Neutron diffraction investigations of the magnetic structure of the copper–chromium chalcogenide spinel $CuCr_2S_4$

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(Submitted 14 March 1979)
Zh. Eksp. Teor. Fiz. 77, 404–408 (July 1979)

Neutron-diffraction investigations were made of the copper–chromium chalcogenide spinel $CuCr_2S_4$ at temperatures 77 and 4.2 K. A new distribution of the electrons among the ions of the copper and chromium was observed. At 77 K all the copper ions are in the $3d^{10}$ configuration, half of the chromium ions are in the $3d^3$ configuration, and the other half in the $3d^2$ configuration. At $T=4.2$ K, approximately 25% of the copper ions are in the $3d^9$ configuration and 75% in $3d^{10}$ configuration. A corresponding change takes place also in the ratio of the trivalent and tetravalent ions of chromium.

PACS numbers: 75.25. + z, 75.50.Dd

Among the chalcogenide spinels, a particular place is occupied by spinels whose tetrahedral positions are occupied by copper ions; they have metallic electric conductivity. The numerous investigations notwithstanding, the valence states of the ions in these compounds have not been established for a long time. Thus, Lotgering[1] has proposed that in the spinel $CuCr_2X_4$ (X=S, Se, Te) the copper ions are monovalent, i.e., the following cation distribution is realized:

$$Cu^+[Cr^{3+}Cr^{4+}]X_4^{2-}. \tag{1}$$

According to Goodenough[2] the copper ions in these compounds are divalent:

$$Cu^{2+}[Cr_2^{3+}]X_4^{2-}. \tag{2}$$

In a recent investigation of nuclear magnetic resonance of the nuclei Cr^{53} and $Cu^{63,65}$ and of the fine structure of the x-ray emission spectra of chromium[3] and copper[4] in $CuCr_2S_4$ at room temperature, it was shown that in this compound the copper ions are monovalent in the magnetic $3d^3$ configuration. Between the chromium ions of different valence there is a rapid exchange of electrons which is responsible for the metallic conductivity. It was observed in Ref. 3 that a temperature $T \leqslant 60$ K the NMR spectra acquire additional lines corresponding to the nuclei of the chromium and copper ions. With decreasing temperature, the intensities of these lines increase, whereas the intensities of the remaining lines decrease. To explain the low-temperature NMR spectrum it was proposed that in this compound the electrons become redistributed among the copper and chromium ions, as a result of which divalent copper ions with configuration $3d^9$ appear and the numbers of trivalent and tetravalent chromium ions are no longer equal.

Reliable information on the redistribution of the electrons along the copper and chromium ions can be obtained from an experiment on neutron diffraction. The change of the configuration of the ions leads to a change of their magnetic moments and consequently should manifest itself in a change of the picture of the magnetic scattering of the neutrons.

The magnetic structure amplitudes of the first six reflections for the spinel structure can be written in the form

$$F_{111}=2^{5/2}\bar{f}_T+8\bar{f}_O,\quad F_{222}=16\bar{f}_O,\quad F_{220}=8\bar{f}_T,$$
$$F_{400}=8\bar{f}_T+16\bar{f}_O,\quad F_{311}=2^{5/2}\bar{f}_T-8\bar{f}_O,\quad F_{331}=2^{5/2}f_T+8\bar{f}_O, \tag{3}$$

where $\bar{f}_{T,O}$ are the average magnetic-scattering amplitudes for the tetrahedral and octahedral positions. The magnetic-scattering amplitude is connected with the spin magnetic moment of the ion by the relation

$$f=\frac{e^2\gamma}{m_0c^2}\varphi(g)S=0.539\varphi(g)S\cdot 10^{-12}\text{ cm}.$$

Here $\varphi(g)$ is a form factor that takes into account the angular dependence of the magnetic-scattering amplitude.

It is seen from (3) that a transition from the cation distribution (1) to the cation distribution (2) should lead to a noticable increase of the magnetic reflections (111), (222), (400), and (331), to the appearance of a magnetic contribution to the intensity of the (220) reflection, and to a decrease of the intensity of the (311) reflection.

The neutron diffraction patterns were obtained for powders of the compound $CuCr_2S_4$ at temperatures 88 and 4.2 K. Since the Curie temperature of this compound is quite high (~398 K), the temperature dependence of the magnetic moments can be neglected in the calculation of the intensities of the magnetic reflections at 88 and 4.2 K (the intensity error is $\leqslant 2\%$).

A comparison of the experimental and calculated values of the intensities has shown that at 88 K the copper ions are in a monovalent state, i.e., the cation distribution (1) is realized. A comparison of the experimental data with the calculated ones for the cation distribution (2) leads to a considerable deterioration of the unreliability factor (from 5 to 30%):

$$R=\sum_{hkl}|I_{\text{calc}}-I_{\text{exp}}|\Big/\sum_{hkl}I_{\text{exp}}.$$

The experimental and the calculated values of the intensities are given in Table I.

TABLE I. Experimental and calculated values of the intensities of the magnetic reflections at $T=88$ K.

(hkl)	$Cu^+[Cr^{3+}Cr^{4+}]S_4^{2-}$				$Cu^{2+}[Cr_2^{3+}]S_4^{2-}$			
	$I_{\text{nuc}}^{\text{calc}}$	$I_{\text{mag}}^{\text{calc}}$	I^{calc}	I^{exp}	$I_{\text{nuc}}^{\text{calc}}$	$I_{\text{mag}}^{\text{calc}}$	I^{calc}	I^{exp}
(111)	1047	4548	5595	4980	1047	9943	11040	4980
(220)	5881	0	5881	5800	5881	346	6227	5800
(311)	11406	2307	13713	14260	11406	1930	13336	14260
(222)	1303	2675	3478	4120	1303	3845	5148	4120
(400)	3251	1296	4547	4480	3251	2851	6102	4480
(331)	686	890	1576	1830	686	1958	2644	1830
R	0.048				0.302			

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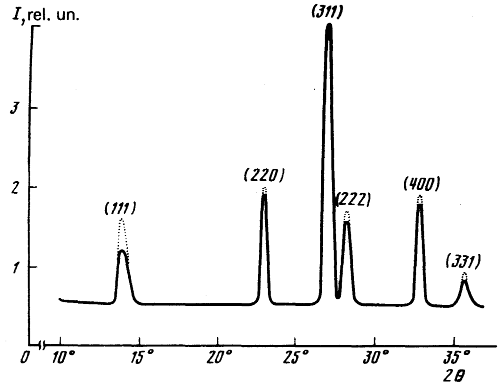

FIG. 1. Sections of the neutron diffraction patterns of $CuCr_2S_4$: solid line—88 K, dashed—4.2 K.

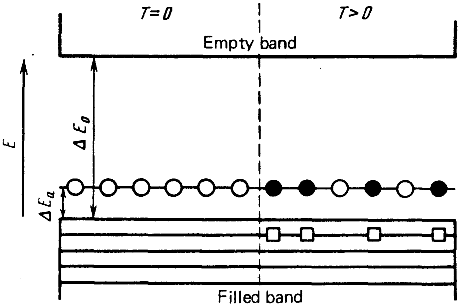

FIG. 2. Electron energy level schemes in the compound $CuCr_2S_4$: ○—Cu^{2+} ions; ●—Cu^+ ions; □—Cr^{4+} ions.

If the configurations of the Cu and Cr ions do not change with decreasing temperature, then the diffraction patterns should likewise remain unchanged. However, the diffraction pattern (Fig. 1) obtained at $T=4.2$ K shows the intensities of some reflections to increase substantially, and this increase reaches ~30% for the (111) reflection. As noted above, the increase of the intensity due to the decrease of the magnetic moment when the temperature changes from 88 to 4.2 K, and also due to the increase of the Debye–Waller factor, cannot exceed 2–3%. Consequently, the only possible cause of the increase of the intensity of the magnetic reflections can be the increase of the magnetic-scattering amplitudes $\bar{f}_{T,0}$ as a result of the change of the valence state of the cations.

Table II lists the calculated and experimental intensities of the diffraction maxima at 4.2 K for different cation distributions. It is seen that on going from the cation distribution (1) to the cation distribution (2) the intensities of the reflections increase (with the exception of the (311) reflection). However, the experimental values of the increments of the intensities are much less than the calculated ones. In this connection, it is natural to assume that at 4.2 K the redistribution of the electrons among the copper and chromium ions has not yet been completed. In this case the cation distribution can be written in the form

$$Cu^{+}_{1-x}Cu^{2+}_{x}[Cr^{3+}_{1+x}Cr^{4+}_{1-x}]S^{2-}_{4}. \tag{4}$$

Minimization of the nonreliability factor R with respect to the quantity x has shown that at $T=4.2$ K the best agreement between calculation and experiment is observed at $x\approx 0.25$ ($R_{\min}=0.026$).

TABLE II. Experimental and calculated values of the intensities of the magnetic reflections at $T=4.2$ K.

(hkl)		$Cu^+[Cr^{3+}Cr^{4+}]S_4^{2-}$	$Cu^{2+}[Cr_2^{3+}]S_4^{2-}$	$Cu^{+}_{0,75}Cu^{2+}_{0,25}[Cr^{3+}_{1,25}Cr^{4+}_{0,75}]S^{2-}_{4}$
	I_{exp}	I_{calc}	I_{calc}	I_{calc}
(111)	6820	5595	11040	6807
(220)	5930	5881	6227	5909
(341)	14000	13713	13336	13569
(222)	4300	3778	5148	4248
(400)	4600	4547	6102	4821
(331)	2030	1576	2644	1806
R	–	0.064	0.189	0.026

Thus, the neutron-diffraction analysis data confirm the previously predicted[3] assumption that the electrons become redistributed among the copper and chromium ions.

The redistribution of electrons among the copper and chromium ions in $CuCr_2S_4$ can be explained by assuming that the system of electron energy levels in $CuCr_2S_4$ takes the form shown in Fig. 2. At the temperature of absolute zero the copper ions are in $3d^9$ configuration and the chromium ions in $3d^3$ configuration. With increasing temperature, ionization of the copper ions sets in and they capture electrons from the filled band. As a result, the copper ions become monovalent ($3d^{10}$ configuration), and the chromium ions, from which one electron each is removed, become tetravalent ($3d^3$ configuration). The temperature at which all the copper ions become ionized depends on the energy gap ΔE. Therefore the redistribution of the electrons among the copper ions and chromium ions takes place in a certain temperature interval $0-TK$, which depends on ΔE_a.

Since the ions in the tetrahedral and octahedral positions in chalcogenide spinels become antiferromagnetically ordered, the compound $CuCr_2S_4$ should be ferrimagnetic at $T=0$ K. Above the temperature at which all the copper ions are ionized, this compound will be ferromagnetic. Thus, we have an unusual activation transition from the ferrimagnetic to the ferromagnetic state. It follows also from this analysis that with increasing temperature a change should be observed in the character of the electric conductivity. The electric conductivity should first increase, reach a maximum, and then decrease with further increase of temperature, just as in metals. Unfortunately, for lack of single-crystal samples of $CuCr_2S_4$ we were unable to measure the electric conductivity, and there are no data on the electric conductivity below 78 K in the scientific literature. Thus, the question of the change of the character of the electric conductivity of the compound $CuCr_2S_4$ remains open.

In conclusion, we are grateful to S. F. Dubinin and V. G. Vologin of the Institute of Metal Physics of the Urals Scientific Center of the USSR Academy of Sciences for the opportunity of carrying out the neutron-diffraction investigations at low temperatures.

[1] P. K. Lotgering, Sol. St. Comm. 2, 55 (1964).
[2] J. B. Goodenough, Colloque Int. CNRS 157, 72 (1965).
[3] N. M. Kovtun, V. T. Kalinnikov, A. A. Shemyakov, V. K. Prokopenko, and A. A. Babitsina, Pis'ma Zh. Eksp. Teor. Fiz. 25, 162 (1977) [JETP Lett. 25, 148 (1977)].
[4] M. M. Ballal and C. Mande, Sol. St. Comm. 19, 325 (1976).

Translated by J. G. Adashko

A new conservation law for the Landau-Lifshitz equations

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(Submitted 7 February 1979)
Zh. Eksp. Teor. Fiz. 77, 409–413 (July 1979)

An explicit expression for a new conservation law, which arises when allowance is made for the magnetic-dipole interactions, is obtained for the case of waves of stationary profile propagating in a uniaxial ferromagnet in a direction perpendicular to the anisotropy axis. It is shown that the new first integral allows the determination of the dependence of the amplitude of stationary-profile waves of all types on the velocity and the characteristic parameter of the magnetic medium. The dependence thus found is in complete agreement with previous numerical calculations.

PACS numbers: 75.30. – m

The analysis of the self-localized solutions of the Landau–Lifshitz equations is of indubitable interest not only in connection with the development of the theory of moving domain boundaries in magnetically ordered media, but also in connection with the search for magnetic solitons. Our previous[1] qualitative and numerical analysis of the self-localized solutions of the Landau–Lifshitz equations allowed us to give an essentially complete classification of waves of stationary profile. It was shown, in particular, that there exist in uniaxial ferromagnets, besides the well-known solutions, self-localized solutions corresponding to both "slow" and "fast" waves of stationary profile. The slow stationary-profile wave is a solitary wave with respect to one of the angular variables and a wave of the type of a moving domain boundary with respect to the other angular variable. The fast stationary-profile waves are characterized by the fact that the magnetic-moment vector executes precession about the anisotropy axis and the fact that, as the velocity of the stationary-profile wave approaches the lower cutoff velocity for spin waves, the nutational motion of the magnetic-moment vector gets excited.

Further investigations have shown that the Landau–Lifshitz equations for stationary-profile waves propagating in a direction perpendicular to the anisotropy axis admit in the case when the local magnetic fields (the magnetic-dipole interactions) are taken into account of the existence not only of the well-known conservation law connected with the invariance of the Lagrangian under spatial translation, but also of another distinctive law of conservation (of the first integral).

V. I. Arnold proposed the use of the Hénon–Heiles method[2] to demonstrate numerically the existence of the new first integral and the analogy with the dynamics of the material particle to seek the explicit form of the conservation law. The numerical computations confirmed the existence of the new first integral, and simple transformations of the Landau–Lifshitz equations allowed in the case of the simplest form of uniaxial-anisotropy energy the derivation of an explicit expression for it. Knowing the new first integral, we can obtain for the dependence of the characteristic amplitude of the slow or fast magnetic soliton on the velocity and parameter of the uniaxial magnetic medium explicit expressions that are in complete agreement with the results of the numerical analysis.[1]

2. The Landau–Lifshitz equations for stationary-profile waves propagating in a uniaxial ferromagnet in a direction perpendicular to the anisotropy axis can be written in terms of the dimensionless variables obtained by choosing the characteristic dimension of the Bloch–Landau domain boundary as the unit of length and the reciprocal of the precession frequency in the anisotropy field as the unit of time in the form

$$\mu_x'+m_zm_y=-um_x',\quad \mu_y'-(1+\varepsilon)m_zm_x=-um_y',\quad \mu_z'+\varepsilon m_xm_y=-um_z'. \tag{2.1}$$

Here u is the velocity of the stationary-profile wave, $\varepsilon=2\pi M_s^2/K$ is the parameter of the magnetic medium (M_s is the saturation magnetization and K is the uniaxial anisotropy constant), and, finally,

$$\mu=[\mathbf{mm}'] \tag{2.2}$$

is the "angular momentum" of the unit magnetic-moment vector.

The well-known conservation law (first integral) of the Landau–Lifshitz equations (2.1) is the quadratic form

$$(m_x')^2+(m_y')^2+(m_z')^2=(1+\varepsilon)m_x^2+m_y^2+\mathscr{H}, \tag{2.3}$$

where $\mathscr{H}$ is the constant of the first integration. In terms of angular variables with the polar axis directed along the anisotropy axis, the first integral (2.3) assumes the form[1]

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