Mem. Fac. Lit. & Sci., Shimane Univ., Nat. Sci., 1, pp. 23–29,
2 text-figs., March 15, 1968

Magnetic Properties of Doubly Antiferromagnetic Arrangements

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(Received November 30, 1967)

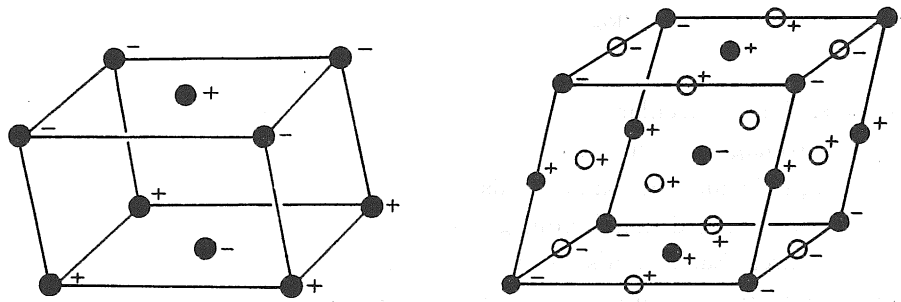
Abstracts. The molecular field treatment of the properties of magnetically dilute antiferromagnetic crystals are given. The system is composed of two kinds of magnetic ions or same kinds of magnetic ions with different environment and is arranged antiferromagnetically along a direction alternately in low temperature. Each kinds of antiferromagnetic lattices are again divided into oppositely directed sublattices. Transitions from ordered antiferromagnetic ground state to paramagnetic state is studied. Susceptibility versus temperature curve above the Néel point is like that of ferrimagnetics. Specific heat discontinuity are compared with Onsager's result.

1. Introduction

In this paper the theory of the magnetic properties of an alternant spin systems with two kinds of antiferromagnetic linear chain coupled mutually. Many compounds containing a low density of ions of iron-group transition metals exhibit paramagnetic susceptibilities in room temperatures. Measurements in low temperatures, however, revealed the existence of ordered states below a critical temperature. Néel[1] showed that negative exchange interactions in certain structures should give rise to a cooperative ordering of ionic magnetic moments. In the ordered state, the magnetic ions are so aligned that they form two or more spontaneously magnetised and interpenetrant sublattices whose magnetisations are differently oriented to give zero resultant magnetisation, so that the ordering does not reveal itself directly as in case of ferro and ferrimagnetism. In recent years this kind of ordering known as antiferromagnetism has been a great increase in number of materials, and it is probably the most kinds of magnetic order in the magnetically dilute compounds containing ions of the iron-group 3d transition series. In such crystals the magnetic ions are separated by the non-magnetic ions such as oxygen, halogen or sulfur ions. Superexchange effect through such intervening ions must be

responsible for the coupling between the magnetic ions.

Suppose that a set of one kind of alternant spin array (A) forms the sublattice (A', A''), The other kind of spins (B) forms sublattice (B', B''). The directions of magnetisation in these sublattices are assumed to be parallel or antiparallel to each other ; A', A'' represent the lattice of positive direction and B', B'' that of negative direction. Examples of medels of crystal lattices of this type are shown in Fig. 1. Molecular field approximation is applied to determine the properties of such crystals.



(a) (b)

Fig. 1. Examples of models of crystal lattice with four antiferromagnetic sublattices. (a) corner and base-centered spins have differant environment. (b) ●and ○represent two kinds of spins with different environment.

2. The Molecular Field Models and Curie Points

At absolute zero all sublattices are saturated magnetically. A metal ion in each sublattice behaves according to the molecular field hypothesis as though it were acted upon by an effective field, representing its interaction with the ions on each sublattice. The molecular fields acting on lattices A', A'', B', B'' may be written :

$$\begin{aligned} H_{A'} &= \alpha' M_{A'} + \alpha'' M_{A''} + \beta' M_{B'} + \beta'' M_{B''}, \\ H_{A''} &= \alpha'' M_{A'} + \alpha' M_{A''} + \beta'' M_{B'} + \beta' M_{B''}, \\ H_{B'} &= \beta' M_{A'} + \beta'' M_{A''} + \gamma' M_{B'} + \gamma'' M_{B''}, \\ H_{B''} &= \beta'' M_{A''} + \beta' M_{A''} + \gamma'' M_{B'} + \gamma' M_{B''}, \end{aligned} \qquad (1)$$

where the Weiss field coefficients α', α'', β', β'', γ', γ'' are a measure of the strength of the exchange interaction between the spins of an ion of each sublattice. Thus, in the cases in which we are interested these values are negative (antiferromagnetic). Yafet and Kittel[2] discussed the possible types of magnetic ordering of ferrites by means of the molecular field treatment and showed that ferrimagnetic antiparallel arrangement, triangular arrangement and doubly antiferromagnetic arragement are possible ground state of spins, and

provided the magnetic ions are assumed to be distributed among the A and B sites of the spinel structure for

$$\beta' = \beta'' = -n.$$

Let C_A and C_B denote the molal Curie constant for sublattice A and B. In the disordered state the magnetic moments are given by :

$$M_{A'} = \frac{C_{A'}}{2T} H_{A'} \quad ; \quad M_{B'} = \frac{C_{B'}}{2T} H_{B'} . \tag{2}$$

These are derived by taking the limiting behavior of the Brillouin function at very small arguments, because the magnetisations M's and therefore H's, are always small above the temperature. The vanishing of the characteristic determinant of the following four linear homogeneous equations yields the Curie points :

$$\begin{aligned}
&\alpha_1 M_{A'} + \alpha_2 M_{A''} - M_{B'} - M_{B''} = (2T/\lambda Cn) M_{A'} \\
&\alpha_2 M_{A'} + \alpha_1 M_{A''} - M_{B'} - M_{B''} = (2T/\lambda Cn) M_{A''} \\
&-M_{A'} - M_{A''} + \gamma_1 M_{B'} + \gamma_2 M_{B''} = (2T/\mu Cn) M_{B'} \\
&-M_{A'} - M_{A''} + \gamma_2 M_{B'} + \gamma_1 M_{B''} = (2T/\mu Cn) M_{B''}
\end{aligned} \tag{3}$$

where $\alpha' = n\alpha_1$, $\alpha'' = n\alpha_2$, $\gamma' = n\gamma_1$, $\gamma'' = n\gamma_2$, (α_1, α_2, γ_1, γ_2 are negative (antiferromagnetic) and $C_{A'} = \lambda C$, $C_{B'} = \mu C$.

The four solutions for T_c are :

$$\begin{aligned}
T_{c1} &= \frac{1}{2} Cn\mu(\gamma_1 - \gamma_2), \\
T_{c2} &= \frac{1}{2} Cn\lambda(\alpha_1 - \alpha_2), \\
T_{c3} &= \frac{1}{2} Cn\{\alpha\lambda + \beta\mu \pm [(\alpha\lambda - \beta\mu)^2 + 4\lambda\mu]^{\frac{1}{2}}\},
\end{aligned} \tag{4}$$

where $\alpha_1 + \alpha_2 = 2\alpha$, $\gamma_1 + \gamma_2 = 2\gamma$.

The $-$ sign in T_{c3} gives a negative value and must be rejected. Again, if $\gamma_1 = \gamma_2$ and $\alpha_1 = \alpha_2$, $T_{c1} = T_{c2} = 0$, and T_{c3} is left. This is the ordinary Curie temperature. T_{c1} and T_{c2} are the antiferromagnetic Curie points of lattice B and A, respectively. The type of ordering below upper Curie points among these is, ferrimagnetic for T_{c3} and antiferromagnetic in the corresponding lattice for T_{c1} and T_{c2}. Yafet and Kittel examined the highest T_c among the solutions, depending on the ratio λ/μ and the molecular field coefficients, several cases occur.

For the case $\alpha_2\gamma_2 > 1$, the upper Curie point is at either T_{c1} or T_{c2}. Suppose it is at T_{c1}. Then the B lattice becomes ordered first. At T_{c2}, the A lattice which still sees no field from B, also becomes ordered antiferromagnetcally and no other transition occurs down to 0°K, that is, the doubly antiferroma-

gnetic arrangement is stable. Even for the case $\alpha_2\gamma_2<1$, antiferromagnetic arrangement is a possible case. The antiferromagnetic order, therefore, is assumed to be the ground state.

3. Susceptibility above the Curie Point

The molecular field calculation also leads to expression for the paramagnetic susceptibility above the Curie (Néel) temperature. Solving (3) for $M_{A'}$, $M_{A''}$, $M_{B'}$ and $M_{B''}$ including now the applied field H, we can derive $1/\chi = (M_{A'}+M_{A''}+M_{B'}+M_{B''})/H$. By simple but lengthy algebra, the following expression for the inverse volume susceptibility (assuming that H is parallel to the prefered axis of the magnetisations of each sublattice)

$$\frac{1}{\chi}=\frac{T}{C}+\frac{1}{\chi_0}-\frac{\sigma}{T-\theta} \tag{5}$$

where the constants C, χ_o , θ and σ are the following functions of the parameter of the theory n, α, β, C_A and C_B (or λ, μ, C),

$$C=C_A+C_B\,;\ \theta=Cn\lambda\mu(1-\alpha-\gamma)=\frac{nC_AC_B}{C}(1-\alpha-\gamma) \tag{6}$$

$$\frac{1}{\chi_0}=\frac{4\theta}{Cn}-\frac{4(\lambda\alpha+\mu\gamma)}{Cn\lambda\mu}\ ;\ \sigma=\frac{1}{2}Cn^2\lambda\mu\{\lambda(2\alpha-1)-\mu(2\gamma-1)\}$$

$1/\chi$ versus T curve coincide with that of ferrimagnetism. The significant point about this expression for χ is that it shows a hyperbolic dependence on temperature and is convex above the Curie point. For $T\gg T_c$ the curve has an asymptote

$$\lim_{T\to\infty}\frac{1}{\chi}=\frac{T+\Theta}{C}\qquad\left(\frac{1}{\chi_0}=\frac{\Theta}{C}\right) \tag{7}$$

which is characteristic for two sublattice antiferromagnetism.

4. Magnetic Transitions at T_{c1} and T_{c2}

In the ordered state the exchange energy is simply the self-energy of the sublattices in their molecular fields, i. e.

$$E=-\tfrac{1}{2}\sum\boldsymbol{H}_i\cdot\boldsymbol{M}_i=-n[\alpha_1M^2{}_{A'}+\alpha_2M_{A'}\cdot M_{A''}+\gamma_1M^2{}_{B'}+\gamma_2M_{B'}\cdot M_{B''}]$$

in the antiferromagnetic arrangements

$$=-n[(\alpha_1-\alpha_2)M^2{}_{A'}+(\gamma_1-\gamma_2)M^2{}_{B'}] \tag{8}$$

The magnetic contribution to the specific heat, therefore, noticing that the exchange energy is the magnetic part of the thermodynamic internal energy, is

$$C=\frac{dE}{dT}=-2n(\alpha_1-\alpha_2)M_{A'}\frac{dM_{A'}}{dT}-2n(\gamma_1-\gamma_2)M_{B'}\frac{dM_{B'}}{dT} \qquad (9)$$

which is related to the M and the gradient of the M versus T curve. Whenever there is a strong variation of M with temperature a correspondingly high specific heat should be expected. In particular sharp maxima in specific heat are expected near Néel points, T_{c1} and T_{c2}.

The $1/\chi$ versus T curve is convex above T_{c2}. As the temperature is lowered below this, ordering will arise in the sublattices A' and A'' in the half numbers of magnetic ions. The other spins on B' and B'' are still in paramagnetic state and contribute to the paramagnetic susceptibility. In addition to this susceptibility of ordered state ($\chi_\perp$ or $\chi_{/\!/}$ or powder susceptibility) of the half number of spins arise. The $1/\chi$ vs. T curve is continuous in this point but bent discontinuously.

At the lower Curie point T_{c1} the whole spins will be in order and also the curve will be bent. The behavior is shown in Fig. 2.

The above situations are based on the assumption that A and B antiferromagnetic lattices will arrange separately in different Curie point T_{c1} and T_{c2}. Even when the B lattice becomes disordered, we imagine that A lattice can persist solely ordered state. On the contrary, when the exchange interaction among B lattice ions coupled through the A lattice ions, if the B lattice become disordered, the A lattice can not persist ordered state, because even if the exchange interaction among A lattice along a line antiferromagnetic linear chain cannot persist long-range order by Onsager's theory.[3] Hence, there will be no ordered state between T_{c1} and T_{c2}, and the inverse susceptibility curve become straight. The slope is $\mu/(\lambda+\mu)$ times that of the envelope in paramagnetic region. (if $\lambda=\mu$ the slope is twice as large in the paramagnetic region)

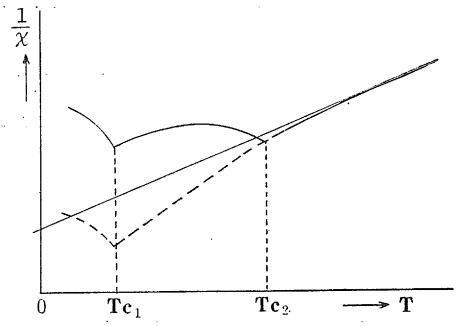


Fig. 2. Expected 1/ vs T curve.
——sublattice A and B ordered separately.
·····antiferromagnetic linear chain.

In the case where A and B sublattices can preserve order separately, two peaks of specific heat must be observed. In the linear chain model, only one specific heat may be possible corresponding the lower Curie point T_{c1}.
For different Weiss coefficient β', β'', the four solutions for T_c are complicated expresions containing six parameters. T_{c1} and T_{c2} will be modefied. Molecular field models represent a first order approximation to the calculation of the equilibrium properties of an ordered magnetic crystal, and give rough order for the Curie temperature.

5. Comparison with Experiment

Only few examples are known for the doubly antiferromagnetic crystals. Such a crystal was first found in the paramagnetic resonance experiment. $CuSO_4 \cdot 5H_2O$[4)5)] and $Mn(COOH)_2 \cdot 2H_2O$[6)] crystal is considered to behave as an isolated linear chain in the liquid helium temperature. Specific heats and susceptibilities are measured also in $CuSO_4 \cdot 5H_2O$ and $CuSeO_4 \cdot 5H_2O$. The results are considered to coincide qualitatively with the $1/\chi$ vs. T curve. The discontinuity in the specific heat expected at the Neél point by the molecular field approximation differs with experiment. The magnetic contribution does not fall immediately to zero as the temperature increases through the Neél point. There is a distinct tails which disappear slowly with temperature. Below the Néel point the specific heat will varies more rapidly than the molecular field model predicts. For these short-range order effect, advanced statistical approximations are needed.
Specific heat peak arise only below 0.01°K. The result also seams to assert the presence of linear chain. The specific heat curve has a broad maximum which correspond to the Onsager's result. Onsager showed that the linear lattice with Ising interactions can not have long-range order and only short-range order can exist. The specific curve may be expected. But the specific heat peak can not be expected for the two-dimentional Ising crystals. It may correspond to T_{c1} Cu^{2+} ions with spin $S = \frac{1}{2}$ well correspond to the Ising model. But in these ciystals, the magnetic ions are seqarated by many nonmagnetic ions and the the exchange interactions are very week. The ordered state will occur near 0°K. Recently, doubly antiferromagnetic crystal is expected in Cr_2F_5. This crystal is not so magnetically dilute and higher Curie temperature is expected. The crystal will have the partial order in relatively higher temperatures. Many data is hoped for the expected doubly antiferromagnetic crystals.

The author wishes to express his thanks to Professor E. Asami for his continual encouragement.

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