

DISPERSION RELATION FOR SPIN WAVES IN  $\text{CuFeS}_2$ 

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The spin wave dispersion relation in the case of  $\text{CuFeS}_2$  is studied. It was found that the spin wave frequencies as functions of the direction of  $\vec{q}$  are anisotropic. The possibility of experimental verification by the method of inelastic scattering of neutrons is discussed.

## 1. Introduction

The aim of the present paper is to derive the spin wave dispersion relation of the magnetic lattice of chalcopyrite.

The crystal structure of chalcopyrite was determined in 1932 by Pauling and Brockway by means of X-Rays [1]. They found the space group  $1\bar{4}2d$  with the atoms positions as follows

$$\begin{aligned} \text{At} & \left( 000; \frac{1}{2} \frac{1}{2} \frac{1}{2} \right) + \\ 4\text{Cu} & \left( 000; 0 \frac{1}{2} \frac{1}{4} \right) \\ 4\text{Fe} & \left( 00 \frac{1}{2}; 0 \frac{1}{2} \frac{3}{4} \right) \\ 8\text{S} & \left( x \frac{1}{4} \frac{1}{8}; \bar{x} \frac{3}{4} \frac{1}{8}; \frac{3}{4} x \frac{7}{8}; \frac{1}{4} x \frac{7}{8} \right) \end{aligned}$$

Where  $x = 0.73 \pm 0.01$ ,  $a = 5.24 \text{ k}\text{\AA}$  and  $c = 10.30 \text{ k}\text{\AA}$ .

In 1958, Corliss *et al.* [2] studied the magnetic structure of chalcopyrite using the neutron diffraction method, and found an antiferromagnetic structure at room temperature. The space group  $1\bar{4}2d$  holds also for the magnetic structure in which the two iron ions and probably also the two copper ions are tetrahedrally bonded to a common sulfur atom and have parallel spins directed along the  $c$  axis. Values of  $3.85 \mu_B$  and  $0 \pm 0.2 \mu_B$  were found for the magnetic moments of the iron and copper ions respectively. Since the copper moment does not participate significantly to the whole magnetic moment, the chalcopyrite lattice can be considered as two interpenetrating body centered tetragonal sublattices consisting of iron — ions only — (placed in the corner points and body centered points). One of the

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two lattices consists of atoms with spins „up” and the other with spins „down” (see Fig. 1). The primitive unit cell is given by the basic vectors  $\vec{a}_1$   $\vec{a}_2$   $\vec{a}_3$ . In the present paper it is assumed that the coupling of spins of the two iron cations  $Q$  and  $R$  is caused by an intermediate sulphur anion  $S$  (Fig. 2). According to Kramers and Anderson [3], [4] such a „super-

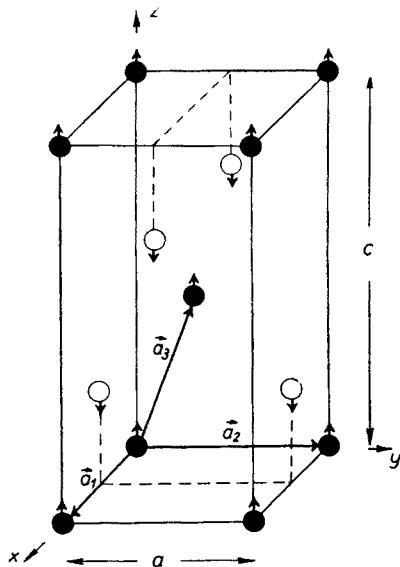


Fig. 1

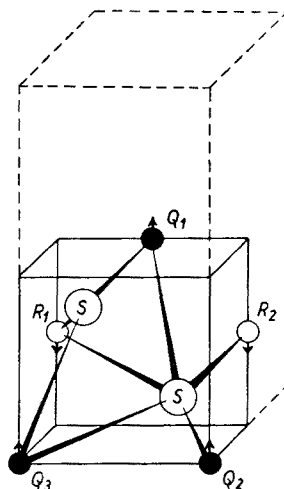


Fig. 2

Fig. 1. The magnetic unit cell of  $\text{CuFeS}_2$ . Black and white circles indicate the positions of Fe ions (Cu and S ions are omitted). The arrows symbolize the order of spins according to the two sublattice. The primitive unit cell is given by the basic vectors  $\vec{a}_1$   $\vec{a}_2$   $\vec{a}_3$ .

Fig. 2. Geometrical relations between Fe and S ions. Small circles: iron ions, large circles: sulphur ions. Conceivable superexchange couplings between two iron ions are given in Table I.

exchange” is possible only when the wave functions of the electrons of  $Q$  and  $R$  overlap those of  $S$ .

Therefore, the interaction falls off rapidly with increasing distances  $Q-S$  and  $S-R$ . Furthermore, the indirect interaction depends on the angle  $QSR$  in such a way that the strongest and weakest interactions occur at angles of  $180^\circ$  and  $90^\circ$ , respectively. In table I are given the angles  $QSR$  and the distances  $Q-S$  and  $S-R$  for the most favourable configurations of iron and sulphur ions respectively.

Interaction	Distances in $Q-S$	$\text{\AA}$ $S-R$	Angle	Exchange Integral
$Q_1-S-R_1$	2.3	2.3	$109^\circ$	$I_1$
$Q_2-S-R_2$				
$Q_1-S-Q_2$	4.4	2.3	$145^\circ$	$I_2$
$Q_1-S-Q_3$	2.3	4.4		
$Q_2-S-R_1$	2.3	4.4		
$Q_3-S-R_2$	4.4	2.3	$145^\circ$	$I_3$

Since the dependence of the interaction on angle and distance is not known quantitatively, it is impossible to decide whether the interactions  $Q_1-S-Q_2$  and  $Q_2-S-R_1$  are stronger or weaker than the interaction  $Q_1-S-R_1$  (the smallest distances and the most unfavourable angle). For these reasons we cannot estimate precisely whether the interactions  $Q_1-S-Q_2$  and  $Q_2-S-R_1$  can be neglected with respect to the  $Q_1-S-R_1$  interaction.

## 2. The spin wave dispersion relation

In this situation the Hamiltonian of the whole spin system will consist of the three kinds of exchange interaction mentioned above and the effective anisotropy field acting on each of them. Thus we have

$$H = 2J_1 \sum_{l,m} \vec{S}_l \cdot \vec{S}_m + 2J_2 \sum_{l,m} \sum_{nei} \vec{S}_l \cdot \vec{S}_m + 2J_3 \left( \sum_{l,l'} \vec{S}_l \cdot \vec{S}_{l'} + \sum_{mm'} \vec{S}_m \cdot \vec{S}_{m'} \right) - 2D \left[ \sum_l (S_l^z)^2 + \sum_m (S_m^z)^2 \right] \quad (1)$$

where  $l$  refers only to atoms in one sublattice and  $m$  refers only to atoms in the other one.

The symbol „ $\sum_{nei}$ ” indicates that the sum goes over all „nearest neighbour” pairs of spins and the symbol „ $\sum_{nnei}$ ” indicates that the sum goes over all next nearest neighbour pairs of spins.

$D$  is the anisotropy energy constant and  $I_1 I_2 I_3$  are exchange integrals defined in table I. Assuming the  $+C$  direction to be in the  $z$  direction we introduce spin deviation operators  $\eta_l, \eta_m$  to represent the deviations of  $S_l^z, S_m^z$  from what would be expected in the perfectly ordered state, *i.e.*

$$\eta_l = S - S_l^z \quad \eta_m = S + S_m^z$$

Define

$$a_l^* a_l = \eta_l \quad \text{and} \quad b_m^* b_m = \eta_m \quad (2)$$

where

$$[a_l, a_{l'}^*] = \delta_{ll'} \quad [b_m, b_{m'}^*] = \delta_{mm'} \quad (3)$$

and all other commutators are equal zero. Then  $a_l$  and  $b_m$  annihilate while  $a_l^*$  and  $b_m^*$  create spin deviation on the  $l$ th and  $m$ th atoms respectively.

Thus if we introduce  $S_l^\pm = S_l^x \pm i S_l^y$   $S_m^\pm = S_m^x \pm i S_m^y$  it gives

$$\begin{aligned} S_l^+ &= (2S)^{1/2} f_l a_l & S_l^- &= (2S)^{1/2} a_l^* f_l & f_l &= \left(1 - \frac{n_l}{2S}\right)^{1/2} \\ S_m^+ &= (2S)^{1/2} b_m^* f_m & S_m^- &= (2S)^{1/2} f_m b_m & f_m &= \left(1 - \frac{n_m}{2S}\right)^{1/2} \end{aligned} \quad (4)$$

Writing Hamiltonian (1) in terms of these operators and retaining second order terms with respect to these operators we obtain the spin wave Hamiltonian.

$$\begin{aligned}
 H = \text{const} + 2J_1S \sum_{l,m} \text{nei} (a_l b_m + a_l^* b_m^* + a_l a_l^* + b_m^* b_m) + 2J_2S \sum_{l,m} \text{nei} (a_l b_m + a_l^* b_m^* + a_l^* a_l + b_m^* b_m) + \\
 + 2J_3S [\sum_{ll'} \text{nei} (a_l^* a_{l'} + a_l a_{l'}^* - a_l^* a_l - a_l^* a_{l'}) + \sum_{mm'} \text{nei} (b_m^* b_{m'} + b_m b_{m'}^* - b_m^* b_m - b_m^* b_{m'}') + \\
 + 4DS (\sum_l a_l^* a_l + \sum_m b_m^* b_m). \quad (5)
 \end{aligned}$$

Fourier transforms are defined by

$$\begin{aligned}
 a_l &= \left(\frac{2}{N}\right)^{\frac{1}{2}} \sum_q e^{-i\vec{q} \cdot \vec{R}_l} a_q & b_m &= \left(\frac{2}{N}\right)^{\frac{1}{2}} \sum_q e^{i\vec{q} \cdot \vec{R}_m} b_q \\
 a_l^* &= \left(\frac{2}{N}\right)^{\frac{1}{2}} \sum_q e^{i\vec{q} \cdot \vec{R}_l} a_q^* & b_m^* &= \left(\frac{2}{N}\right)^{\frac{1}{2}} \sum_q e^{-i\vec{q} \cdot \vec{R}_m} b_q^*
 \end{aligned} \quad (6)$$

where  $q$  runs over all possible values in first Brillouin zone. Then

$$[a_q, a_{q'}^*] = [b_q, b_{q'}^*] = \delta_{qq'} \quad (7)$$

and all other comutators are zero.

The Hamiltonian is easily diagonalized by the following transformation (see for instance [5])

$$\begin{aligned}
 a_q &= \frac{1}{\sqrt{2}} (Q_q + iP_q) & b_q &= \frac{1}{\sqrt{2}} (R_q + iS_q) \\
 a_q^* &= \frac{1}{\sqrt{2}} (Q_q - iP_q) & b_q^* &= \frac{1}{\sqrt{2}} (R_q - iS_q)
 \end{aligned} \quad (8)$$

Hence

$$\begin{aligned}
 [Q_q, P_{q'}] &= [R_q, S_{q'}] = i\delta_{qq'} & [Q_q, Q_{q'}] &= 0 \text{ etc.} \\
 Q_q &= \frac{1}{\sqrt{2}} (\alpha_{1q} + \alpha_{2q}) & P_q &= \frac{1}{\sqrt{2}} (\beta_{1q} + \beta_{2q}) \\
 R_q &= \frac{1}{\sqrt{2}} (\alpha_{1q} - \alpha_{2q}) & S_q &= \frac{1}{\sqrt{2}} (\beta_{1q} - \beta_{2q})
 \end{aligned} \quad (9)$$

Hence

$$\begin{aligned}
 [\alpha_{1q}, \beta_{1q'}] &= [\alpha_{2q}, \beta_{2q'}] = \delta_{qq'} & [\alpha_{1q}, \alpha_{2q'}] &= 0 \text{ etc.} \\
 H &= \text{const} - \sum_q A_q + \frac{1}{2} \sum_q (A_q + B_q) (\alpha_{1q}^2 + \beta_{2q}^2) + \\
 &+ \frac{1}{2} \sum_q (A_q - B_q) (\alpha_{2q}^2 + \beta_{1q}^2)
 \end{aligned}$$

where

$$A_q = 4J_3 S \gamma_3(q) + 4J_1 S \gamma_1 + 4J_2 S \gamma_2 - 4J_3 S \gamma_3 + 8DS$$

$$B_q = 4J_1 S \gamma_1(q) + 4J_2 S \gamma_2(q)$$

Thus, for the spin waves dispersion relation we have the following expression:

$$\hbar\omega(q) = 2SJ_1\gamma_1\{[1 - J_3(\gamma_3 - \gamma_3(q))/J_1\gamma_1 + J_2\gamma_2/J_1\gamma_1 + 2D/J_1\gamma_1]^2 - [J_1\gamma_1(q) + J_2\gamma_2(q)]^2\} J_1^2\gamma_1^2$$

where

$$\gamma_1 = 4 \quad \gamma_2 = 8 \quad \gamma_3 = 8$$

and

$$\gamma_1(q) = \sum_{\vec{R}_l - \vec{R}_m} n e^{i\vec{q}(\vec{R}_l - \vec{R}_m)}$$

$$\gamma_2(q) = \sum_{\vec{R}_l - \vec{R}_m} n e^{i\vec{q}(\vec{R}_l - \vec{R}_m)}$$

$$\gamma_3(q) = \sum_{\vec{R}_l - \vec{R}_m} n e^{i\vec{q}(\vec{R}_l - \vec{R}_m)}$$

Therefore

$$\begin{aligned} \hbar\omega(q) = 2J_1 S \gamma_1 \left\{ \left[ 1 + \frac{2J_3}{J_1} \cos \frac{aq_x}{2} \cos \frac{aq_y}{2} \cos \frac{cq_z}{2} + 2(J_2 - J_3)/J_1 + E_A \right]^2 - \right. \\ \left. - \left[ \cos \frac{aq_x}{2} \left( \frac{1}{2} \cos \frac{cq_z}{4} + \frac{J_2}{J_1} \cos \frac{cq_z}{8} \cos aq_x \right) + \cos \frac{aq_y}{2} \left( \frac{1}{2} \cos \frac{cq_z}{4} + \right. \right. \right. \\ \left. \left. \left. + \frac{J_2}{J_1} \cos \frac{cq_z}{8} \cos aq_y \right) \right]^2 \right\}^{1/2} \end{aligned}$$

Where

$$E_A = 2D/J_1\gamma_1 \quad (12)$$

For the case of long  $\lambda$ , the spin wave energy can be expanded in powers of  $q$  which gives

$$\begin{aligned} \left[ \frac{\hbar\omega(q)}{2J_1 S \gamma_1} \right]^2 = 2 \left( 1 + \frac{2J_2}{J_1} \right) E_A + E_A^2 + \frac{\left( 1 + \frac{2J_2}{J_1} \right) \left( 1 + \frac{10J_2}{J_1} - \frac{4J_3}{J_1} \right) - \frac{4J_3}{J_1} E_A}{8} a^2(q_x^2 + q_y^2) + \\ + \frac{\left( 1 + \frac{2J_2}{J_1} \right) \left( 2 + \frac{J_2}{J_1} - \frac{16J_3}{J_1} \right) - \frac{16J_3}{J_1} E_A}{32} c^2 q_z^2 + \dots \quad (13) \end{aligned}$$

If  $J_2$  and  $J_3$  can be neglected with respect to  $J_1$  and  $E_A$  is small then we have

$$\left[ \frac{\hbar\omega(q)}{2J_1 S \gamma_1} \right]^2 = 2E_A + \frac{1}{8} a^2(q_x^2 + q_y^2) + \frac{1}{16} c^2 q_z^2 + \dots \quad (14)$$

### 3. Discussion

The verification of formula (14) can be carried out experimentally by the techniques of neutron spectrometry used by Brockhouse [6]. Brockhouse uses monochromatised incident neutron beams measures the energy and momentum of the neutrons scattered inelastically.

If we restrict ourselves in [14] to spin waves moving in [001] and [100] directions, then we obtain two relations

$$\begin{aligned}\hbar\omega(q_x) &= 2J_1S\gamma_1 \left( 2E_A + \frac{a^2q_x^2}{8} \right)^{1/2} \\ \hbar\omega(q_z) &= 2J_1S\gamma_1 \left( 2E_A + \frac{C^2q_z^2}{16} \right)^{1/2}\end{aligned}\quad (14)$$

which can be compared with experiment.

The constant term  $E_A$  allows for the presence of an anisotropy field and can be also estimated experimentally from the value of

$$\omega(q) \quad \text{for} \quad q = 0$$

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