

Magnetic Properties of the Antiferromagnet $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

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(Received 23 September 1964)

We use a Green-function technique to derive expressions for the Néel temperature and the susceptibility above the Néel temperature for the case of an antiferromagnet with an antiferromagnetic nearest-neighbor interaction and a ferromagnetic next-nearest-neighbor interaction. Comparing the results thus obtained with the experimental data on $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, we find for the nearest- and next-nearest-neighbor exchange interaction constants, respectively, $J_1/k_B = 6.78$ °K and $J_2/k_B = 0.89$ °K, corresponding to a ratio $J_2/J_1 = 0.131$ which is close to an estimate by Marshall. The value of J_1 agrees also reasonably well with the value obtained from low-temperature perpendicular susceptibility measurements. We also give an expression for the critical field necessary for spin-flopping and estimate that this field changes by only about 10% between absolute zero and the Néel temperature.

1. INTRODUCTION

IN recent years, Green-function methods have been used by many authors to discuss both ferromagnetism and antiferromagnetism, following the work by Bogolyubov and Tyablikov.¹ For a general discussion of this method we refer to the literature.² Recently, two of the present authors³ have extended this method to discuss the susceptibility of an anisotropic Heisenberg antiferromagnet with nearest-neighbor interactions, while the third author has, on the one hand,⁴ discussed antiferromagnetism in layer structures, considering both nearest-neighbor and next-nearest-neighbor interactions, and, on the other hand,⁵ pointed out that for lattices corresponding essentially to weakly interacting layers (such as FeCl_2 and CoCl_2) or to weakly interacting chains (such as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) molecular field and cluster approximation methods are not suitable, since they do not adequately cope with one- or two-dimensional systems at temperatures near or below the Néel temperature, while Green function methods can deal with all temperatures.

In the present paper we shall be concerned with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Its Néel temperature is⁶ 4.33°K and the spins of the copper ions are arranged in layers parallel within the a - b plane and along the a axis, but antiparallel in adjacent planes.

Marshall⁷ was the first to treat this substance theoretically, using a cluster method and the Ising model. As an isolated antiferromagnetic chain cannot support long-range order, he assumed that the strong antiferromagnetic coupling between nearest neighbors (the chains along the c axis) led to antiferromagnetic chains which were stabilized by a (weaker) ferromagnetic next-nearest-neighbor coupling in the a - b plane. From the susceptibility measurements he estimated that the ratio J_2/J_1 of the next-nearest-neighbor to the nearest-neighbor exchange constants was about 0.138. Nagai⁸ applied a cluster method to the Heisenberg model and found $J_2/J_1 = 0.55$, while Oguchi,⁹ using a generalized molecular field method, found a value of 0.3.

2. CALCULATION OF THE EXCHANGE CONSTANTS

We shall use the following Hamiltonian to describe $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$:

$$\mathcal{H} = 2 \sum_{nn} J_1 (\mathbf{S}_i \cdot \mathbf{S}_j) - 2 \sum_{nnn} J_2 (\mathbf{S}_i \cdot \mathbf{S}_k) - g\mu H \sum_i S_{iz}, \quad (1)$$

where the first sum is over nearest-neighbor pairs, the second sum over next-nearest-neighbor pairs, and the third sum over all the spins in the lattice. The various terms leading to anisotropy in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ are all small and can to a good approximation be neglected.

As in Ref. 3 (we use as far as possible the same notation as in that paper), we denote spins on one sublattice by \mathbf{g} and those on the other sublattice by \mathbf{f} , and the corresponding magnetizations by $\langle S_+ \rangle$ and $\langle S_- \rangle$. As we are here dealing with the spin- $\frac{1}{2}$ case, the situation is simpler than the general case, considered in Ref. 3. Using the normal Green function method approach and the Bogolyubov-Tyablikov decoupling,^{3,4} we find the following expressions for the spin correlation functions

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$(S^\pm = S_x \pm iS_y)$:

$$\langle S_{g'}^- S_{g'}^+ \rangle = \frac{\langle S_+ \rangle}{N} \sum_{\kappa} e^{i[\kappa \cdot (\mathbf{g}-\mathbf{g}')]}$$

$$\times \left\{ \left[\frac{1}{e^{\beta E_1} - 1} + \frac{1}{e^{\beta E_2} - 1} \right] + \frac{2(J_1 z + J_2 z') (\langle S_+ \rangle - \langle S_- \rangle)}{E_1 - E_2} \right\}, \quad (2)$$

$$\langle S_{g'}^- S_{f'}^+ \rangle = \frac{\langle S_+ \rangle \langle S_- \rangle}{N} \sum_{\kappa} e^{i[\kappa \cdot (\mathbf{g}-\mathbf{f}')]}$$

$$\times \frac{4J_1 z' \gamma_{\kappa}}{E_1 - E_2} \left[\frac{1}{e^{\beta E_1} - 1} - \frac{1}{e^{\beta E_2} - 1} \right], \quad (3)$$

where $\beta = 1/k_B T$ (k_B : Boltzmann's constant; T : absolute temperature), where the summations are over the N values of the reciprocal lattice vector κ in the first Brillouin zone, where E_1 and E_2 are the solutions of

$$[E - g\mu H + 2J_1 z \langle S_+ \rangle - 2J_2 z' \langle S_- \rangle (1 - \mu_{\kappa})] \times [E - g\mu H + 2J_1 z \langle S_- \rangle - 2J_2 z' \langle S_+ \rangle (1 - \mu_{\kappa})] - 4J_1^2 z^2 \gamma_{\kappa}^2 \langle S_+ \rangle \langle S_- \rangle = 0, \quad (4)$$

where z and z' are the numbers of nearest and next-nearest neighbors, respectively, and where

$$\gamma_{\kappa} = \frac{1}{z} \sum_{n} e^{i(\kappa \cdot \delta)}, \quad \mu_{\kappa} = \frac{1}{z'} \sum_{n'n''} e^{i(\kappa \cdot \delta')}. \quad (5)$$

Putting $\mathbf{g} = \mathbf{g}'$ and $H = 0$ in (2), we find for the sublattice magnetization S_0 below the Néel temperature

$$\frac{1}{S_0} = \frac{1}{N} \sum_{\kappa} \frac{4S_0 [J_1 z + J_2 z' (1 - \mu_{\kappa})]}{E_0} \coth \frac{1}{2} \beta E_0, \quad (6)$$

where

$$E_0 = 2S_0 \left[\{J_1 z + J_2 z' (1 - \mu_{\kappa})\}^2 - J_1^2 z^2 \gamma_{\kappa}^2 \right]^{1/2}. \quad (7)$$

At the Néel temperature, T_N , $S_0 \rightarrow 0$, and we get for T_N from Eq. (6).

$$T_N = \frac{1}{2k_B} \left[\frac{1}{N} \sum_{\kappa} \frac{1}{J_1 z (1 - \gamma_{\kappa}) + J_2 z' (1 - \mu_{\kappa})} \right]^{-1}. \quad (8)$$

Equation (8) gives us one relation between J_1 and J_2 . A second relation is obtained from the Curie-Weiss

constant, which follows from susceptibility measurements up to room temperatures—which are high compared to the Néel temperature of 4.33°K. Using the value¹⁰ of 5°K for the Curie-Weiss constant, we have

$$\frac{1}{2} (J_1 z - J_2 z') = 5k_B. \quad (9)$$

The sum in Eq. (8) was evaluated in the limit $N \rightarrow \infty$. The contribution of the singularity at $\kappa = 0$, was calculated analytically and the remainder of the sum computed numerically. Combining then Eqs. (8) and (9), we find for J_1 and J_2 the values

$$J_1/k_B = 6.78^\circ\text{K}, \quad J_2/k_B = 0.89^\circ\text{K}, \quad J_2/J_1 = 0.131. \quad (10)$$

The value of 0.131 for J_2/J_1 is very close to Marshall's result. A check on the value of J_1 can be obtained from the experimental value of the perpendicular susceptibility χ_{\perp} . In Ref. 3 we showed that χ_{\perp} is temperature independent in the Bogolyubov-Tyablikov approximation.¹¹ Comparing the theoretical value of χ_{\perp} with the experimental one,¹⁰ we find $J_1/k_B = 7.63^\circ\text{K}$. The difference between this value of J_1 and that of Eq. (10) is probably due to the neglect of correlations when using the Bogolyubov-Tyablikov decoupling (compare the discussion in Ref. 3).

3. SPIN FLOPPING

If a sufficiently high field is applied along the a axis, the antiparallel spin-array "flops" from the a to the b direction.¹² We discussed this process in Ref. 3 and noticed that spin-flopping occurs as soon as the free energy change in a perpendicular field exceeds the change in a parallel field. Although the expression for the Hamiltonian is now different from the one used in Ref. 3, Eq. (39) of that paper still holds. This means that the critical field at which flopping starts, H_c , is given by the equation

$$(\chi_{\perp} - \chi_{\parallel}) H_c^2 = K z S_0^2. \quad (11)$$

The quantity K in Eq. (11) is here the anisotropy difference between the a and the b directions. The derivation of (11) is simple, if we just introduce an anisotropy term $K \sum S_{fz} S_{g\theta} S_{g\theta}$ as was done in Ref. 3, but (11) remains valid if the complete biaxial anisotropy of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is taken into account. The derivation of (11) in the latter case, however, is much more involved.

The critical field H_c is only slightly temperature-dependent. In Ref. 3 we found a value of 1.4 for the ratio $H_c(T_N)/H_c(T=0)$ for the spin- $\frac{1}{2}$ case. If we

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¹¹ Compare, however, M. E. Lines, *Phys. Rev.* **135**, A1336 (1964).

¹² N. J. Poulis, J. van den Handel, J. Ubbink, J. A. Poulis, and C. J. Gorter, *Phys. Rev.* **82**, 552 (1951).

repeat the calculations for the present case, we find

$$\frac{H_c(T_N)}{H_c(T=0)} = \left[\frac{3T_N(1+\alpha)}{2(J_1+2J_2)} \right]^{1/2}, \quad (12)$$

with

$$\alpha = \frac{1}{N} \sum_{\kappa} \frac{J_{1z} - J_{2z}'(1-\mu_{\kappa})}{J_{1z} + J_{2z}'(1-\mu_{\kappa})} \cdot \frac{2T_N}{J_{1z}(1-\gamma_{\kappa}) + J_{2z}'(1-\mu_{\kappa})}. \quad (13)$$

The numerical value of α is 0.68, and using Eq. (10) for J_1 and J_2 , we find $H_c(T_N)/H_c(T=0) = 1.1$.

ACKNOWLEDGMENTS

We wish to thank the Department of Scientific and Industrial Research for the award of a maintenance grant to one of us (A.C.H.) during the tenure of which the above research was carried out.

Optical Properties and Band Structure of Wurtzite-Type Crystals and Rutile*

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(Received 6 October 1964)

The fundamental reflectivity of several optically anisotropic materials (hexagonal ZnS, CdS, CdSe, and rutile) has been measured at room temperature with linearly polarized light of wavelength longer than 1100 Å. Measurements were performed with the electric vector parallel and perpendicular to the c axis of the crystal. From these reflection measurements, extended with unpolarized light to the region between 1100 and 550 Å, the optical constants have been determined by means of the Kramers-Kronig technique. The structure in the optical data of the wurtzite materials is interpreted in terms of the electronic band structure as due to direct allowed interband transitions. The interpretation is based on the existing knowledge about the related zincblende and diamond-type materials and the fact that the band structure of wurtzite along the c axis can be derived from that along the [111] axis of zincblende by applying a small hexagonal crystal field as a perturbation. The optical data on rutile reflect the ionic character of the material.

I. INTRODUCTION

THE determination of the optical constants of semiconductors at energies beyond the fundamental absorption edge by means of reflectivity and absorption measurements is a powerful way of studying the band structure of these materials.¹⁻⁵ In particular the work on cubic crystals of the diamond and zincblende structure, together with recent band-structure calculations, has provided very detailed and consistent knowledge about the position and symmetry of the electronic states involved in the direct interband transitions observed optically. A systematic correlation of all the energy gaps at critical points, i.e., points with singularities in the joint density of states of the valence and conduction bands, in the isoelectronic sequences demonstrates the similarity of the band structure of the group IV elements, III-V, II-VI, and even I-VII

compounds.^{5,6} Such similarity is also borne out by theoretical calculations.^{7,8} Birman suggested that the band structure of the hexagonal wurtzite type crystals at points of \mathbf{k} space along the hexagonal axis (c) can be derived by perturbation theory from that of the corresponding zincblende type materials along a [111] direction.⁹ Hence one expects the electronic states of both types of materials to be very similar at $\mathbf{k}=0$ and along the directions just mentioned. Reflectivity measurements with unpolarized light have indeed shown that the spectra look very similar to those of the hypothetical zincblende analog as deduced from the isoelectronic sequences.¹⁰ Also very small shifts in the position of the first absorption edge, of 0.02 eV to 0.03 eV, have been seen under different orientations of linearly polarized light with respect to the hexagonal axis of the crystals.¹¹⁻¹³ Moreover, the materials exhibit a very small long-wavelength birefringence.¹⁴ Measure-

* This work was supported in part by the Advanced Research Projects Agency under Contract SD-182.

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