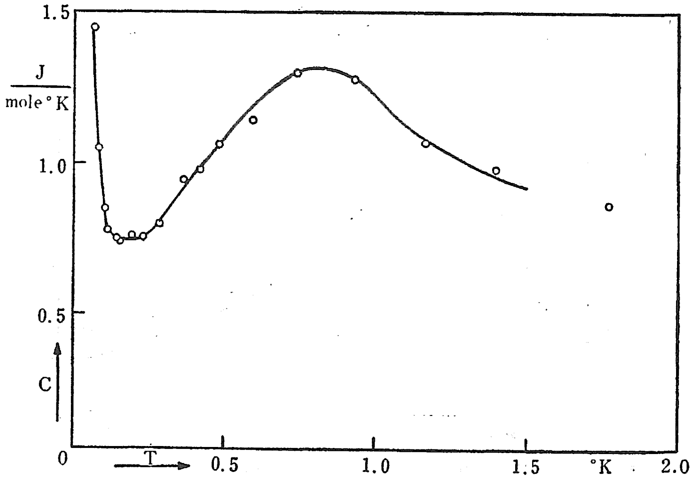

Fig. 3. The specific heat of $CuSeO_4 \cdot 5H_2O$ as a function of temperature below 1.5°K.

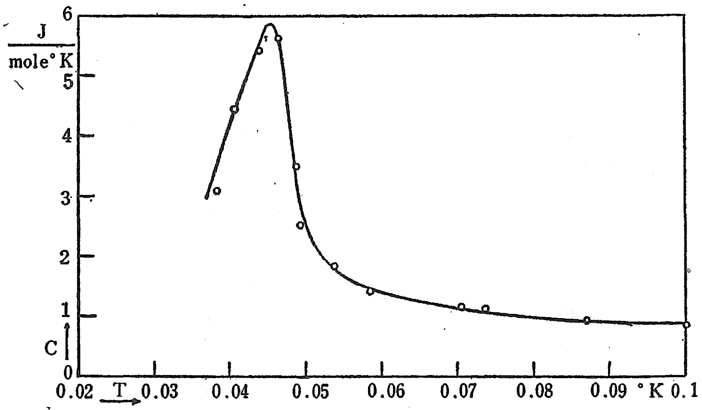

Fig. 4. The specific heat fo $CuSeO_4 \cdot 5H_2O$ as a function of temperature below 0.1°K.

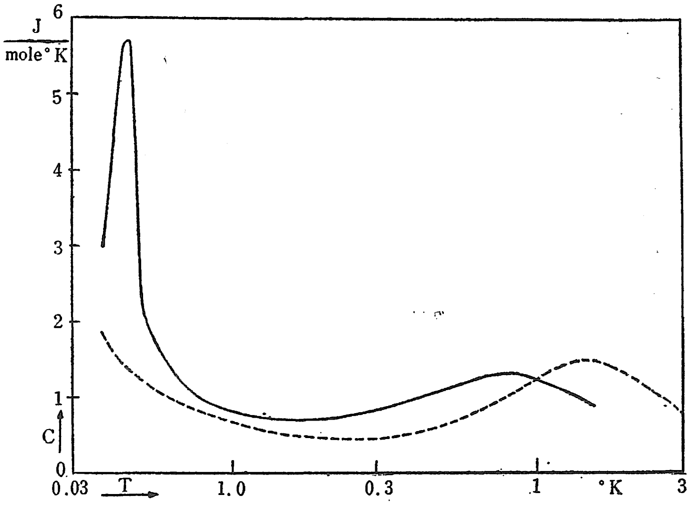

Fig. 5. Comparison of the specific heat ersus temperature curves of $CuSO_4.\ 5H_2O$ (dashed line) and $CuSeO_4.\ 5H_2O$ (solid line). The temperatures are plotted on a logarithmic scale.

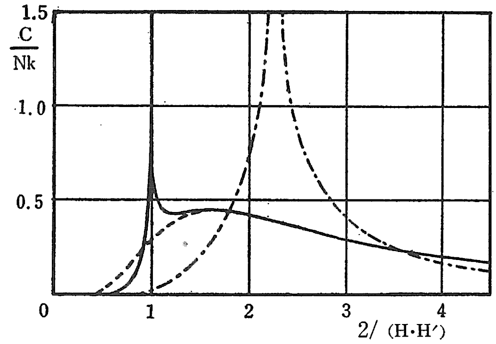

Fig. 6. Specific heats for varying degrees of anisotropy.
—— $J'/J=1/100$; —·— $J'/J=1$ (quadratic crystal) ------ ; $J'=0$ (linear chain).

calculations of Onsager7) a specific curve of Fig. 6 must be expected.

The simiarity between the curves of Fig. 6 makes it probable that there is a practically isolated linear chains of magnetic ions in $CuSO_4 \cdot 5H_2O$ and $CuSeO_4 \cdot 5H_2O$ to which only half the number of copper ions belong.

The susceptibility of $CuSO_4 \cdot 5H_2O$ has been measured as a function of temperature by de Haas and Gorter8) (powder) and Benzie and Cooke9) (singlecrystal). Between room temperature and about 2°K the susceptibility follows a Curie-Weiss law, $\chi = C/(T-\Theta)$; the Curie-Weiss constant is in the liquid helium temperature range equal to $\Theta = -0.60$°K. Kobayashi10) found a similar behaviour for the susceptibility of $CuSeO_4 \cdot 5H_2O$, Θ being equal to -0.46°K.

Haseda *et al* performed susceptibility measurements. The results obtained are shown in Figs. 7 and 8. The C/χ versus temperature curve will be a straight line if the susceptibility follows a Curie-Weiss law, the slope of the line corresponding to the inverse of the Curie constant and the intercept with the abscissa indicating the Weiss constant. It may be seen from Figs. 7 and 8 that the susceptibility follows no longer the Curie-Weiss law with $C=g^2\mu_B S(S+1)/3k$ and $\Theta=0.6$°K, but tends to amother Curie-Weiss law with a Θ' of about $+0.02$°K and a Curie constant C' which equals nearly about ½C.

The C/χ versus T curve is shown in Fig. 9.. Again the curve can be divided into two

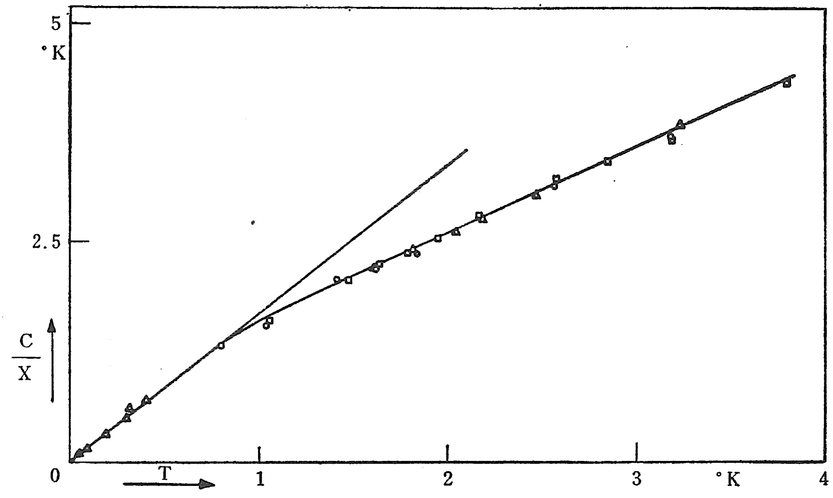

Fig. 7 The ratio of the Curie constant C and the adiabatic susceptibility χ of $CuSO_4 \cdot 5H_2O$ plotted as a function of temperature below 4°K.
○ α axis ☐ β axis △ γ axis

straight lines. The line which descrives the susceptibility between 0.1 and 0.8°K corresponds to a Curie-Weiss law with $C'=0.53C$ and $\Theta'=+0.03$°K. Below 1°K the susceptibility no longer follows a Curie-Weiss law but shows a weak maximum at $T=0.05$°K. Between 0.05 and 0.03°K the susceptibility decreases.

The susceptibilities of copper sulphate and copper selenate follow a Curie-Weiss law above 1°K with a negative Weiss constant of the order of 0.5°K, whereas below 1°K the susceptibilities are described by a Curie-Weiss law with $C'\approx\frac{1}{2}C$ and a Θ' which is small and positive. For $CuSeO_4 \cdot 5H_2O$ the susceptibility shows a maximum at 0.05°K which is near the temperature of the lambda type amomaly in the specific heat suggesting

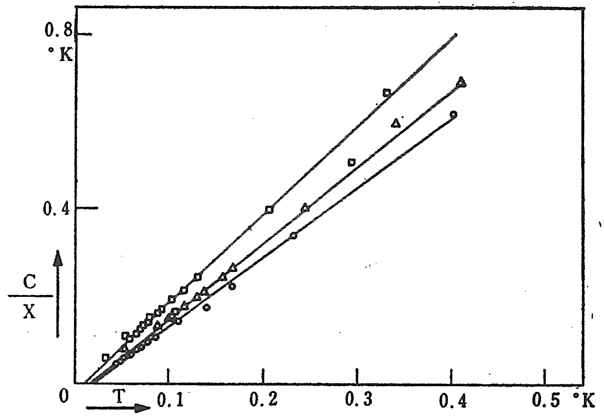

Fig. 8 The ratio of the Curie constant and the adiabatic susceptibility of $CuSO_4 \cdot 5H_2O$ plotted versus temperature below 0.4°K. The intercept with the abscissa indicates the Curie-Weiss constant.

○ α axis □ β axis △ γ axis

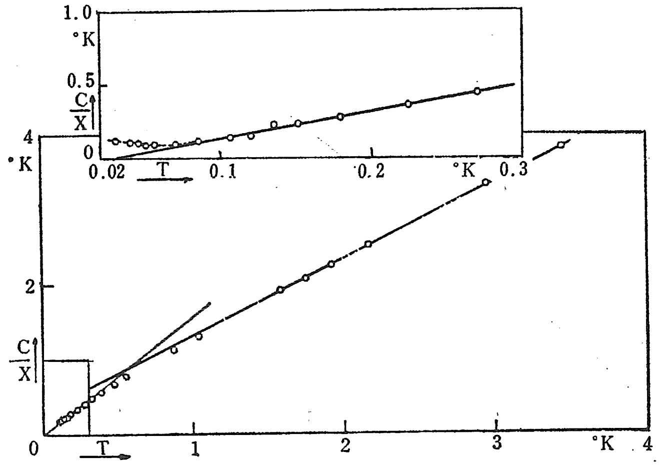

Fig. 9 $CuSeO_4 \cdot 5H_2O$. The ratio of the Curie constant C and the adiabatic susceptibility χ measured in the direction of the crystalline c axis as a function of temperature. The region below 0.3°K. is shown on an enlarged scale.

that this anomaly corresponds to a transition to the antiferromagnetic state.

The present results are in nice agreement with the removal in two steps of the magnetic entropy of the copper ions.

A tentative explanation for these thermal and magnetic behaviour given by Geballe and Giauque are treated theoretically by using the molecular field theory in the following sections.

II. Linear chain model and molecular field theory

Crystallographic investigations on the isomorphous crystals $CuSO_4 \cdot 5H_2O$ and $CuSeO_4 \cdot 5H_2O$ were made by Beevers and Lipson.[10] Their results are given in Fig. 10. It may be seen that there are two copper ions in the unit cell on the inequivalent positions (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, 0)$ each surrounded by an approximate octahedron of oxygen atoms, belonging to four water molecules and two sulphate ions. Each copper ion has a copper neighbours of the similar type at a distance of 6.12Å, two more at a distance of 5.97Å, whereas

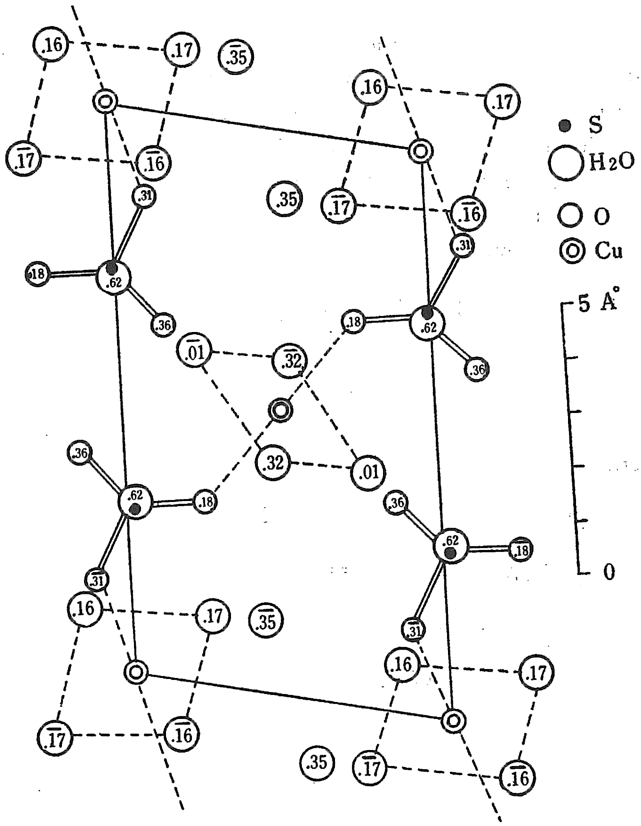

Fig. 10 Projection of the crystal structure of copper sulphate pentahydrate on a plane normal to the c axis (after Beevers and Lipson). The distances to the plane of the drawing are given in percentages of $c_0=5.97$ A. The dashed lines between the various oxygen atoms are drawn to show the tetragonal environments of the Cu^{2+} ions ; the dashed line connecting two oxygens belonging to sulphate groups correspond to the crystal field axes.

there are two pairs of near neighbours of dissimilar type at distances of 5.65Å and 6.8Å Other copper ions are more than 8Å apart.

The crystal structure support the presence of two independent systems of copper ions (I and II) with different environments. In one of the system (I) the magnetic interaction energy is of the order of 1°K whereas the interionic interactions are much smaller in the other system (II) and also between I and II. 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 a number of steps in the superexchange as follows

$$\text{—— Cu}^{++}\text{ —— OH}_2\text{ —— OH}_2\text{ —— Cu}^{++}\text{ ——} \qquad \text{A}$$

The magnetic exchange interaction between copper ions at inequivalent positions can be supposed through the path

$$\text{—— Cu}^{++}\text{ —— O —— S —— O—— Cu}^{++}\text{ ——} \qquad \text{B}$$

while for the exchange interaction of ions of system II ((0, 0, 0) superexchange with path less than three oxygen atoms between two copper ions is not found. The path A may be the most favourable one for exchange interaction occurring in the crystal. The exchange canstant of path A, path B, and between the ion of system II are denoted by J_1, J_2, and J_{12}. They are estimated of the order of 1°K, 0.1°K, and 0.01°K, respectively.

We assume that at 0°K all copper ions are arranged alternately, that is, antiferromagnetically along the direction parallel to the a-, b- and c-axis. The crystal lattice can be divided into four sublattices, two of which are the sublattices of up and down spin of the system I, the other two are those of system II.

If the central spin Si which interacts with its neighbouring spins is on the sublattice of system I, the interaction energy on the average, given by

$$-\,2\,J_1 z \mathbf{S}i\mathbf{S}_{\mathrm{I}}^{\mp}\,2 - J_{12}z_{12}\mathbf{S}i\mathbf{S}_{\mathrm{II}}^{\mp} \qquad (1)$$

where $\mathbf{S}_{\mathrm{I}}^{\mp}$ and $\mathbf{S}_{\mathrm{II}}^{\mp}$ are the average values of spins of the sublattice around the central spin, z_1 and z_{12} are the number of nearest neighbour spins on the system I and system II around the central spin on the system I ($z_1=2_1$, $z_{12}=4$ in this case). the ∓ sign depends on whether the central spin is on the sublattice of up spin or not.

The total magnetic moment of each sublattice $M_{\mathrm{I}}^{\pm}$ and $M_{\mathrm{II}}^{\pm}$ is then

$$\mathbf{M}_{\mathrm{I}}^{\pm} = \frac{1}{4}\,\mathrm{N}g\mu_{\mathrm{B}}\,\mathbf{S}_{\mathrm{I}}^{\pm}, \qquad \mathbf{M}_{\mathrm{II}}^{\pm} = \frac{1}{4}\mathrm{N}\,g\mu_{\mathrm{B}}\,\mathbf{S}_{\mathrm{II}}^{\pm}. \qquad (2)$$

where N is the total number of magnetic ions, (2) becomes

$$-g\mu_{\mathrm{B}}\,\mathbf{S}i\,\mathbf{H}i^{\pm} \qquad (3)$$

Here

$$\mathbf{H}_i^{\pm} = -\alpha\,\mathbf{M}_{\mathrm{I}}^{\mp} - \beta\mathbf{M}_{\mathrm{II}}^{\mp} \qquad (4)$$

is the molecular field acting on the spins of system I, and

$$\alpha = -\frac{8J_1\ z_1}{\mathrm{N}g^2\mu_{\mathrm{B}}^2}, \qquad \beta = -\frac{8J_{12}\ z_{12}}{\mathrm{N}g^2\mu_{\mathrm{B}}^2} \qquad (5)$$

are the molecular field coefficients and are positive together if J_1 and J_{12} are negative.

Boltzmann statistics gives for the magnetic moment of sublattices in the internal magnetic field (4)

$$M_{I}^{\pm} = \frac{1}{4} N g \mu_B S B_s \left(- \frac{g \mu_B S \; (\alpha M_{I}^{\mp} + \beta M_{II}^{\mp})}{kT} \right) \qquad (6)$$

and similarly

$$M_{II}^{\pm} = \frac{1}{4} N g \mu_B S B_s \left(- \frac{g \mu_B S \; (\beta M_{I}^{\mp} + \gamma M_{II}^{\mp})}{kT} \right) \qquad (7)$$

where Bs is the Brillouin function, $S = \frac{1}{2}$ for Cu^{++} and

$$\gamma = - \frac{8 J_2 z_2}{N g^2 \mu_B^2} \, . \qquad (8)$$

M_I and M_{II} must satisfy the equations (6) and (7) simultaneously. The solutions are given by putting

$$M_{I}^{+} = - M_{I}^{-} = M_{I}, \qquad M_{II}^{+} = - M_{II}^{-} = M_{II} = - M_{I} \qquad (9)$$

M_I and M_{II} are total magnetic moment of sublattice of each kind of ion. Then

$$M_I = \frac{1}{4} N g \mu_B S \, B_s \left(\frac{g \mu_B S \; (\alpha - \beta) \; M_I)}{KT} \right) \qquad (10)$$

and

$$M_{II} = \frac{1}{4} N g \mu_B S \, B_s \left(\frac{g \mu_B S \; (\beta + \gamma) \; M_{II})}{KT} \right) \qquad (11)$$

The above equations which give the temperature dependence of the magnetic moment of sublattices resembles the ferromagnetic case. After long range order vanishes, short range order still persist in the sublattices of system I, then Nèel temperature can be obtained from the equation (11) as in the case of ferromagnetism

$$T_N = \frac{\frac{1}{4} N g^2 \mu_B^2 \; (\beta + \gamma) \; S \; (S+1)}{3k} = - \frac{2 \; (J_{12} z_{12} + J_2 z_2) \; S \; (S+1)}{3k}$$

or

$$T_N = \frac{1}{4} \; (\beta + \gamma) \; C \qquad (12)$$

where C is a Curie constant defined as

$$C = \frac{N g^2 \mu_B^2 \; S \; (S+1)}{3k} \qquad (13)$$

The susceptibility above T_N can be derived by expanding Brillouin function in the equations (6) and (7), when external field is added to the molecular field, as

$$M_{I}^{\pm} = \frac{C}{4T} \; (H - \alpha M_{I}^{\mp} - \beta M_{II}^{\mp}) \qquad (14)$$

$$M_{II}^{\pm} = \frac{C}{4T} \; (H - \beta M_{I}^{\mp} - \gamma M_{II}^{\mp}) \qquad (15)$$

From (14) and (15), we obtain the susceptibilities of the sublattice I and II

$$\chi_I = \frac{M_I^{+} + M_I^{-}}{H} = \frac{1 - \frac{(\beta - \gamma) \; C}{4T}}{1 + \frac{(\alpha + \gamma) \; C}{4T} + \frac{C^2}{16 T^2} \; (\alpha \gamma - \beta^2)} \qquad (16)$$

and

$$\chi_{\mathrm{II}} = \frac{M^{\overset{+}{\mathrm{II}}} + M^{\overset{-}{\mathrm{II}}}}{H} = \frac{1 + \frac{(\alpha-\beta)\ C}{4T}}{1 + \frac{(\alpha+\gamma)\ C}{4T} + \frac{C^2}{16T^2}\ (\alpha\gamma-\beta^2)} \tag{17}$$

When the Nèel temperature is reached, only the sublattices of system II become disordered and paramagnetic, partial order may still persist in the sublattices of system I, the susceptibility of system I is smaller and $\chi \sim \chi_{\mathrm{II}}$ holds. When the temperature is raised, the sublattices of system I also become perfectly disordered, paramagnetic susceptibility is added, hence

$$\frac{C}{\chi_{\mathrm{II}}} \approx 2T + \frac{1}{2}\ (\beta-\gamma)\ C \tag{18}$$

and

$$\frac{C}{\chi_{\mathrm{I}}+\chi_{\mathrm{II}}} \approx 4T - \beta C \tag{19}$$

and the slope of the C/χ versus temperature curve decreases to one half of the slope in the range of lower temperatures. The Curie-Weiss constant is determineded as

$$\Theta = -\frac{1}{4}\ (\beta-\gamma)\ C, \qquad \Theta' = \frac{1}{4}\ \beta C \tag{20}$$

These results are coincident fairly well with the results of experimental work of Haseda *et al.*

The ordering energy of the lattice is the interaction of magnetic moment with the internal field, then

$$E = \frac{1}{2}\ \alpha\ M_{\mathrm{I}}^2 + \beta M_{\mathrm{I}}\ M_{\mathrm{II}} + \frac{1}{2}\ \gamma\ M_{\mathrm{II}}^2 \tag{21}$$

The specific heat is derived by differentiating the energy (21) with respect to temperature and using the equation of magnetization near the Curie point for ferromagnetism for sublattice magnetization, we get finite value. Above the Néel point, the specific heat of the disordered sublattices is zero, but there exist the specific heat of remaining partially ordered linear chain. But we may expect the finite jump of specific heat.

III. Final Comments

The calculation presented in the previous section is performed using the rather simple molecular field theory. In spite of this, Nèel temperature and the temperature dependency of susceptibility of two kinds of isomorphous crystals which contain dissimilar copper ions.

The specific heat anomaly take place at the Nèel point associated with the magnetic transition in the lower temperture range rather than in the higher temperature region of Onsager's theory of linear chain. To explain the specific heat curve quantitatively, elaborate calculation method, for example Bethe-Peierls- Weiss method etc. will be necessary.

References

1) J. J. Fritz and H. L. Pinch ; J. Am. Chem. Soc. **79** (1959) 3644.
2) T. Haseda and A. R. Miedema : Physica **27** (1961) 1102.
3) T. Watanabe and T. Haseda : J. Chem. Phys. **29** (1958) 1429.

4) T. H. Geballe and W. F. Giauque : J. Am. Chem. Soc. **74** (1952) 3513.
5) G. Duijckaerts : Soc. Roy. Scien. de Liège **10** (1951) 284.
6) A. R. Miedema, H. van Kempen, T. Haseda and W. J. Huiskamp : Physica **28** (1962) 119.
7) L. Onsager : Phys. Rev. **65** (1944) 117.
8) W. J. de Haas and C. J. Gorter : Comm. Kamerlingh Onnes Lab., Leiden No. 210d (1930).
9) R. J. Benzie and A. H. Cooke : Proc. Phys. Soc. **64** (1951) 124.
10) C. H. Beevers and H. Lipson : Proc. Roy. Soc. **A 146** (1934) 570.