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Magnetostriction Studies of Magnetic Phase Transitions in the Copper Metaborate CuB_2O_4

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Abstract—The field dependences of the longitudinal and transversal magnetostriction of the copper metaborate CuB_2O_4 were measured at various temperatures below the Néel point in magnetic fields directed along the tetragonal axis or in the basal plane. Magnetostriction was found to exhibit jumps at magnetic-field-induced phase transitions to a commensurate weak ferromagnetic state, as well as to grow smoothly in fields above and below the critical level. The magnetostriction observed in a magnetic field directed along the tetragonal axis is shown to be primarily caused by volume dilatation of the crystal. The experimental data obtained were used to construct the magnetic phase diagram of copper metaborate magnetized along the tetragonal axis.

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1. INTRODUCTION

Copper oxide compounds are characterized by a wide variety of magnetic order. Crystals of these compounds that have been investigated include the collinear three-dimensional antiferromagnet Bi_2CuO_4 [1], the spin-Peierls chain magnet $CuGeO_3$ [2, 3], the spin-glass $CuGa_2O_4$ [4], the antiferromagnet $LiCu_2O_2$ with a broken ladder structure [5], the triclinic ferrimagnet $Cu_5Bi_2B_4O_{14}$ [6], and other magnetic structures.

The tetragonal copper metaborate CuB_2O_4 occupies a specific place in the rich variety of these structures. The magnetic properties of this compound, which has a complex magnetic structure, have been studied by various experimental techniques, including neutron scattering [7, 8], μSR [9, 10], magnetic resonance [11], and magnetic measurements [12]. Neutron studies have revealed that, for $T < T_{spont} = 9.5$ K (where T_{spont} is the temperature of the spontaneous phase transition), the magnetic state of the crystal is incommensurate with the modulation wave vector directed along the tetragonal axis. Within the temperature range 1.8 to 0.9 K, the crystal undergoes a sequence of three phase transitions to new states, which are likewise modulated [8, 13]. Resonance and magnetic measurements [13] suggest that, above 9.5 K and up to the Néel temperature T_N = 20 K, the ground state is also modulated and has a long modulation period. When acted upon by a magnetic field perpendicular to the tetragonal axis, the modulated states transfer to a field-induced weak ferromagnetic state, with the spontaneous magnetic moment lying in the basal plane of the crystal.

The magnetic phase diagram of copper metaborate in a perpendicular field is presented in [13]. However, the phase transitions occurring in a magnetic field applied along the tetragonal crystal axis have not been adequately investigated thus far. Magnetic resonance studies performed in this magnetic field orientation [11] revealed anomalies in the resonance properties, which indicate a transition from the incommensurate phase to a commensurate weak ferromagnetic phase. The temperature of this transition was found to be the lower than T_{spont} the higher the magnetic resonance frequency. This implies that a magnetic field applied along the tetragonal axis also initiates a transition between the incommensurate and commensurate phases and that the critical transition field is temperature-dependent. This observation has been recently confirmed in a study of optical second-harmonic generation performed on CuB_2O_4 [14].

This publication reports on a continuation of the investigation of the phase diagram of the copper metaborate CuB_2O_4 by the magnetostriction technique, which is a traditional approach used in the study of magnetic phase transitions. Particular attention was directed at measuring the magnetostriction with the crystal magnetized along the tetragonal axis.

2. EXPERIMENTAL RESULTS

Magnetostriction was measured by the capacitive technique. Two copper capacitor cells were used to measure the transversal and longitudinal magnetostric-

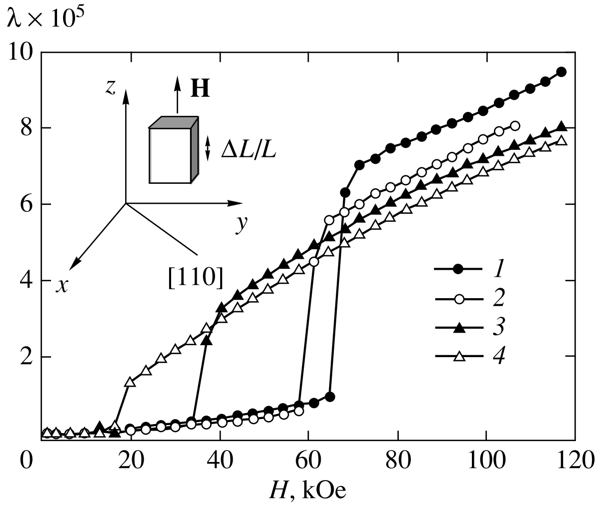

Fig. 1. Magnetic field dependences of longitudinal magnetostriction measured along the tetragonal axis of copper metaborate at various temperatures T: (*1*) 5.5, (*2*) 6.5, (*3*) 8.5, and (*4*) 9.5 K. The inset shows the geometry of the experiment.

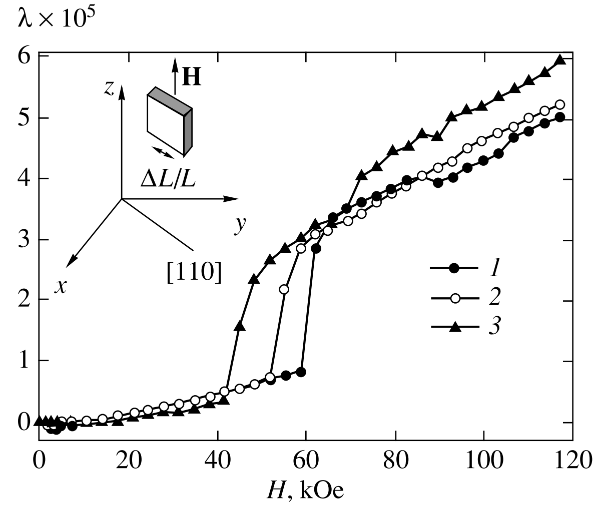

Fig. 2. Magnetic field dependences of transversal magnetostriction measured at **H** ∥ c at various temperatures T: (*1*) 5.5, (*2*) 6.5, and (*3*) 7.5 K. The inset shows the geometry of the experiment.

tion. Each cell consisted of a screened planar capacitor in which one electrode is fixed while the other shifts when acted upon by magnetostriction of the sample. The magnetostriction-induced capacitance variation was measured by an Andeen–Hagerling AX 2550A high-precision bridge. The capacitor cell was placed in a superconducting solenoid (Cryogenic Ltd.) producing magnetic fields of up to 12 T. The temperature of the cell housing the sample, controlled by a helium gas flow in the 5- to 15-K interval, could be maintained constant during the measurement of the field dependences of magnetostriction. To increase the measurement accuracy, the external magnetic field was varied stepwise, with the sample kept at each point for a few seconds before each measurement.

The samples were platelets with linear dimensions of up to 7 mm and a thickness of about 2 mm cut along the [100] and [110] planes. All the measurements were conducted in the following mode: cooling down to a given temperature with no magnetic field applied, and, after this, measurement of the field dependence of magnetostriction at this temperature.

Figure 1 presents the field dependences of longitudinal magnetostriction measured along the tetragonal axis at several temperatures. All the graphs have a characteristic shape, namely, a sharp magnetostriction jump at a critical field and a smooth monotonic course with increasing field above and below the critical value. These graphs differ in steepness by several times at fields below and above the jump. Also, a comparison of the field dependences obtained at different temperatures in fields above the critical level shows that magnetostriction falls off under heating of the crystal. We may add also that both the magnitude of the jump in magnetostriction and the corresponding critical field decrease with increasing temperature and tend to zero as the temperature T_{spont} is approached.

The field dependences of transversal magnetostriction measured in the [110] direction in the basal plane with the field also oriented along the tetragonal axis have a similar pattern. Figure 2 plots the field dependences obtained at three temperatures. The graphs are seen to exhibit the same characteristic features as those of longitudinal magnetostriction measured in the same orientation of the magnetic field.

Figure 3 displays the field dependences of longitudinal magnetostriction obtained in the basal plane in the

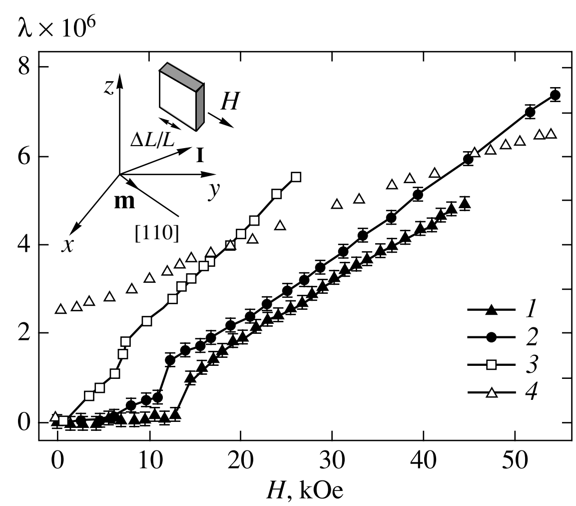

Fig. 3. Magnetic field dependences of longitudinal magnetostriction measured in the basal plane at various temperatures T: (*1*) 5.0, (*2*) 5.8, (*3*) 7.1, and (*4*) 12.8 K. The inset shows the geometry of the experiment.

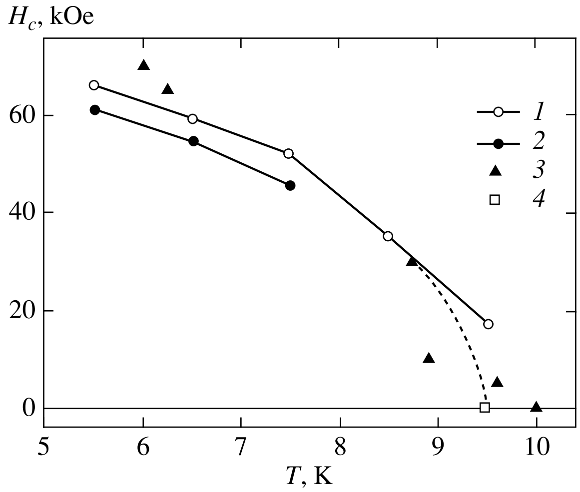

Fig. 4. Temperature dependence of the critical field of the phase transition from the incommensurate to commensurate state as derived from experimental data on (*1*) longitudinal magnetostriction, (*2*) transversal magnetostriction, (*3*) optical measurements [14], and (*4*) heat capacity [10].

[110] direction at several temperatures, including those above T_{spont}. Here, the critical fields for $T < T_{spont}$ are substantially lower than those measured at the same temperatures but under magnetization along the tetragonal axis. In addition, the magnetostriction jumps are one order of magnitude smaller than in the two preceding cases. Note one more remarkable feature: in this case, magnetostriction measured at the same field increases with increasing temperature.

3. DISCUSSION OF THE RESULTS

In summing up the experimental results, one should point out two characteristic features of the field dependences of magnetostriction, namely, a jump (or some other feature) at a critical field and a smooth increase of magnetostriction with increasing field both above and below the critical value.

The critical fields at which longitudinal magnetostriction in the basal plane undergoes jumps below 10 K can be identified with the magnetic-field-induced phase transition of copper metaborate from the incommensurate to commensurate weak ferromagnetic phase. Such transitions have been detected by resonance [11, 13], magnetic [12], and neutron diffraction [15] measurements. It was shown in [13], in particular, that the transitions to the commensurate, weak ferromagnetic phase occurring at temperatures above 9.5 K are of the second order. The field dependences of magnetization reveal kink points at the critical fields at these temperatures.

It appears only natural to assume that the magnetostriction jumps observed under magnetization along the tetragonal crystal axis are also associated with phase transitions taking place between the incommensurate and commensurate phases. Below $T_{spont} = 9.5$ K, this transition is also first-order. Figure 4 plots the temperature dependence of the phase-transition critical fields derived from measurements of the longitudinal and transversal magnetostriction for $\mathbf{H} \parallel c$. Comparison with an analogous dependence obtained under magnetization in the basal plane reveals that, in both cases, the critical fields decrease under crystal heating and tend to zero at the spontaneous transition temperature T_{spont}. The absolute fields obtained for $\mathbf{H} \parallel c$ are, however, substantially higher than those observed under magnetization in the basal plane. Moreover, in this orientation, the critical fields as derived from measurements of the longitudinal and transversal magnetostriction at the same temperatures are markedly different. We believe that this difference should be assigned to inaccuracies in the sample orientation with respect to the magnetic field.[1] The critical fields at which magnetostriction undergoes jumps are close to the phase transition fields derived from optical measurements [14] (see Fig. 4). The spontaneous transition temperature T_{spont} as extracted from heat capacity measurements with no magnetic field applied [10] is also specified in Fig. 4.

The temperature dependence of the phase-transition critical field for $\mathbf{H} \parallel c$ is essentially the magnetic phase diagram of a crystal for the given magnetic field orientation. Below the phase boundary lies a spiral structure, and above it lies a commensurate weak ferromagnetic phase. The existence of a phase transition in a magnetic field oriented in the basal plane (in which the magnetic moments forming the spiral structure are confined) comes as no surprise. A magnetic field distorts the spiral structure and transforms it first to a fanlike structure and, subsequently, to the commensurate phase. At the same time, the phase transition occurring in a magnetic field oriented along the wave vector of a structure appears at first glance strange, because in this orientation the spiral and commensurate phases have equal energies in a magnetic field. We are inclined to assign the origin of the phase transition in this case to the existence of two copper ion subsystems in CuB_2O_4. It is known [8, 16] that the twelve copper ions in the CuB_2O_4 cell occupy two nonequivalent positions to form an ordered subsystem with a Néel temperature $T_N = 20$ K (subsystem *A* consisting of four Cu^{2+} ions) and a weakly ordered subsystem that is partially polarized by exchange interaction with the ordered subsystem (subsystem *B* consisting of eight Cu^{2+} ions). Although subsystem *B* is only weakly ordered, it plays an important role in the formation of a modulated state by forming, together with subsystem *A*, a spiral magnetic structure. As shown from magnetic measurements in strong fields [17], subsystem *B*, when magnetized along the tetragonal axis, saturates at low temperatures

[1] Preliminary magnetic measurements suggest that the strongest angular dependence of the transition critical field is indeed observed for magnetic field orientations close to the tetragonal axis. Measurements of the angular dependence will be published at a later date.

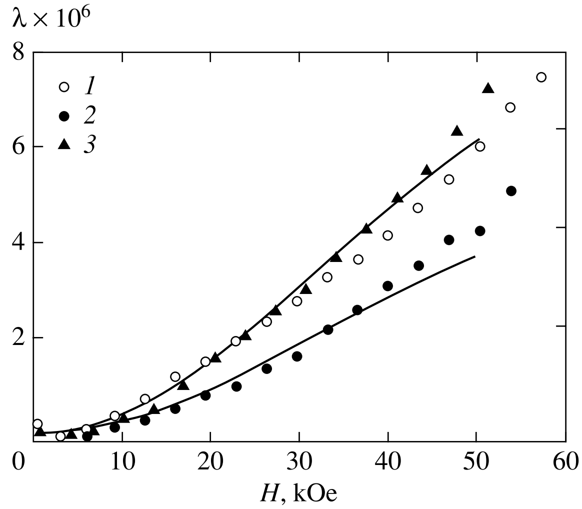

Fig. 5. Initial parts of the field dependences of (*1*, *2*) longitudinal and (*3*) transversal magnetostriction measured at (*1*) 5.5 and (*2*, *3*) 6.5 K in fields **H** || *c*. Solid lines are plots of Eq. (1).

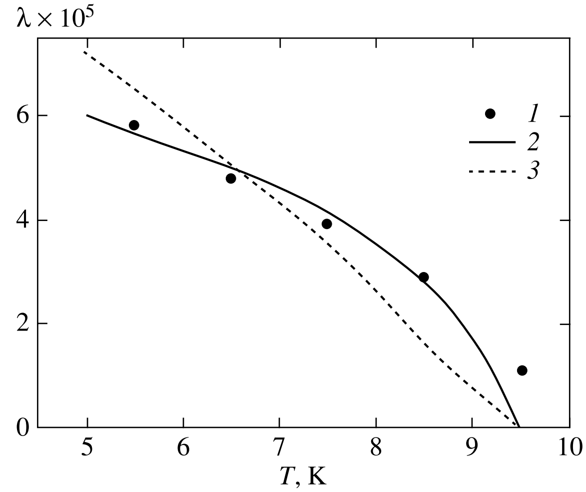

Fig. 6. (*1*) Temperature dependences (*1*) of the jump in longitudinal magnetostriction obtained at **H** || *c* and (*2*, *3*) of the normalized magnetization (*2*) $m_c(T)$ and (*3*) $m_c^2(T)$.

in fields of a few tens of kilooersteds by aligning primarily with the magnetic field. As a result, the contribution of this subsystem to the formation of the spiral structure varies and, after the field has reached a certain critical value, a transition to the commensurate phase occurs.

The jump in magnetostriction is evidently associated with a change in the magnetic state of the copper metaborate at the phase transition. Similar field dependences of magnetostriction have been observed in dysprosium and holmium single crystals [18, 19], in which the magnetostriction in the spiral state is negligible and increases in a jump at the transition from the spiral to ferromagnetic state. An analysis of the field dependences of longitudinal and transversal magnetostriction under magnetization along the tetragonal axis suggests that in our case magnetostriction in the spiral state is likewise close to zero. The weak magnetostriction observed below the critical field may originate from parts of the crystal that still reside in the commensurate state. It was reported in [15] that, when the magnetic field is applied in the basal plane, the (002) neutron peak characteristic of the commensurate phase is weakly seen in the incommensurate phase as well. The intensity of this peak grows slowly with increasing field and reaches a maximum in a jump at the phase transition.

It is significant that, when magnetization is performed along the tetragonal axis, the jumps in magnetostriction and the smooth elongation of the crystal both above and below the critical field have the same signs both along the axis and in the basal plane. This means that the magnetostriction observed under this field orientation reflects primarily volume dilatation of the crystal and is caused by the strain dependence of the exchange energy. In this case, magnetostriction is governed by the crystal magnetization only and does not depend on its direction. Therefore, following [19, 20], the magnetostriction-induced elongation can be written as

$$\left(\frac{\Delta L}{L}\right) = [\lambda_1(\alpha_x^2 + \alpha_y^2) + \lambda_2\alpha_z^2]m^2. \qquad (1)$$

Here, as is the case with uniaxial crystals, the magnetostriction constants λ_1 and λ_2 are responsible for elongation in the basal plane and along the tetragonal axis, respectively; α_i are the directional cosines of the direction along which the magnetostriction is measured; and m is the magnitude of the total crystal magnetization normalized against the saturation magnetization. Figure 5 presents the initial parts of the field dependences of longitudinal and transversal magnetostriction measured at 5.5 and 6.5 K in a magnetic field aligned with the tetragonal axis. The experimental curves obtained for both types of magnetostriction at a temperature of 6.5 K fit well to Eq. (1), in which we used the experimental field dependence of magnetization [17] measured at this temperature in a magnetic field directed along the tetragonal axis.

Recalling that the magnetostriction in the spiral state is close to zero, the magnetostriction jump at the phase transition should be determined for any temperature by the square of the magnetization in a magnetic field equal to the critical value. Figure 6 displays the temperature dependence of the jumps in longitudinal magnetostriction observed at the phase transition in a field along the tetragonal axis. Also shown are the normalized temperature dependences of $m_c^2(T)$ and $m_c(T)$ based on experimental field dependences of longitudinal magnetization [17] measured at different temperatures in a magnetic field directed along the tetragonal axis. The quantity $m_c(T)$ is actually the magnetization at the phase transition at temperature T. Contrary to what one might expect from Eq. (1), the behavior of the magnetostriction jumps is fitted better by the $m_c(T)$ temperature dependence. The field dependences taken from [17] also suggest that it is the weak subsystem that provides the major contribution to the magnetization m at low temperatures; therefore, in the case in question, both the jump in magnetostriction and its smooth growth above the critical field are dominated by the weak subsystem of the copper ions.

With magnetization performed in the basal plane, only the longitudinal magnetostriction was measured. Therefore, one cannot establish with certainty whether the effect in these conditions is due to volume magnetostriction only or whether it also contains a contribution of linear magnetostriction. Note, however, that for $\mathbf{H} \perp c$ the jumps in magnetostriction at the phase transitions and the magnitude of the magnetostriction in both states are an order of magnitude smaller than their respective values observed at $\mathbf{H} \parallel c$. In addition, we mentioned above the anomalous temperature dependence of magnetostriction in this case, namely, that magnetostriction increases with increasing temperature. It is conceivable that magnetization in the basal plane also gives rise to a linear magnetostriction contribution, which has the opposite sign. If these contributions have different temperature dependences (for instance, if the linear contribution decreases under heating faster than the volume magnetostriction), this interplay of the contributions could account for both the small total magnetostriction and its unusual temperature dependence. We note one more feature of longitudinal magnetostriction in the basal plane, more specifically, its practically linear dependence on the applied field at all temperatures (both above and below the phase transition).

The field dependence of magnetostriction measured at $T = 12.8$ K reveals a very low (less than 0.4 kOe) critical field for transition to the weak ferromagnetic state. The resolution of the superconducting solenoid in this field range is not high enough to establish whether the magnetostriction anomaly observed in these conditions is a jump or a kink point in the field dependence. Resonance and magnetic studies [13] suggest, however, that for $T > T_{spont}$ the phase transition to the weak ferromagnetic state induced by the application of a magnetic field in the basal plane is second-order. Therefore, the magnetostriction in this case also apparently changes continuously at the transition point rather than in a jump.

4. CONCLUSIONS

We have performed measurements of the longitudinal and transversal magnetostriction of the copper metaborate CuB_2O_4 with the magnetic field oriented along the tetragonal axis or in the basal plane. It has been established that the field dependences of magnetostriction in magnetic fields of either orientation exhibit anomalies as a transition occurs from the incommensurate phase to the magnetic-field-induced commensurate weak ferromagnetic phase. Below the spontaneous transition temperature $T_{spont} = 9.5$ K, the phase transition in a magnetic field is first-order. When measured in a magnetic field oriented along the tetragonal axis, both the smooth growth of the magnetostriction with the field and its jumps at the phase transitions are initiated primarily by volume magnetostriction associated with the weakly ordered copper ion subsystem. The experimental data obtained were used to construct the magnetic phase diagram of the copper metaborate magnetized along the tetragonal axis.

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REFERENCES

1. G. Petrakovskii, K. Sablina, A. Pankrats, A. Vorotinov, A. Furrer, B. Roessli, and P. Fischer, J. Magn. Magn. Mater. **140–144**, 1991 (1995).
2. G. A. Petrakovskiĭ, K. A. Sablina, A. M. Vorotynov, A. I. Kruglik, A. G. Klimenko, A. D. Balaev, and S. S. Aplesnin, Zh. Éksp. Teor. Fiz. **98** (4), 1382 (1990) [Sov. Phys. JETP **71**, 772 (1990)].
3. G. A. Petrakovskiĭ, Izv. Vyssh. Uchebn. Zaved., Fiz., No. 1, 91 (1998).
4. G. A. Petrakovskii, K. S. Aleksandrov, L. N. Bezmaternikh, S. S. Aplesnin, B. Roessli, F. Semadeni, A. Amato, C. Baines, J. Bartolome, and M. Evangelisti, Phys. Rev. B: Condens. Matter **63** (18), 184 425 (2001).
5. A. M. Vorotynov, A. I. Pankrats, G. A. Petrakovskiĭ, K. A. Sablina, W. Paszkowicz, and H. Szymczak, Zh. Éksp. Teor. Fiz. **113** (5), 1866 (1998) [JETP **86**, 102 (1998)].
6. G. A. Petrakovskiĭ, K. A. Sablina, A. I. Pankrats, L. A. Velikanov, A. D. Balaev, O. A. Bayukov, V. I. Tugarinov, A. M. Vorotynov, A. D. Vasil'ev, G. V. Romanenko, and Yu. G. Shvedenkov, Fiz. Tverd. Tela (St. Petersburg) **44** (7), 1280 (2002) [Phys. Solid State **44** (7), 1339 (2002)].
7. B. Roessli, J. Schefer, G. A. Petrakovskii, B. Ouladdiaf, M. Boehm, U. Staub, A. Vorotinov, and L. Bezmaternikh, Phys. Rev. Lett. **86** (9), 1885 (2001).
8. M. Boehm, B. Roessli, J. Schefer, A. S. Wills, B. Ouladdiaf, E. Lelièvre-Berna, U. Staub, and G. A. Petrakovskii, Phys. Rev. B: Condens. Matter **68** (2), 024 405-1 (2003).
9. M. Boehm, B. Roessli, J. Schefer, B. Ouladdiaf, A. A. Amato, C. Baines, U. Staub, and G. Petrakovskii, Physica B (Amsterdam) **318** (1), 277 (2002).
10. G. Petrakovskii, D. Velikanov, A. Vorotinov, A. Balaev, K. Sablina, A. Amato, B. Roessli, J. Schefer, and U. Staub, J. Magn. Magn. Mater **205** (1), 105 (1999).

11. A. I. Pankrats, G. A. Petrakovskiĭ, and N. V. Volkov, Fiz. Tverd. Tela (St. Petersburg) **42** (1), 93 (2000) [Phys. Solid State **42** (1), 96 (2000)].

12. G. A. Petrakovskiĭ, A. D. Balaev, and A. M. Vorotynov, Fiz. Tverd. Tela (St. Petersburg) **42** (2), 313 (2000) [Phys. Solid State **42** (2), 321 (2000)].

13. A. I. Pankrats, G. A. Petrakovskiĭ, M. A. Popov, K. A. Sablina, L. A. Prozorova, S. S. Sosin, H. Szymczak, R. Szymczak, and M. Baran, Pis'ma Zh. Éksp. Teor. Fiz. **78** (9), 1058 (2003) [JETP Lett. **78** (9), 569 (2003)].

14. R. V. Pisarev, I. Sanger, G. A. Petrakovskii, and M. Fiebig, Phys. Rev. Lett. **93** (3), 037 204-1 (2004).

15. J. Schefer, M. Boehm, B. Roessli, G. A. Petrakovskii, B. Ouladdiaf, and U. Staub, Appl. Phys. A: Mater. Sci. Process. **74** (6), 1740 (2002).

16. G. A. Petrakovskii, M. A. Popov, B. Roessli, and B. Ouladdiaf, Zh. Éksp. Teor. Fiz. **120** (4), 926 (2001) [JETP **93**, 809 (2001)].

17. G. A. Petrakovskiĭ, A. I. Pankrats, V. I. Tugarinov, K. A. Sablina, L. N. Bezmaternykh, H. Szymczak, R. Szymczak, M. Baran, A. Nabialek, and B. Kundys, Ukr. Fiz. Zh. **50** (2005) (in press).

18. S. Legvold, J. Alstad, and J. Rhyne, Phys. Rev. Lett. **10** (2), 509 (1963).

19. A. E. Clark, B. F. DeSavage, and R. Bozorth, Phys. Rev. **138** (1A), A216 (1965).

20. E. Callen and H. Callen, Phys. Rev. **139** (2A), A455 (1965).

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