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Antisymmetric Exchange in the CuB_2O_4 A Subsystem

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The space distribution of the components of the microscopic Hamiltonian of the antisymmetric Dzyaloshinskii–Moriya exchange with respect to the exchange bond pairs of the A subsystem of Cu^{2+} ions in the crystallographic 4b positions of CuB_2O_4 has been obtained using symmetry analysis. The possibility of the coexistence of two different types of the exchange spatial distribution is demonstrated. The component of the antisymmetric exchange vector **D** parallel to the tetragonal axis has a weakly ferromagnetic distribution for all of the directions of the bonds between the nearest magnetic neighbors. Each exchange bond has an additional component of the antisymmetric exchange parallel to the bond projection on the tetragonal plane. The spatial distribution of these components is helicoidal with the modulation vector in the tetragonal crystal plane.

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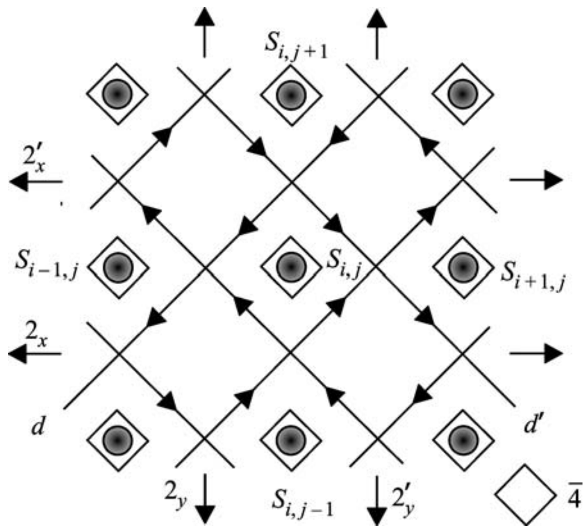
In the last decade, copper metaborate, CuB_2O_4, has been one of the most intensively investigated magnetic substances with an incommensurate magnetic structure (IMS) [1–10]. Recent studies have pointed to the existence of interesting magnetoelectric effects in this crystal [11–14]. For this reason, future intense investigations of the physical properties of CuB_2O_4 associated with its diverse magnetic phases can be expected. However, many publications with "qualitative" IMS interpretations and without any quantitative analysis of the body of experimental data do not clarify the type of various magnetic structures in this substance and the mechanisms of their formation.

The diversity of magnetic phases in CuB_2O_4 (and, accordingly, the difficulty of their description) is mainly determined by the existence of two magnetic subsystems which feature magnetic interactions radically different in their magnitude and form. The A subsystem of Cu^{2+} ions in the crystallographic 4b positions coupled by the strongest antiferromagnetic exchange transits to the magnetically ordered state at $T_N = 20$ K. The studies reported in [6] imply a long-period modulated character of magnetic ordering at $T < T_N$. However, the form (the directions of the modulation and polarization vectors) and the mechanism of this modulation have not yet been determined. In relatively low fields h_{c1}, this state transits to the weakly ferromagnetic state with the ferromagnetism vector in the tetragonal plane [1, 8. 11–14]. The nonzero magnetic moment on the ions in the 8d positions of the second magnetic subsystem B can be revealed at much lower temperatures $T \sim 10$ K. The magnetization of this subsystem remains far from saturation even at $T = 1.8$ K; this implies that the exchange interactions between the spins of this subsystem are low and, probably, quasi-one-dimensional. Meanwhile, the intersubsystem exchange bonds are geometrically frustrated: every spin of the B subsystem interacts with the spins of both antiferromagnetic sublattices of the A subsystem along identical exchange ways. At $T_S = 9.5$ K, the transverse helical IMS appears in CuB_2O_4 with the modulation vector directed along the tetragonal axis c, which increases rapidly and reaches $k = 0.15$ *rlu* at $T = 1.8$ K. The critical fields h_{c2} destroying this IMS reach several tens of kilooersteds, which is two orders of magnitude higher than the critical field h_{c1} of the high-temperature IMS at $9.5 \text{ K} < T < 20$ K.

Interest in the magnetic properties of CuB_2O_4 was largely determined by the initial suggestion regarding the relativistic mechanism of the formation of the helicoidal magnetic structure at $T < T_S$ [2, 3, 5]. A necessary condition for the uniform Dzyaloshinskii–Moriya (UDM) antisymmetric exchange in magnetic substances,

$$H_U = \sum_i \mathbf{D}[\mathbf{S}_i \times \mathbf{S}_{i+1}], \qquad (1)$$

which forms the helicoidal structure, is the absence of the inversion operation among the crystal symmetry elements. However, this condition is not sufficient. Even under this condition, combinations of other symmetry elements can lead to the formation of another, staggered spatial distribution of the Dzyaloshinskii–Moriya antisymmetric exchange (SDM) over the exchange bond pairs, which gives rise to a



Symmetry elements of CuB_2O_4: the second-order axes 2_x and 2_y, the fourth-order inversion axes $\bar{4}$, and the inclined planes *d*. The second-order screw axes are not shown.

weakly ferromagnetic skew of the antiferromagnetic sublattices [18, 19],

$$H_S = \sum_i (-1)^i \mathbf{D}[\mathbf{S}_i \times \mathbf{S}_{i+1}]. \quad (2)$$

The concurrent presence of the symmetry operations transforming separate components of the vector product of magnetic moments by both rules, (1) and (2), means that these components of vector **D** should be zero. Therefore, although the inversion center in a crystal is often absent, this mechanism of the formation of the IMS is less common than the competition of the symmetric Heisenberg exchanges. A more recent symmetry analysis of the phenomenological expansion of free energy (the Ginzburg–Landau functional) showed that the Lifshitz invariant describing the appearance of the helicoidal structure at T_S with $\mathbf{k} \parallel \mathbf{c}$ cannot be constructed only on the order parameter of the A subsystem [7]: the formation mechanism of this IMS is based on the intersubsystem coupling. In [9], it was shown that this mechanism is the geometrically frustrated intersubsystem isotropic exchange. The corresponding invariant was obtained in [10]. However, the formation mechanism of the high-temperature IMS is not fully understood to date. Moreover, the IMS formation at $T < T_S$ is, as before, attributed to the presence of the Dzyaloshinskii–Moriya interaction in the A subsystem or to its combination with the competition of isotropic exchanges [20–22]. An erroneous symmetry analysis [23] based on the mirror plane between the spins of the A subsystem, which was absent in the system, led to the conclusion regarding the possibility of the coexistence of two helicoidal IMSs with different, right and left-handed, chiralities in the quasi-antiferromagnetic sublattices of this subsystem. Another extremity is claiming the absence of the Dzyaloshinskii–Moriya interaction in the A subsystem proposed in [24]. This disagreement between the interpretations of the possible interactions in CuB_2O_4 and the corresponding phases is explained by the absence of the symmetry analysis of the allowed spatial distribution of vector **D** over the exchange bond pairs in the magnetic ion lattice, which could make it possible to write the microscopic Hamiltonian of the antisymmetric exchange in CuB_2O_4. The objective of this work is to perform such an analysis in the A subsystem of the Cu^{2+} ions.

In the symmetry analysis of the possible antisymmetric combinations of the components of the second-order magnetic invariants, it is convenient to divide all of the symmetry elements of the crystal point group into the "limiting" elements, which limit the possible pair combinations, and the "generating" elements, which transfer pair combinations to each other, i.e., generate the spatial distribution. In the Turov notation for antiferromagnets, this corresponds to the odd and even symmetry elements, respectively [25]. The space group $I\bar{4}2d$ of CuB_2O_4 contains the limiting axes of the second order, 2_x and 2_y, which are parallel to the tetragonal plane and connect the nearest magnetic neighbors of the A subsystem (see figure). The invariant antisymmetric combinations of the second-order magnetic components for them have the form [25]

$$\begin{aligned} &2_x: \text{(a) } m_x l_y - m_y l_x, \quad \text{(b) } m_x l_z - m_z l_x; \\ &2_y: \text{(a) } m_x l_y - m_y l_x, \quad \text{(b) } m_y l_z - m_z l_y, \end{aligned} \quad (3)$$

where m_α and l_α are the local components of the ferro- and antiferromagnetism vectors constructed on the magnetic moments coupled by each separate axis, respectively. For example, in the notation of the figure,

$$\begin{aligned} &2_x: \mathbf{m}(\mathbf{r}) = \mathbf{S}_{ij} + \mathbf{S}_{ij-1}; \quad \mathbf{l}(\mathbf{r}) = \mathbf{S}_{ij} - \mathbf{S}_{ij-1}, \\ &2'_x: \mathbf{m}(\mathbf{r}) = \mathbf{S}_{ij} + \mathbf{S}_{ij+1}; \quad \mathbf{l}(\mathbf{r}) = \mathbf{S}_{ij} - \mathbf{S}_{ij+1}, \\ &2_y: \mathbf{m}(\mathbf{r}) = \mathbf{S}_{ij} + \mathbf{S}_{i-1j}; \quad \mathbf{l}(\mathbf{r}) = \mathbf{S}_{ij} - \mathbf{S}_{i-1j}, \\ &2'_y: \mathbf{m}(\mathbf{r}) = \mathbf{S}_{ij} + \mathbf{S}_{i+1j}; \quad \mathbf{l}(\mathbf{r}) = \mathbf{S}_{ij} - \mathbf{S}_{i+1j}. \end{aligned} \quad (4)$$

The spins of the A subsystem are in the tetrahedral environment of the nearest magnetic neighbors pairwise shifted along the **c** axis (see figure). Hereinafter, the third subscript in the coordinate symbols is omitted for the sake of simplicity, and the spins are uniquely specified by two subscripts in each group under consideration.

The generating symmetry elements in CuB_2O_4 are the axes and planes parallel to the tetragonal axis $\mathbf{z} \parallel \mathbf{c}$: the fourth-order inversion axes passing through the magnetic ions, the inclined planes *d* between the ions, and the second-order helical axes parallel and normal to the tetragonal axis. All of them constitute the invariant combination of groups (a) in Eqs. (3),

$$S^x_{i-1j}S^y_{ij} - S^y_{i-1j}S^x_{ij} + S^x_{i+1j}S^y_{ij} - S^y_{i+1j}S^x_{ij} + S^x_{ij-1}S^y_{ij} - S^y_{ij-1}S^x_{ij} + S^x_{ij+1}S^y_{ij} - S^y_{ij+1}S^x_{ij}. \quad (5)$$

Therefore, the z component of the antisymmetric exchange is the SDM exchange,

$$H_S = D^z_S \sum_{ij} (-1)^{i+j} \mathbf{e}_z([\mathbf{S}_{ij} \times \mathbf{S}_{i+1,j}] + [\mathbf{S}_{ij} \times \mathbf{S}_{i,j+1}]). \quad (6)$$

The second invariant constructed on the combinations of groups (b) in Eqs. (3) has the form

$$S^y_{i-1j}S^z_{ij} - S^z_{i-1j}S^y_{ij} - S^y_{i+1j}S^z_{ij} + S^z_{i+1j}S^y_{ij} + S^x_{ij-1}S^z_{ij} - S^z_{ij-1}S^x_{ij} - S^x_{ij+1}S^z_{ij} + S^z_{ij+1}S^x_{ij}. \quad (7)$$

Correspondingly, the x and y components of the antisymmetric exchange are written in the form of the UDM exchange,

$$H_U = D^{xy}_U \sum_{ij} (\mathbf{e}_x[\mathbf{S}_{ij} \times \mathbf{S}_{i+1,j}] - \mathbf{e}_y[\mathbf{S}_{ij} \times \mathbf{S}_{i,j+1}]). \quad (8)$$

Taking into account the permutation properties of the coordinate subscripts, the equivalent general Hamiltonian represented in the form of the mixed product,

$$H_D = \sum_{\mathbf{r},\mathbf{r}'} \mathbf{D}_{\mathbf{r},\mathbf{r}'}[\mathbf{S}_\mathbf{r} \times \mathbf{S}_{\mathbf{r}'}], \quad (9)$$

allows one to perform a similar analysis of the distribution of the axial vector $\mathbf{D}_{\mathbf{r},\mathbf{r}'}$ itself [26] with the same result: the Dzyaloshinskii–Moriya antisymmetric exchange in the 4b subsystem of Cu^{2+} magnetic ions has the weakly ferromagnetic (SDM) component of vector $\mathbf{D}^z_S$ along the tetragonal axis for all of the exchange bonds between the nearest magnetic neighbors and the two-dimensional distribution of the helicoidal (UDM) components D^{xy}_U and $-D^{xy}_U$ over the exchange bond pairs. Each pair of the exchange bonds with the projections along the a and b directions in the tetragonal plane has either x or y component of $\mathbf{D}_{\mathbf{r},\mathbf{r}'}$, respectively.

Compound $Ba_2CuGe_2O_7$ is a tetragonal antiferromagnet with an incommensurate magnetic structure where the mirror plane is the limiting symmetry element [27]. This symmetry element keeps another antisymmetric combination of the spin components and, together with generating axis $\bar{4}$ identical to that in CuB_2O_4, also leads to the corresponding two-dimensional distribution of the UDM exchange in the tetragonal plane [28]. This distribution results in the helical structure with the wave vector lying in the tetragonal plane.

A conclusion on the relativistic formation mechanism of the incommensurate magnetic structure can be made only after eliminating the exchange mechanism of competition between the symmetry exchanges of different magnetic neighbors. The presence of this competition can directly be determined by analyzing the spin wave spectrum as it was done for $Ba_2CuGe_2O_7$ [27]. The dispersion curve of the spin waves recorded for different directions of the wave vector contains complete information on the spatial distribution of the main exchange interactions and their anisotropy. The exchange with the second nearest neighbors $J_2 > 0.25\,J_1$, which begins the formation of the incommensurate magnetic structure, considerably affects the spin wave spectrum, particularly if this exchange direction differs from that of the J_1 exchange between the nearest neighbors. Previous analysis of the spin wave spectrum for the A subsystem at $T > T_S$ demonstrated that the spectrum for all directions of the wave vector is described with a high accuracy by the model with the single exchange interaction between the nearest neighbors [4]. Therefore, an attempt to describe the low-temperature incommensurate magnetic structure in CuB_2O_4 using the combination of the relativistic mechanism and the major contribution of the competing exchange with the second-nearest neighbors [22] contradicts the abovementioned analysis: the incommensurate magnetic structure at $T \leq 9.5$ K cannot be induced by the competition of exchanges between the spins of the A subsystem.

The complex incommensurate structure appearing in CuB_2O_4 in the coexistence of different types of antisymmetric exchange is radically different from the helicoid with the wave vector along the tetragonal axis. Its detailed analysis will be presented later; the antisymmetric exchange distribution obtained above gives not only the weakly ferromagnetic invariant

$$I_S \sim m_x l_y - l_x m_y,$$

but also the invariant

$$I_U \sim m_y \frac{\partial m_z}{\partial x} - m_z \frac{\partial m_y}{\partial x} - m_x \frac{\partial m_z}{\partial y} + m_z \frac{\partial m_x}{\partial y} - l_y \frac{\partial l_z}{\partial x} + l_z \frac{\partial l_y}{\partial x} + l_x \frac{\partial l_z}{\partial y} - l_z \frac{\partial l_x}{\partial y}, \quad (10)$$

which is a particular case of the generalized Lifshitz invariant [29].This long-period incommensurate magnetic structure appears, together with the appearance of the magnetic order at T_N, as in the classical incommensurate magnetic substances with the relativistic mechanism [27, 28, 30, 31]. At a temperature T_S, as soon as the necessary magnetization appears, the incommensurate magnetic structure is formed in the B subsystem of the Cu^{2+} ions and removes the frustration with respect to the symmetric exchange between the subsystems with the wave vector $\mathbf{k} \parallel \mathbf{c}$ [9, 10]. The intermediate mixed structure near T_S produces the satellite neutron-scattering peaks [3] identified as the soliton lattice signs.

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