ISSN 1063-7761, Journal of Experimental and Theoretical Physics, 2021, Vol. 132, No. 4, pp. 586–587. © Pleiades Publishing, Inc., 2021.
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Contribution for the JETP special issue in honor of I.E. Dzyaloshinskii's 90th birthday

Anomalous Spin-Flop in Antiferromagnetic $Cu(pz)_1(ClO_4)_2$

V. I. Marchenko[a,*]

[a] *Kapitsa Institute for Theoretical Physics, Russian Academy of Sciences, Moscow, 119334 Russia*

**e-mail: mar@kapitza.ras.ru*

Received December 8, 2020; revised December 8, 2020; accepted December 10, 2020

Abstract—An explanation is proposed for the anomalous spin-flop in antiferromagnetic $Cu(pz)_2(ClO_4)_2$. Due to the closeness of the monoclinic and tetrahedral lattices, the spin-flop in a small magnetic field can be accompanied by a transition from one to another antiferromagnetic vector. These two vectors transform into each other under the action of symmetry elements lost during monoclinic lattice distortions.

DOI: 10.1134/S1063776121040166

Povarov, Smirnov, and Landee [1] discovered an unusual phenomenon in antiferromagnetic $Cu(pz)_2(ClO_4)_2$ (pyrazine pz = $C_4H_4N_2$). A transition that looks like the spin-flop in a magnetic field according to the behavior of the magnetization is accompanied by an unexpected change in the sign of one of the anisotropy constants, according to the measurements of the antiferromagnetic resonance spectrum.

Copper atoms are located at the sites of an almost square rhombic lattice (Fig. 1a). The parameters of the crystal investigated in [1] are

$$a = 14.072\ \text{Å},\quad b = 9.786\ \text{Å},$$

$$c = 9.7810\ \text{Å},\quad \beta = 96.458°.$$

The antiferromagnetic exchange within the atomic planes (b, c) greatly exceeds the exchange between the planes [2]. As a result, a natural two-dimensional order with oppositely directed average spins of the nearest neighbors is established in each plane. According to neutron diffraction data [2], the observed three-dimensional exchange magnetic structure in $Cu(pz)_2(ClO_4)_2$ is specified by one antiferromagnetic vector ℓ, composed of four sublattices with the signature shown in Fig. 1a:

$$\ell = \mathbf{s}_1 - \mathbf{s}_2 + \mathbf{s}_3 - \mathbf{s}_4. \tag{1}$$

If $b = c$ and $\beta = 90°$, then the lattice becomes tetrahedral. In this case, regardless of the structure of the microscopic exchange Hamiltonian, if there is an antiferromagnetic state ℓ described above, then, due to symmetry, an alternative magnetic state

$$\tilde{\ell} = \mathbf{s}_1 - \mathbf{s}_2 - \mathbf{s}_3 + \mathbf{s}_4. \tag{2}$$

with the signature shown in Fig. 1b is possible.

The energies and, in general, all the characteristics of states (1) and (2) are the same.[1] Macroscopically, these states differ only in the rotation of the easy axis by 90° in the basal plane.

In an external magnetic field at low temperatures, the energies of the states under discussion are

$$\begin{aligned} E_\ell &= E_0 + \frac{\beta_1}{2}\ell_z^2 + \frac{\beta_2}{2}\ell_y^2 - \frac{\chi_\perp}{2}[\boldsymbol{\ell}\times\mathbf{B}]^2,\\ E_{\tilde\ell} &= E_0 + \frac{\beta_1}{2}\tilde\ell_z^2 + \frac{\beta_2}{2}\tilde\ell_y^2 - \frac{\chi_\perp}{2}[\tilde{\boldsymbol{\ell}}\times\mathbf{B}]^2, \end{aligned} \tag{3}$$

where E_0 is the ground state energy, $\beta_1 > \beta_2 > 0$ are anisotropy constants, and $\chi_\perp$ is the magnetic susceptibility perpendicular to the vectors ℓ and $\tilde\ell$, $|\ell| = |\tilde\ell| = 1$.

In a magnetic field parallel to the basal plane, $\ell_z = \tilde\ell_z = 0$. In this case, if the field is oriented at an angle of 45° to the easy axes ($B_x = \pm B_y$), the energies of the two alternative states remain the same. In the general case, the degeneracy is lifted, and the state in which the easy axis is oriented at an angle closer to the optimal one (90°) with respect to the field has the minimum energy in a small field.

Taking into account the existing small differences between the crystal lattice and the tetrahedral lattice, the exchange energies of the states $\boldsymbol{\ell}$ and $\tilde{\boldsymbol{\ell}}$ become different. As a rule, the crystal in the paramagnetic phase contains crystallites rotated relative to each other by 90° in the basal plane. According to neutron diffraction data, in crystallites in which translation **b** is

[1] Compare with case III in §3 of Dzyaloshinskii's paper [3].

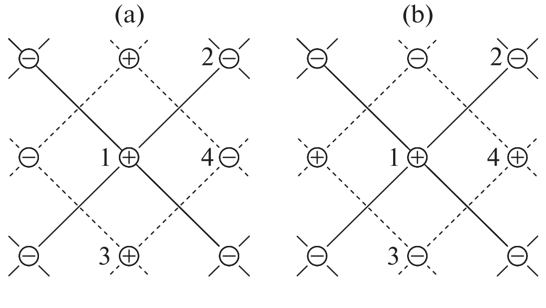

Fig. 1. A stack of alternating planes of copper atoms in the almost tetrahedral crystal of $Cu(pz)_2(ClO_4)_2$. Translation **b** is the horizontal diagonal of a rhombus, and translation **c** is the vertical diagonal.

horizontal, the state ℓ is realized (see Fig. 1). Counting the energy from the average value of the two discussed states in a given crystallite, we assign to state ℓ a small negative exchange contribution $-\alpha/2$, and to state $\tilde{\ell}$, a positive contribution $+\alpha/2$. Since the state $\tilde{\ell}$ is stable in the tetrahedral lattice, it should remain stable under small perturbations even in case of weak monoclinicity.

Generally speaking, as symmetry decreases, other magnetic characteristics, such as the susceptibility and the anisotropy constants, should also become slightly different in the states $\tilde{\ell}$ and ℓ. In addition, due to the loss of orthogonality ($\beta = 96.458°$), there arises an additional contribution of the form $\beta_3\ell_y\ell_z$ to the anisotropy, which leads to a weak deviation of the antiferromagnetic vectors from the basal plane. This should give rise to the partition into domains with opposite signs of shear deformation, which breaks the orthogonality. Such domains are characterized by different signs of the constant β_3. However, these effects should be small compared to the main effect—the splitting α of the ground state energy.

In the case when the magnetic field is parallel to the basal plane, formulas (3) can be rewritten as

$$\begin{aligned} E_\ell &= E_0 - \frac{\alpha}{2} + \frac{\beta_2 - \chi_\perp B^2}{4} + \frac{A^-}{4}\cos 2(\theta - \psi^-), \\ E_{\tilde{\ell}} &= E_0 + \frac{\alpha}{2} + \frac{\beta_2 - \chi_\perp B^2}{4} + \frac{A^+}{4}\cos 2(\tilde{\theta} - \psi^+), \end{aligned} \tag{4}$$

where

$$\tan\theta = \frac{\ell_y}{\ell_x}, \quad \tan\tilde{\theta} = \frac{\tilde{\ell}_y}{\tilde{\ell}_x}, \quad \tan\varphi = \frac{B_y}{B_x},$$

$$A^\pm = \sqrt{(\chi_\perp B^2\cos^2 2\varphi \pm \beta_2)^2 + (\chi_\perp B^2 \sin 2\varphi)^2},$$

$$\tan\psi^\pm = \frac{\chi_\perp B^2 \sin 2\varphi}{\chi_\perp B^2 \cos 2\varphi \pm \beta_2}.$$

Hence, it is obvious that the equilibrium orientations of the antiferromagnetic vectors are $\theta = \psi - + \pi/2$ and $\tilde{\theta} = \psi^+ + \pi/2$. A spin-flop transition occurs under the condition $E_\ell = E_{\tilde{\ell}}$:

$$A^+ - A^- = 4\alpha.$$

The solution of this equation gives the critical field of anomalous spin-flop

$$B_c(\varphi) = B_{sf}\left(\frac{\cos^2 2\varphi_c \sin^2 2\varphi_c}{\cos^2 2\varphi - \cos^2 2\varphi_c}\right)^{1/4}, \tag{5}$$

where $B_{sf} = \sqrt{\beta_2/\chi_\perp}$ is the field of conventional spin-flop and φ_c is the critical angle defined by the relation $\cos 2\varphi_c = 2\alpha/\beta_2$. Anomalous spin-flop is observed in the range of angles $0 \le \varphi < \varphi_c$ under the condition $\alpha < \beta_2/2$. The critical field attains its minimum at $\varphi = 0$, which is equal to $B_c(0) = B_{sf}\sqrt{\cos 2\varphi_c}$.

According to formula (5), as approaching the critical angle φ_c, the critical field should exhibit a sharp increase, which corresponds to experimental observations in antiferromagnetic $Cu(pz)_2(ClO_4)_2$ as $\varphi \to 10°$ [1]. The magnetic resonance spectrum in a field $B > B_c$ at $\varphi = 0$ should coincide with the spectrum of oscillations of the vector ℓ in the basal plane when the field is directed along the c axis. The value of the parameter $\Delta_a = 14 \pm 2$ GHz in the empirical formula proposed in [1], however, turns out to be slightly larger than the expected value $\Delta_x = 11 \pm 2$ GHz [1], which can be attributed to the above-mentioned differences in the characteristics due to monoclinic deformations.

I am pleased that this note has been accepted for publication in the issue of the journal dedicated to the 90th birthday of Igor Iekhielievich Dzyaloshinskii, who, with his remarkable articles in JETP, has largely determined the current state of the theory of antiferromagnetism.

ACKNOWLEDGMENTS

I am grateful to A.I. Smirnov and S.S. Sosin for helpful discussions and comments.

FUNDING

This work was supported by the Russian the Russian Foundation for Basic Research, project no. 19-02-00194.

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Translated by I. Nikitin