

ANISOTROPIC EXCHANGE INTERACTIONS BETWEEN PAIRS OF Cu^{++} IONS IN KCuF_3

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Exchange interactions in one-dimensional antiferromagnetic KCuF_3 are considered. An expression for the anisotropic exchange contribution to the Hamiltonian is derived on the basis of the perturbation theory and symmetry. It is shown how the phenomenological anisotropic parameters of the model are related to the superexchange mechanisms.

1. Introduction

Recent studies [1] on KCuF_3 suggest the one-dimensional antiferromagnetic model for that compound. The spins of Cu^{++} ions along the c -axis are strongly coupled by antiferromagnetic exchange, forming a linear chain, while coupling between the spins along the a -axis and the b -axis is very weak. The intrachain isotropic interaction is found on the basis of Bonner and Fisher's theory [2] as $J/k = -190^\circ\text{K}$, whereas the interchain isotropic interaction J'/k is of order 1°K and positive.

On the other hand, Ikebe and Date [3] suggested a strong influence of the anisotropic exchange interactions on the ESR line width.

The purpose of the present paper is to discuss a microscopic model, based on perturbation theory and providing a description of the relevant interactions in KCuF_3 .

2. Microscopic model

We use the results of the preceding paper [4], where the third order of perturbation theory was applied to a pair of ions in the crystal field with orbitally nondegenerate ground levels. The wave functions of the individual ions A and B are:

$$\Psi_{A t_A a_i \Gamma_i \mu}(q_A); \quad \Psi_{B t_B b_j \Gamma_j \nu}(q_B) \quad (1)$$

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where t_A determines the type of the ion and its nearest environment (*i.e.* the electronic configuration and ligand-field group G), $\Gamma_i(\Gamma_j)$ are irreducible representations of the point group $G_A(G_B)$, $\mu(\nu)$ labels the row of the representation, α is a supplementary quantum number and \hat{q} —the spatial and spin coordinates of the ion. For the ground level we use the notation g , and for excited levels $n, n' \dots$

We take as perturbation the Hamiltonian containing [5] the spin-orbit coupling terms for the two ions A and B and the exchange interaction term between them:

$$\begin{aligned} \hat{\mathcal{H}}' = & \lambda_A \hat{L}_A \cdot \hat{S}_A + \lambda_B \hat{L}_B \cdot \hat{S}_B - \\ & - 2 \left\{ \sum_{\substack{n_A, n'_A \\ n_B, n'_B}} J_k(n_A n_B; n'_A n'_B) |n_A n_B\rangle \langle n'_A n'_B| \right\} (\hat{S}_A \cdot \hat{S}_B). \end{aligned} \quad (2)$$

The index "k" in J indicates to which ion pair AB the microscopic exchange integral refers.

The second order of perturbation theory gives the terms responsible for single-ion anisotropy, the Dzialoshynski-Moriya term $\vec{D} \cdot (\hat{S}_A \times \hat{S}_B)$, and biquadratic term $j(\hat{S}_A \cdot \hat{S}_B)^2$. For the case of spin $S_A = S_B = \frac{1}{2}$ the first term reduces to a constant, while the third term is proportional to $(\hat{S}_A \cdot \hat{S}_B)$. The second term vanishes when the point group of the pair contains the spatial inversion operator.

The terms arising from the third order of perturbation theory can be divided into two parts:

$$\tilde{\mathcal{H}}_{AE}^{(3)} + \tilde{\mathcal{H}}_r^{(3)} \quad (3)$$

$\tilde{\mathcal{H}}_r^{(3)}$ represents those terms which for the case $S_A = S_B = \frac{1}{2}$, either reduce to a constant (or zero) or are proportional to $(\hat{S}_A \cdot \hat{S}_B)$ as is the case for the triple term $j(\hat{S}_A \cdot \hat{S}_B)^3$. $\tilde{\mathcal{H}}_{AE}^{(3)}$ consists of the terms responsible for the anisotropic exchange interactions; for arbitrary spins, it is of the following form:

$$\begin{aligned} \tilde{\mathcal{H}}_{AE}^{(3)} = & \hat{S}_A \cdot Q^a \cdot \hat{S}_A (\hat{S}_A \cdot \hat{S}_B) + \{A \rightarrow B\} + \\ & + \hat{S}_A \cdot Q^b (\hat{S}_A \cdot \hat{S}_B) \cdot \hat{S}_A + \{A \rightarrow B\} + \\ & + (\hat{S}_A \cdot \hat{S}_B) \hat{S}_A \cdot Q^c \cdot \hat{S}_A + \{A \rightarrow B\} + \\ & + \hat{S}_A \cdot A \cdot \hat{S}_A (\hat{S}_A \cdot \hat{S}_B) + (\hat{S}_A \cdot \hat{S}_B) \hat{S}_A \cdot A \cdot \hat{S}_A + \{A \rightarrow B\}. \end{aligned} \quad (4)$$

The explicit forms of the tensors are:

$$\begin{aligned} Q^a = & - \sum'_{\substack{n_A, n'_A \\ (\neq g_A)}} \frac{2\lambda_A^2}{\Delta E_{n_A} \Delta E_{n'_A}} \{ \vec{L}_{gn}^A \vec{L}_{mn'}^A J(n'_A g_B; g_A g_B) \} \\ Q^b = & - \sum'_{n_A, n'_A} \frac{2\lambda_A^2}{\Delta E_{n_A} \Delta E_{n'_A}} \{ \vec{L}_{gn}^A J(n_A g_B; n'_A g_B) \vec{L}_{n'g}^A \} \end{aligned}$$

$$Q^c = - \sum'_{n_A, n'_A} \frac{2\lambda_A^2}{\Delta E_{n_A} \Delta E_{n'_A}} \{J(g_A g_B; n'_A g_B) \vec{L}_{n'_A}^A \vec{L}_{ng}^A\}$$

$$\Lambda = J(g_A g_B; g_A g_B) \sum'_{n_A} \frac{\lambda_A^2}{(\Delta E_{n_A})^2} \{\vec{L}_{gn}^A \vec{L}_{ng}^A\} \quad (5)$$

where

$$\vec{L}_{nn'}^A = \langle n_A | \hat{L}_A | n'_A \rangle$$

$$\Delta E_{n_A} = E_{n_A} - E_{g_A} \quad (6)$$

3. Application of the model to KCuF_3

A. Crystal field

The two crystal structure types were established [6] for KCuF_3 as (a) and (d) (see Fig. 1). In both, the local point group of the ligand-field for a Cu^{2+} ion is D_{2h} . The appropriate energy levels scheme is shown in Fig. 2. $\Gamma_{r\mu}^+$ and $\Gamma_{t\mu}^+$ are irreducible representations

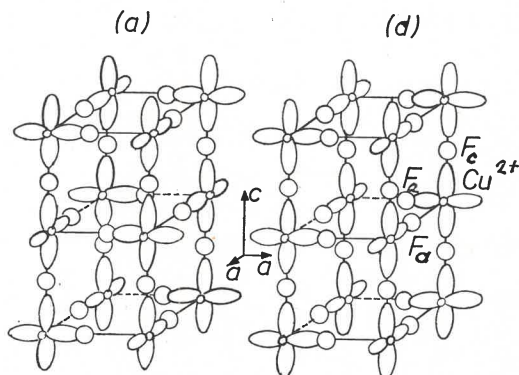


Fig. 1. Crystal structure of KCuF_3 and the charge distribution of electronic holes on the Cu^{2+} ions after [1]

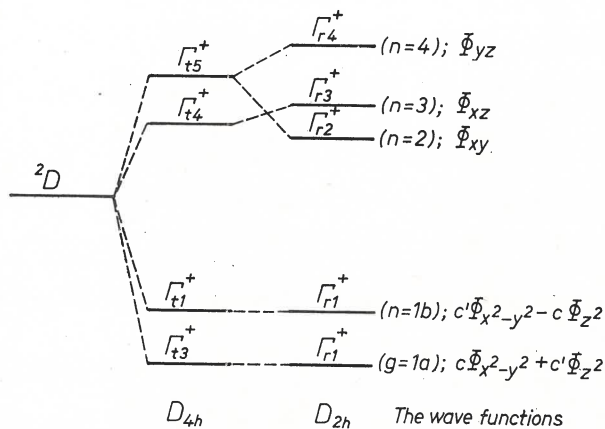


Fig. 2. Energy level scheme for a Cu^{2+} ion in a crystal field of symmetry D_{2h}

of the orthorhombic (index r) and tetragonal (t) point groups. Here $t_A = t_B$ and all $\Gamma_{r\mu}^+$'s are one-dimensional representations. The energy separations after [1] are:

$$\Delta E_2 = 9.100 \text{ cm}^{-1}$$

$$\Delta E_3 = 10.400 \text{ cm}^{-1}$$

$$\Delta E_4 = 12.000 \text{ cm}^{-1}$$

and ΔE_1 is of order 10^3 cm^{-1} [7].

Knowing the wave functions, we can easily calculate the matrix elements of the angular momentum operator \hat{L}_i , i.e. the vectors \vec{L}_{nm}^i .

B. Symmetry considerations

The point group G_k of a crystal field acting on a pair k of two Cu^{++} ions is the intersection $D_{\infty h} \cap G_c$, where G_c is the local point group of the midpoint on the line joining the pair. Then a local z -axis of the system of two ions is chosen along the line joining the ions.

We obtain the following point groups for the two neighbouring ions in (d) type structure: $D_{\infty h} \cap D_{2h} = D_{2h}$ for ions along the c -axis; and $D_{\infty h} \cap C_{2v} = C_{2v}$ for ions along the a -axis; whereas in (a) type structure both G 's are C_{2v} .

The term $V_{\text{ex}} = -2J_{\text{eff}} \hat{S}_A \cdot \hat{S}_B$ in Eq. (2) has to transform according to the regular symmetric representation Γ_1 of the group G_k . For the zero-order wave functions of a system consisting of two ions, we can choose those antisymmetrized linear combinations of the wave functions (1) of the unperturbed Hamiltonian which transform according to the irreducible representations of the group G_k .

Hence, an arbitrary state of a pair $|n_A n'_B\rangle$ from the basis defined above has to transform like the tensor product of the irreducible representations corresponding to the individual states $|n_A\rangle$ and $|n'_B\rangle$:

$${}^2\Gamma_{n_A}^+ \otimes {}^2\Gamma_{n'_B}^+ = (D^{\frac{1}{2}} \otimes D^{\frac{1}{2}}) \otimes (\Gamma_{n_A}^+ \otimes \Gamma_{n'_B}^+). \quad (7)$$

The product representation $(\Gamma_{n_A}^+ \times \Gamma_{n'_B}^+)$ is reducible and we have to decompose it into the irreducible representations Γ_i of the group G_k , as desired:

$$(D^0 \oplus D^1) \otimes \sum_i a_i \Gamma_i. \quad (8)$$

Using the relations for the characters of the reducible product representations $\{\Gamma_{n_A}^+, \Gamma_{n'_B}^+\}$ [8], we derive the following rules for the various states of the pair:

| State | Reducible product representation | Irreducible representation | |
|--------------------|---|----------------------------|----------------|
| $ n_A n_B\rangle$ | $\{\Gamma_{n_A}^+, \Gamma_{n_B}^+\}$ | $G_k = D_{2h}$ | $G_k = C_{2v}$ |
| | for $n_A = n_B = 1a, 1b, 2, 3, 4$ | Γ_3^- | Γ_1 |
| $ n_A n'_B\rangle$ | $\{\Gamma_{n_A}^+, \Gamma_{n'_B}^+\} + \{\Gamma_{n'_A}^+, \Gamma_{n_B}^+\}$ | Γ_p^+ | $2\Gamma_p$ |

for

| n_A | n'_B | p is |
|-------|--------|--------|
| 1a | 1b | 1 |
| 1a | 2 | 2a |
| 1a | 3 | 3a |
| 1a | 4 | 4a |
| 2 | 3 | 4 |
| 2 | 4 | 3 |
| 3 | 4 | 2 |

(9)

The matrix elements $\langle n_A n'_B | V_{ex} | n''_A n'''_B \rangle$ are non-zero only if the direct product $\Gamma_l \otimes \Gamma_1 \otimes \Gamma_r$ contains, on decomposition, the representation Γ_1 . Here, Γ_l and Γ_r are representations according to which the "bra" and "ket" transform respectively. We thus have the general condition: $\Gamma_l = \Gamma_r$, and for the two special cases:

$$1^0. \langle n_A g_B | V_{ex} | n'_A g_B \rangle \neq 0 \text{ if } \Gamma_{n_A}^+ = \Gamma_{n'_A}^+ \quad (10a)$$

since the Γ^+ 's here are one-dimensional, the condition (10a) reduces to:

$$n_A = n'_A; \quad (10b)$$

$$2^0. \langle n_A g_B | V_{ex} | g_A g_B \rangle \equiv 0 \text{ for all } n_A \text{ except}$$

$$n_A = g_A \quad \text{for } G_k = D_{2h}$$

$$n_A = g_A \text{ or } 1b \text{ for } G_k = C_{2v}. \quad (10c)$$

From the above and Eq. (5), we see there exist the following relevant exchange integrals: for both G_k 's: $J(00; 00)$; $J(20; 20)$; $J(30; 30)$; $J(40; 40)$ and, additionally, for $G_k = C_{2v}$ $J(10; 00) = J(00; 01)$.

Finally, we obtain the components of the tensors as:

$$Q_{ij}^a = - \frac{8\lambda^2 J_k(10; 00)}{\Delta E_{1b}} \gamma_{ij} \quad (11)$$

where the following coefficients γ_{ij} are non-zero:

$$\gamma_{xx} = - \frac{(c + \sqrt{3} c') (c \sqrt{3} - c')}{\Delta E_4}$$

$$\gamma_{yy} = + \frac{(c - \sqrt{3} c') (c \sqrt{3} + c')}{\Delta E_3}$$

$$\gamma_{zz} = + \frac{cc'}{\Delta E_2} \quad (11a)$$

$$Q^c = Q^a \quad (12)$$

$$Q_{ij}^b = -8\lambda^2 \beta_{ij} \quad (13)$$

where the following β 's are non-zero:

$$\begin{aligned}\beta_{xx} &= J_k(40; 40) \left(\frac{c + \sqrt{3}c'}{\Delta E_4} \right)^2 \\ \beta_{yy} &= J_k(30; 30) \left(\frac{c - \sqrt{3}c'}{\Delta E_3} \right)^2 \\ \beta_{zz} &= J_k(20; 20) \left(\frac{c}{\Delta E_2} \right)^2\end{aligned}\quad (13a)$$

$$A_{ij} = 4\lambda^2 \beta'_{ij} \quad (14)$$

where the coefficients β' correspond to β with all $J(n0; n0)$ changed to $J(00; 00)$.

A detailed discussion of the terms included to the part $\tilde{\mathcal{H}}_r^{(3)}$ of the Hamiltonian (3) with regard to the symmetry considerations is to be found in [4].

C. Reduction of $\tilde{\mathcal{H}}_{AE}^{(3)}$ for $S_A = S_B = \frac{1}{2}$

We have shown [4] that by applying the formulas:

$$\hat{S}_i \hat{S}_j \hat{S}_l = \frac{1}{4} \{ \delta_{ij} \hat{S}_l + \delta_{jl} \hat{S}_i - \delta_{il} \hat{S}_j \} + \frac{1}{8} i \varepsilon_{ijl} \quad (15)$$

one obtains from Eq. (4):

$$\begin{aligned}\tilde{\mathcal{H}}_{AB}^{(3)} &= \text{Tr} \left[\frac{1}{2} Q^a + \frac{1}{2} Q^c + \Lambda - \frac{1}{2} Q^b \right] (\hat{S}_A \cdot \hat{S}_B) + \\ &+ \frac{1}{8} i \sum_{i,j,l} \varepsilon_{ijl} (Q_{ij}^a + Q_{ij}^c - Q_{ij}^b + 2A_{ij}) (\hat{S}_i^A + \hat{S}_i^B) + \\ &+ \frac{1}{2} \sum_{i,l} \hat{S}_i^A (Q_{il}^b + Q_{il}^c) \hat{S}_l^B,\end{aligned}\quad (16)$$

irrespective of the concrete form of the tensors Q^a , Q^b , Q^c and Λ . The tensors Q^a and Q^c exist only for $G_k = C_{2v}$, whereas Q^b and Λ exist for both G_k 's. But since they are diagonal, the second term in Eq. (16) has to vanish completely. As the expression under "trace" is a scalar, the first term contributes only to the isotropic part of the Hamiltonian. Finally, the anisotropic exchange contribution to the Hamiltonian has the following form for both cases $G_k = D_{2h}$ and C_{2v} :

$$\tilde{\mathcal{H}}_{AE}^{(3)} = J'_{kx} \hat{S}_x^A \hat{S}_x^B + J'_{ky} \hat{S}_y^A \hat{S}_y^B + J'_{kz} \hat{S}_z^A \hat{S}_z^B \quad (17)$$

and

$$J'_{ki} = Q_{ii}^b. \quad (18)$$

D. Remarks on superexchange theory

Let us refer the index $k = 1$ to a pair along the c -axis and $k = 2$ to a pair along the a -axis in any of the two types of KCuF_3 structure. The two pairs $k = 1$ and $k = 2$ are not equivalent because of the different charge distribution of the two Cu^{++} ions and

the intervening fluorine ion (see Fig. 1). Our $J_k(n_A n_B; n'_A n'_B)$ can be interpreted from the viewpoint of superexchange theory [9] as J_k^{c-a-c} — the 180° cation-anion-cation exchange interaction integrals. To each J_k , the following three mechanisms contribute: a) electrostatic exchange between the two $3d^n$ ions, of necessarily positive value and usually very small, b) correlation superexchange D , c) delocalization E . Goodenough predicted (Table XII of [9]) two possibilities: 1° — D, E are negative or 2° — D, E are none. It seems reasonable to assume that the case 1° occurs for a pair $k = 1$, and the case 2° for a pair $k = 2$.

Using the values for ΔE given in the text, for $c = 0.578$, $c' = 0.816$ [7], for $\lambda = -935 \text{ cm}^{-1}$, the theoretical value for free Cu^{++} ion [10] and taking the spin-orbit reduction factor for the ion in the crystal environment as 0.75 [7], we estimate the following orders of values for the integrals of Eq. (18):

$$\begin{aligned} J'_{kx} &\approx -10^{-1} J_k(40; 40) \\ J'_{ky} &\approx -10^{-2} J_k(30; 30) \\ J'_{kz} &\approx -10^{-3} J_k(20; 20). \end{aligned} \quad (19)$$

4. Comparison with the purely phenomenological approach

Kurzyński [11] obtained, by group theory, general formulas for the bilinear spin Hamiltonian allowed by the symmetry of an ion pair. For the case $S = \frac{1}{2}$ and $G_k = D_{2h}$ or C_{2v} , Kurzyński derives the following two terms:

$$\begin{aligned} H_0 &= B_0(\hat{S}_x^A \hat{S}_x^B + \hat{S}_y^A \hat{S}_y^B) - 2B_0 \hat{S}_z^A \hat{S}_z^B \\ H_3 &= B_3(\hat{S}_x^A \hat{S}_x^B - \hat{S}_y^A \hat{S}_y^B). \end{aligned} \quad (20)$$

By transforming our Eq. (17) to the form (20), we obtain a reduction of the number of effective parameters to two:

$$\begin{aligned} B'_{k0} &= -\frac{1}{2} J'_{kz} \\ B'_{k3} &= -\frac{1}{2} (J'_{ky} - J'_{kx}). \end{aligned} \quad (21)$$

The part H_0 in (20) is precisely what is called the "pseudodipolar" term resembling the form historically proposed by Van-Vleck.

5. Conclusion

We have discussed the problem of anisotropic exchange interactions between two Cu^{++} ions in KCuF_3 . Starting from a model based on perturbation theory and on performing a group theoretical analysis, we derive an expression for the anisotropic exchange contribution to the spin Hamiltonian. Our phenomenological parameters are related with superexchange mechanisms. However, the question of the strength of the superexchange

integrals $J_k(n0; n0)$ in KCuF_3 still remains open. The inclusion of $\tilde{\mathcal{H}}_{AE}$ into the total Hamiltonian of the antiferromagnetic chain of spins will permit further investigation of the magnetic properties of KCuF_3 .

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