Diagram of corresponding states of easy-axis antiferromagnets

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Experimental investigations are made of the effect of high hydrostatic pressure (up to 15 kbar) on the spin-flop transition field ($H_{\rm tr}$), the Néel temperature (T_N), and the triple-point parameters (T_t,H_t) of the easy-axis antiferromagnets $CuCl_2 \cdot 2H_2O$ and $CuCl_2 \cdot 2D_2O$. The functional relations $H_{\rm tr}/H_t = f(T/T_t)$ are the same for both the antiferromagnets studied and are independent of the value of the hydrostatic pressure; that is, a law of corresponding states holds. Analytical expressions are obtained for the dependence of $H_{\rm tr}$ on pressure and temperature. The limits of applicability of the law of corresponding states are discussed.

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1. A more profound understanding of the dependence of the magnetic properties of solids on temperature can be attained by study of the behavior of magnetic materials under the influence of external actions. One of these actions is hydrostatic pressure, which, without changing the crystalline and magnetic symmetry of the antiferromagnet under investigation (up to 15 kbar in the present research), makes it possible to influence substantially the values of such characteristics of the crystal as the interatomic distances, the energy of exchange interaction, the anisotropy, and so on. Thus study of the magnetic characteristics of a magnet at high pressures, together with information about its structure and elastic properties, enables one to investigate the influence of the structural parameters of the crystal on its magnetic properties.

As is well known, in easy-axis antiferromagnets, in a magnetic field parallel to the axis of easy magnetization, flipping of the magnetic sublattices [a spin-flop (SF) transition] occurs in fields $H_{\rm tr} \sim (H_{\rm a} H_{\rm exc})^{1/2}$, where $H_{\rm exc}$ is the exchange field and $H_{\rm a}$ is the anisotropy field.[1] Thus the change of the SF transition field is determined by the change of the values of the exchange and anisotropy interactions under the influence of hydrostatic pressure. Experimental investigations of the effect of pressure on the SF transition field were begun in Refs. 2 and 3, where, by the method of antiferromagnetic resonance, a strong dependence of $H_{\rm tr}$ on the value of the hydrostatic pressure was detected in $CuCl_2 \cdot 2H_2O$. In Ref. 4, an investigation was made of the effect of hydrostatic pressure on the course of the temperature variation of the SF transition field in $CuCl_2 \cdot 2H_2O$. It was observed that the functional dependence $h_{\rm tr} = f(t)$, where $h_{\rm tr} = H_{\rm tr}/H_t$ and $T = T/T_t$, and where H_t and T_t are the triple-point parameters, is independent of the value of the pressure, i.e. a *law of corresponding states* holds. Later[5] it was observed that this law holds also in $CuCl_2 \cdot 2D_2O$. It was shown that the functional relation $h_{\rm tr} = f(t)$ is the same for $CuCl_2 \cdot 2H_2O$ and for $CuCl_2$, i.e. a law of corresponding states likewise holds.[6]

The present paper gives the results of an investigation of the effect of high hydrostatic pressure (up to 15 kbar) on $H_{\rm tr}(t)$,T_N, and the triple-point parameters for antiferromagnetic single crystals of $CuCl_2 \cdot 2H_2O$ and $CuCl_2 \cdot 2D_2O$. A calculation of $H_{\rm tr}(T)$ is made within the framework of the molecular-field-theory approximation. A theoretical interpretation of the law of corresponding states is given, and the limits of its applicability are determined.

2. In the molecular-field-theory approximation, the expression for the free energy of a two-sublattice antiferromagnet in an external field H, parallel to the axis of easy magnetization, has the following form[7]:

$$F=fN=\{\lambda\sigma_1\sigma_2+{}^1/_2\delta(\sigma_1{}^2+\sigma_2{}^2)-{}^1/_2\beta(\sigma_{1z}{}^2+\sigma_{2z}{}^2) -\beta'\sigma_{1z}\sigma_{2z}-\mu H(\sigma_{1z}+\sigma_{2z})-T[\tilde{S}(\sigma_1)+\tilde{S}(\sigma_2)]\}N. \quad (1)$$

Here $\boldsymbol{\sigma}_1 = \mathbf{M}_1(T)/M_0$ and $\boldsymbol{\sigma}_2 = \mathbf{M}_2(T)/M_0$ are the relative magnetizations of the sublattices; λ and δ are the exchange constants corresponding to the intersublattice and intrasublattice interactions; β and β' are the intrasublattice and intersublattice anisotropy constants; μ is the magnetic moment of an atom of a sublattice at $T = 0$, T is temperature; $\tilde{S}$ is the sublattice entropy, which in the molecular-field-theory approximation is determined by the relation

$$d\tilde{S}(\sigma_i)/d\sigma_i=-B_s^{-1}(\sigma_i),$$

where $B_s^{-1}(\sigma_i)$ is the inverse Brillouin function and s is the spin of an atom; N is the number of magnetic ions in each of the sublattices of the antiferromagnet; the Z axis coincides with the direction of easy magnetization.

The effect of hydrostatic pressure on the magnetic properties of the antiferromagnet manifests itself indirectly: under the influence of pressure, the crystal lattice becomes strained, and because of magnetostrictive interaction these strains change the magnetic characteristics of the system. In order to allow for the effect of pressure on the equilibrium parameters of the antiferromagnet, we introduce into the expression (1) for the free energy the energy $E_{\rm m.el}$ of magnetoelastic interaction, the energy E_σ of external stresses, and the internal elastic energy $E_{\rm el}$ of the crystal:

$$E_{\rm el} = {}^1/_2 C_{ijkl} U_{ij} U_{kl},$$

where U_{ij} is the elastic-strain tensor and C_{ijkl} is the elastic-constant tensor;

$$E_{\rm m.el} = d_{ijkl} U_{ij} (\sigma_{1k}\sigma_{1l}+\sigma_{2k}\sigma_{2l}) + d'_{ijk}{}^{l} U_{ij}\sigma_{1k}\sigma_{2k},$$

where d_{ikjl} and d'_{ijkl} are the magnetostriction-coefficient ten-

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sors, and where σ_{1k} and σ_{2k} are the components of the vectors $\boldsymbol{\sigma}_1$ and $\boldsymbol{\sigma}_2$;

$$E_d = U_{ij}\sigma_{ij},$$

where σ_{ij} is the external-stress tensor (for hydrostatic compression, $\sigma_{ij} = P\delta_{ij}$, where P is the value of the pressure).

The structure of the tensor C_{ijkl} is determined by the symmetry of the crystal. For the antiferromagnets investigated in this paper (of the rhombic system), 9 components of the tensor C_{ijkl} are nonzero; the 6 components of the form C_{iikk}, and also C_{1212}, C_{1313}, and C_{2323}. The tensors d_{ijkl} and d'_{ijkl} have the same structure. The stable states of the antiferromagnet are determined by minimization of the free energy with respect to the internal parameters of the system: the components of the vectors $\boldsymbol{\sigma}_1$ and $\boldsymbol{\sigma}_2$ and of the tensor U_{ij}. Supposing, however, that $E_{\rm m.el}$ is much smaller than the magnetic energy of the system, one can determine at once the components of the strain tensor

$$U_{ij} = Pa_i\delta_{ik},$$

$$(a_1 = s_{11}+s_{31}+s_{21};\quad a_2 = s_{22}+s_{21}+s_{23};\quad a_3 = s_{33}+s_{23}+s_{31}), \quad (2)$$

where s_{ij} is the elastic-modulus tensor.[8]

As is well known (see, for example, Ref. 9), in this case the expression for the free energy can be reduced to the form (1) corresponding to a redetermination of the molecular-field constants:

$$\lambda \to \lambda + Pd'_{1111}a_1, \qquad \delta \to \delta + Pd_{1111}a_1,$$
$$\beta \to \beta + P(d_{1111}a_1 - d_{3333}a_3), \quad \beta' \to \beta' + P(d'_{1111}a_1 - d'_{3333}a_3). \quad (3)$$

The investigation of the free energy (1) of the antiferromagnet is similar to that carried out in Refs. 1, 7, and 10. Without dwelling on the calculations, we shall give the results of these papers that are necessary hereafter. To the minimum of the function (1) corresponds an arrangement of the vectors $\boldsymbol{\sigma}_1$, $\boldsymbol{\sigma}_2$, and $\mathbf{H}$ in a single plane. When $\beta - \beta' > 0$, anisotropy of the easy-axis type occurs in the antiferromagnet.[1] We shall furthermore suppose that $\beta > 0$. In this case, to a stable state of the magnet, over the whole range of existence of an ordered state, there corresponds either an antiferromagnetic (AF) phase ($\theta_1 = 0$, $\theta_2 = \pi$, where θ_i is the angle between the direction of the axis of easy magnetization and $\boldsymbol{\sigma}_1$) or to a SF phase ($\theta_1 = -\theta_2 = \theta$, $\sigma_1 = \sigma_2 = \sigma$); i.e., the SF transition occurs in the form of a phase transition of first order.[1,7] The SF transition field $H^0_{\rm tr}$ at $T=0$, the triple-point parameters T_t, H_t, and σ_t, and also T_N are determined by the following relations[1,7,10]:

$$T_N = \frac{(s+1)}{3s}(\lambda - \delta + \beta - \beta'), \quad (4)$$

$$T_t = \frac{(s+1)}{3s}\left(\lambda - \delta - \frac{\beta - \beta'}{2}\right), \quad (5)$$

$$(\mu H_{\rm tr}{}^0)^2 = (\beta - \beta')(2\lambda - \beta - \beta'), \quad (6)$$

$$\mu H_t = (2\lambda - \beta - \beta')\sigma_t, \quad (7)$$

$$\sigma_t = \left[\frac{5}{3}\frac{(s+1)^2}{(s+1)^2+s^2}\frac{(\beta-\beta')}{(\lambda-\delta)}\right]^{1/2}. \quad (8)$$

The expressions for $T_N(P)$ and $T_t(P)$ are obtained by substitution of (3) in (4) and (5):

$$T_N(P) = T_N{}^0 + (d_{3333} - d_{3333})a_3P, \quad (9)$$

$$T_t(P) = T_t{}^0 + {}^1/_2[3(d'_{1111} - d_{1111})a_1 - (d'_{3333} - d_{3333})a_3]P. \quad (10)$$

We shall discuss in more detail the derivation of the expression for the temperature dependence $H_{\rm tr}(T)$ of the SF transition field. The relation $F_{\rm AF} = F_{\rm SF}$, together with the equations for the equilibrium values of the parameters of the magnet in the individual phases, constitutes a system of transcendental equations for $H_{\rm tr}(T)$ and the sublattice magnetizations in the individual phases on the SF transition line. Solutions of this system are usually carried out by numerical methods.[7,10,11] But the case of practical importance is that in which $E_{\rm exc} \gg E_{\rm a}$. It seems possible to carry out an expansion of the free energy in the parameter $\varepsilon = (\beta - \beta')/(\lambda - \delta)$ (usually $\varepsilon = 10^{-2}$–10^{-4}[Ref. 7]) and to obtain an analytic expression for $H_{\rm tr}(T)$.

The free energy of the antiferromagnet in the SF phase has the form

$$f_{\rm SF} = \lambda\sigma^2\cos 2\theta$$
$$-(\beta+\beta')\cos^2\theta - 2\mu H\sigma\cos\theta + \delta\sigma^2 - 2T\tilde{S}(\sigma). \quad (11)$$

After minimization with respect to $\cos\theta$, the energy of $f_{\rm SF}$ simplifies considerably:

$$f_{\rm SF} = -(\lambda-\delta)\sigma^2 - 2T\tilde{S}(\sigma) - (\mu H)^2/(2\lambda - \beta - \beta'). \quad (12)$$

The free energy of the antiferromagnet in the collinear phase is conveniently expressed in terms of linear combinations of the sublattice magnetizations,

$$\sigma_1 = \sigma_+ + \sigma_-; \quad \sigma_2 = \sigma_+ - \sigma_-,$$

namely,

$$f_{\rm AF} = -(\lambda - \delta + \beta - \beta')\sigma_+{}^2 + (\lambda + \delta - \beta - \beta')\sigma_-{}^2$$
$$-2\mu H\sigma_- - T[\tilde{S}(\sigma_+ + \sigma_-) - \tilde{S}(\sigma_+ - \sigma_-)]. \quad (13)$$

In fields close to the SF transition field,

$$H \sim (H_{\rm a}\cdot H_{\rm exc})^{1/2} \sim \varepsilon^{1/2}H_{\rm exc} \ll H_{\rm exc}.$$

It follows from the expression (13) that in this range, the equilibrium values of $\sigma_- \sim H/H_{\rm exc}\varepsilon^{1/2} \ll 1$. After expansion as a series in σ_- and minimization of (13) with respect to this parameter, we get the following expression:

$$f_{\rm AF} = -(\lambda-\delta)\sigma_+{}^2 - 2T\tilde{S}(\sigma_t)$$
$$-[(\beta-\beta')\sigma_+{}^2 + (\mu H)^2/(\lambda + \delta - \beta - \beta' - T\tilde{S}''(\sigma_+))]. \quad (14)$$

On equating (12) to (14) and dropping terms proportional to ε, we get the following expression[12,13] for $H_{\rm tr}(T)$:

$$\mu H_{\rm tr}(T) = [2\lambda(\beta-\beta')]^{1/2}\left[1 + \frac{2\lambda}{-T\tilde{S}'' - \lambda + \delta}\right]^{1/2}\sigma(T). \quad (15)$$

In the relative units $h_{\rm tr} = H_{\rm tr}/H_t$ and $t = T/T_t$, the expression (15) takes the form

$$h_{\rm tr}(t) = \left[\frac{3}{5}\frac{(s+1)^2+s}{(s+1)^2}\right]^{1/2}$$

$$\times\left\{\frac{\lambda-\delta}{2\lambda} + \left[\frac{(s+1)}{3s}t\tilde{S}'' - 1\right]^{-1}\right\}^{1/2}\sigma(t); \quad (16)$$

$\sigma(t)$ is determined from the equation $\partial f_{SF}/\partial\sigma = 0$, which gives

$$\sigma(t) = B_s[3s\sigma/(s+1)t]. \quad (17)$$

Since the triple point T_t lies on a line of phase transitions of second order, the formula for $h_{tr}(t)$ is inapplicable when $(T - T_t)/T_t \ll 1$, and in order to determine the SF transition field in this neighborhood it is necessary to use similitude theory.[14]

The molecular-field constants enter the expression (16) in the form of the parameter $k = (\lambda - \delta)/2\lambda$. The exchange constants vary with pressure less than do the anisotropy constants (see below); furthermore, the parameters λ and δ occur in k in the form of a ratio. This all leads to a weak dependence of k on pressure. In this case, the relation (16) is the mathematical formulation of the law of corresponding states.

It should be noted that the law of corresponding states has a wider sphere of application. It is evident from the relation (16) that the functional relations $h_{tr} = f(t)$ coincide for antiferromagnets for which

1) the spins of the magnetic ions are the same;

2) the parameter k, which determines the ratio between the values of the exchange interactions within and between sublattices, has nearly equal values. In particular, the law of corresponding states is fulfilled for the group of antiferromagnets with magnetic ion Cu^{++} ($s = 1/2$):

$CuCl_2 \cdot 2H_2O$ (T_N=4.36 K), $CuCl_2 \cdot 2D_2O$ (T_N=4.25 K), $CuCl_2$ (T_N=23.9 K), $LiCuCl_3 \cdot 2H_2O$ (T_N=4.4 K).

Figure 1 shows the relation $h_{tr}(t)$ for these crystals. The experimental data are taken from Refs. 5, 6, and 15.

Fulfillment of the law of corresponding states can be expected in antiferromagnets with the same spin of the magnetic ion, and in which the antiferromagnetic exchange interaction between sublattices greatly exceeds the exchange interaction within sublattices ($\lambda \gg \delta$). In this case $k = 1/2$.

In the layered antiferromagnets, for example of the group $(C_nH_{2n+1}NH_3)_2 \cdot CuX_4$, where n = 1, 2, 3, 4, 5, 6, 10 and X = Cl or Br,[16] the value of the ferromagnetic interaction within sublattices greatly exceeds the antiferromagnetic interaction between sublattices ($-\delta \gg \lambda$). From the relations (6) and (15) it follows that for such antiferromagnets

$$H_{tr}(T)/H_{tr}(0) = \sigma(t),$$

i.e., a law of corresponding states again holds.

We note that the relation (16), which formulates the law of corresponding states, was obtained by expansion of the free energy of a two-sublattice antiferromagnet with respect to a small parameter, in the molecular-field approximation. Within the framework of this approximation, the law of corresponding states holds to within terms proportional to ε.

3. Experimental investigations were made on antiferromagnetic single crystals of $CuCl_2 \cdot 2H_2O$ and $CuCl_2 \cdot 2D_2O$. High hydrostatic pressure was produced in an independent chamber (up to 15 kbar) over the temperature interval 1.6–5.4 K. The pressure measurement was made on the basis of the pressure dependence of the superconducting transition temperature, with accuracy $\pm$ 100 bar. The scheme of the apparatus and the method of making the measurements are given in detail in Ref. 17. The results of the investigation of $T_N(P)$ and $T_t(P)$ are shown in Fig. 2. In complete agreement with the deductions of the theory, a linear dependence of T_N and T_t on pressure is observed. It follows from the relations (3) and (4) that the different slope of the lines $T_N(P)$ and $T_t(P)$ in Fig. 2 is caused by the different pressure dependence of the exchange and anisotropy constants.

Measurement of the value of H_{tr} was carried out by two methods: on the basis of the character of the proton resonance[18] in the vicinity of H_{tr}, and on the basis of an investigation of the intensity of the anomalous signal[19] observed in this region. The two methods gave good agreement of the results. The accuracy of measurement of the magnetic field

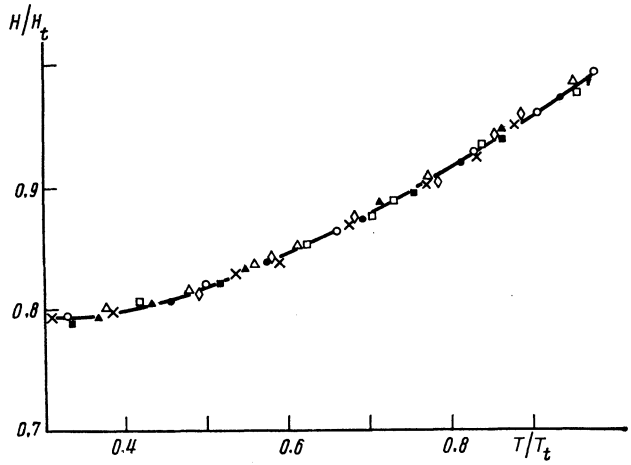

FIG. 1. Diagram of corresponding states for the antiferromagnets $CuCl_2 \cdot 2H_2O$ (● $P = 0$, ◇ 5.3 kbar, ○ 10 kbar), $CuCl_2 \cdot 2D_2O$ (□ $P = 0$, △ 6.9 kbar, × 15 kbar), $CuCl_2$ (▲), and $LiCuCl_3 \cdot 2H_2O$ (■).
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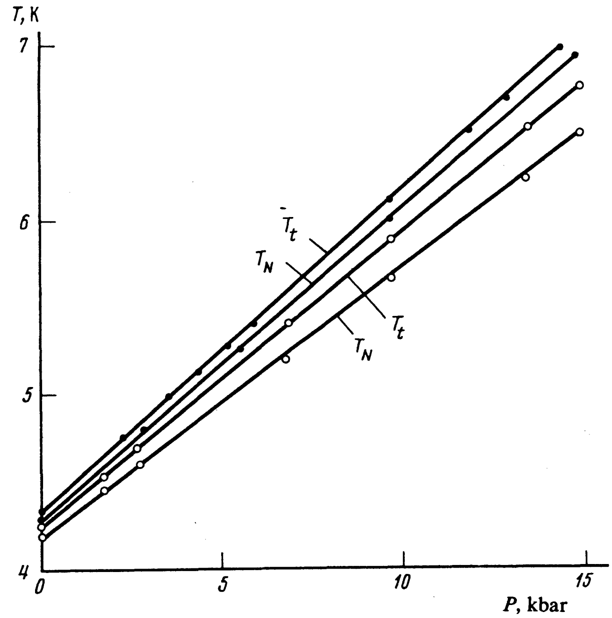

FIG. 2. Pressure dependence of Néel temperature T_N and triple-point temperature T_t for the antiferromagnets $CuCl_2 \cdot 2H_2O$ (●) and $CuCl_2 \cdot 2D_2O$ (○).

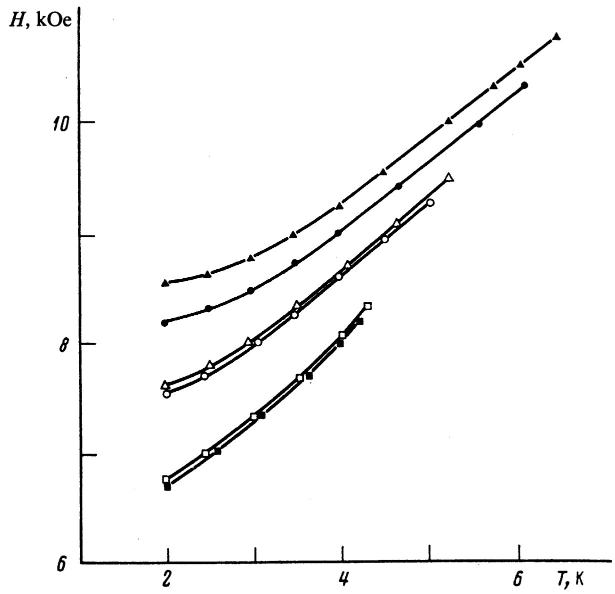

FIG. 3. Temperature dependence of the spin-flop transition field H_{tr} for various pressures, for the antiferromagnets $CuCl_2 \cdot 2D_2O$ (▲ 15 kbar, △ 6.9 kbar, ■ $P=0$) and $CuCl_2 \cdot 2H_2O$ (● 10 kbar, ○ 5.3 kbar, □ $P=0$). Ordinate label: H, kOe

is ± 1 Oe. Figure 3 shows the $H_{tr}(T)$ relation for various pressures. It is characteristic of both antiferromagnets investigated that the function $h_{tr}(t)$ is independent of the value of the hydrostatic pressure over the whole range of variation of P investigated (0–15 kbar); i.e., a *law of corresponding states* holds (Fig. 1).

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