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New high magnetic field phase of the frustrated $S = 1/2$ chain compound $LiCuVO_4$

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Magnetization of the frustrated $S = 1/2$ chain compound $LiCuVO_4$, focusing on high magnetic field phases, is reported. Besides a spin-flop transition and the transition from a planar spiral to a spin modulated structure observed recently, an additional transition was observed just below the saturation field. This newly observed magnetic phase is considered as a spin nematic phase, which was predicted theoretically but was not observed experimentally. The critical fields of this phase and its dM/dH curve are in good agreement with calculations performed in a microscopic model (M. E. Zhitomirsky and H. Tsunetsugu, Europhys. Lett. **92**, 37001 (2010)).

Unconventional magnetic orders and phases in frustrated quantum spin chains are attractive issues, because they appear under a fine balance of the exchange interactions and are sometimes caused by much weaker interactions or fluctuations [1 – 4].

A kind of frustration in quasi one–dimensional (1D) magnets is provided by competing interactions when the intra–chain nearest neighbor (NN) exchange is ferromagnetic and the next–nearest neighbor (NNN) exchange is antiferromagnetic. This type of exchange results in the formation of bound magnon pairs in a high magnetic field near the saturation point [1, 5, 6]. The condensation of bound magnon pairs could provide a nematic spin ordering. Numerical investigations of frustrated chain magnets with different models [7 – 9] have, indeed, predicted a nematic ordering of transverse spin components at zero temperature in a magnetic field range close to the saturation field. The spin nematic phase was introduced phenomenologically [10] as a magnetic state with zero ordered spin components and nonzero spin correlations emerging via a second order phase transition. This spin ordering is analogous to the well known ordering of molecules in nematic phases of liquid crystals [11]. Besides the frustrated spin $S = 1/2$ chains, $S \geqslant 1$ systems with biquadratic exchange were proposed as potential nematics [12]. Nevertheless, the real spin nematics have not been found during a long period.

Recently a new analytical approach for the description of the high field magnetic phase of frustrated chains with a spin-nematic ordering was proposed [13]. The parameters of this curious phase were calculated from the representation of the condensate wave function in terms of the coherent bosonic states. A $S = 1/2$ quasi 1D magnet with the competing interactions of the described type, $LiCuVO_4$, was analyzed as a potential spin nematic. For $LiCuVO_4$, the nematic phase was predicted to exist in the field interval of about 3 T below the saturation field. This work stimulated our high field magnetization measurements on $LiCuVO_4$ single crystals.

$LiCuVO_4$ crystallizes in an inverse spinel structure AB_2O_4 with an orthorhombic distortion. Copper ions share the octahedral sites being arranged in chains directed along the b–axis. These chains are separated by the nonmagnetic ions of Li, V, O. The elementary cell contains four ions $Cu^{2+}(S = 1/2)$ (see Fig.1). Neutron–diffraction experiments [14] indicate that, in the ordered phase at $T < T_N = 2.3$ K and $H = 0$, an incommensurate planar spiral spin structure occurs with the wave vector $k_{ic} = (0.468)\cdot 2\pi/b$ directed along the b–axis. The Curie-Weiss temperature is $\Theta_{CW} = -15$ K. The ordered magnetic moments of Cu^{2+} ions lie within the ab–planes and amount to $0.31\mu_B$ at T=1.6 K. The strong reduction of the ordered component and a small value of T_N/Θ_{CW} indicate a significant influence of quantum fluctuations and frustration on the ground state.

Inelastic neutron–scattering experiments [15] confirmed that the exchange interactions $J_{1,2}$ within chains are dominant, and the NN and NNN intrachain exchange interactions are ferromagnetic and antiferromagnetic, re-

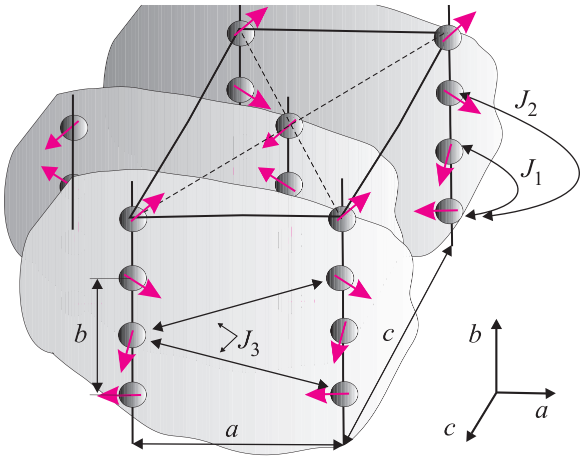

Fig.1. Scheme of Cu^{2+} moments in the crystal structure of $LiCuVO_4$. Copper ions are marked by circles. Arrows constitute a helical spin structure at $H = 0$ below T_N [14]). J_1, J_2, and J_3 are main exchange integrals [15]. The exchange bonds J_1, J_2, J_3 lie in shadowed planes, which are parallel to the ab-planes

spectively. It was shown that the incommensurate structure is due to these competing interactions. In addition, it was found that there is a ferromagnetic exchange between neighboring chains along the a–axis (J_3), and an antiferromagnetic exchange link between different ab–planes (J_4), which is almost five times smaller than J_3.

In a magnetic field H, consecutive magnetic phase transitions were observed [15 – 18]. Below 12 T, the magnetic phases were studied also by means of ESR and NMR techniques [16]. For $\mathbf{H}$ within the ab-plane, the first transition takes place at $\mu_0 H_{c1} \approx 2.5$ T, being interpreted as a spin–flop reorientation of the spin spiral plane perpendicular to H [16]. At $\mu_0 H_{c2} \approx 7$ T, there is a transition to a phase with the collinear spin-modulated structure. The spins in this phase are directed along the magnetic field. This ordering occurs only within separate ab-planes, and adjacent planes are not correlated [16, 18]. A week anisotropy of H_{c2} reveals an exchange nature of this transition. A possible mechanism of this transition was proposed in Refs. [7] and [9]. Further, the saturation of the magnetization was ascribed to dM/dH anomalies observed at $\mu_0 H \approx 40$ T and 45 T for the orientations $\mathbf{H} \parallel c$ and $\mathbf{H} \parallel a$, respectively [15, 17]. However, the true saturation, i.e. the transition to constant M, was not achieved there.

Single crystals of $LiCuVO_4$ with several cubic millimeters were prepared as described in Ref.[19]. The composition of samples is characterized by the relations: Li/V=0.96±0.05, Li/Cu=0.95±0.04, Cu/V=0.99±0.01. Thus, the average composition is $Li_{0.97}CuVO_4$, which means a low concentration of vacancies in the Li-sublattice. This type of crystals has the unit cell parameter c=8.745 Å. The analysis of the quality of samples is discussed in Ref. [20]. The samples used in the present work are from the butch 1 of Ref. [20]. Magnetization curves in magnetic fields of up to 7 T were measured with a commercial SQUID magnetometer (Quantum Design MPMS- XL7). High field magnetization data were taken in magnetic fields of up to 55 T using a pulsed magnet at KYOKUGEN in Osaka University [21].

Experimental curve of dM/dH for $\mathbf{H} \parallel c$ and its field integral $M(H)$ for $\mathbf{H} \parallel a, b, c$ are shown in Fig.2. Each dM/dH curve demonstrates two sharp peaks at

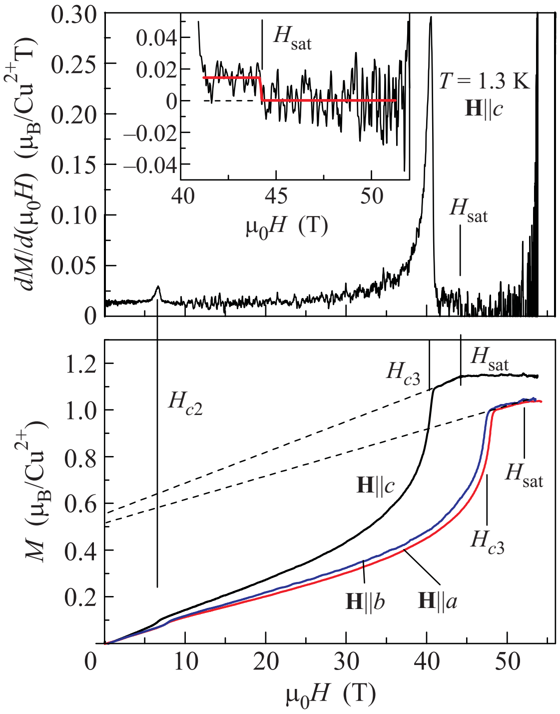

Fig.2. Upper panel: dM/dH curve measured with a pulse field technique. Insert: dM/dH near H_{sat}. The solid line presents the fit by a step-like function. The dashed line marks zero level. Lower panel: $M(H)$ curves at T =1.3 K obtained by integration for $\mathbf{H} \parallel a, b, c$. The solid lines correspond to the magnetization for field descending process. The straight dashed lines present linear fits in the range $H_{c3} < H < H_{sat}$ and extrapolations of these fits to zero field

the fields H_{c2}, H_{c3} and a step at H_{sat}. A strong inflection is seen on the $M(H)$ curve below the field H_{c3}. The lowest transition, marked as H_{c2}, occurs at $H \approx 7$ T for all three field directions. This anomaly corresponds to the transition from a spiral to a collinear spin modulated phase described above. The field derivative of magnetization above H_{c2} is a bit smaller than that in the low field phase. This difference equals 5±1% for $\mathbf{H} \parallel c$, $3.5 \pm 1\%$

for **H** $\|$ a and 2.5$\pm$ 1% for **H** $\|$ b. At this critical field, a jump of magnetization for 14$\pm$2% occurs.

Our intriguing finding in the magnetization curve is a "*fine structure*" near the saturation process, which includes anomalies at H_{c3} and $H_{\rm sat}$. The field H_{c3} is marked by the maximum of dM/dH. Right under H_{c3} (Fig.2), the dM/dH increases abruptly more than by a factor of twenty. The magnetic moment at H_{c3} reaches 95% of the saturation value. Above H_{c3}, the value of dM/dH drops quickly to that in the middle field range. Then, it goes down to zero at the saturation field $H_{\rm sat}$. The value of $H_{\rm sat}$ is determined by the fit of dM/dH curve in the interval above H_{c3} by a Fermi-like step function: $dM/dH = \chi/(\exp((H - H_{\rm sat})/\Delta H) + 1)$ where $H_{\rm sat}$, the derivative $dM/dH = \chi$, and the width of the saturation transition ΔH are fitting parameters. The obtained value of $H_{\rm sat}$ does not depend on the boundaries of the fitting range within 1%. The value of χ is obtained with the accuracy of 20%, ΔH is less then 0.01 T. The magnetic moment in the saturated phase for **H**$\|c$ is $M = 1.15 \pm 0.05$ μ_B/Cu^{2+}, consistent with the expected 1.15 μ_B for g_c=2.3. The fields H_{c3} and $H_{\rm sat}$ are well separated by an interval of 3.9 $\pm$0.1 T for **H** $\|$ c, 4.9$\pm$0.2 T for **H** $\|$ a, b.

The temperature evolution of the $M(H)$ curve for **H** $\|$ c is shown in Fig.3. The small kink of $M(H)$ at $H_{\rm sat}$ is distinguishable below 2 K. Above 2 K, the phase transition at H_{c3} is broadened and the anomaly at $H_{\rm sat}$ is masked. At 1.3 K, the hysteresis is practically negligible, while at higher temperatures it becomes larger and is probably caused by the magnetocaloric effect.

The results of low field measurements are depicted in Fig.4. The dM/dH curves for **H** $\|$ a and **H** $\|$ b have peaks at H_{c1}=2.5 and 3.1 T, respectively, corresponding to the spiral-plane flop transition. The critical fields are listed in Table. The proposed magnetic phases at $T < 2$ K are presented in the lower panel of Fig.4. For **H** $\|$ c, the low field transition is absent, because the spiral-plane flop does not take place in this case. The values of H_{c1} for a and b directions are consistent with those obtained from ESR measurements [16]. The H_{c2} for **H** $\|$ c is close to that observed in the dM/dH curve in Ref. [17]. The field H_{c3} corresponds well to the peak of dM/dH observed in Ref. [15], where this anomaly was ascribed to the saturation field. Nevertheless, the right wing of this dM/dH peak at the high field range of their work appeared much more diffuse than that in the present observation. The interval where the dM/dH decreases twice is for this experiment about 2 T while for our observation this interval is 0.25 T. A large width of the right wing of the dM/dH peak masks the details of saturation in the experiments of Refs. [17] and [15].

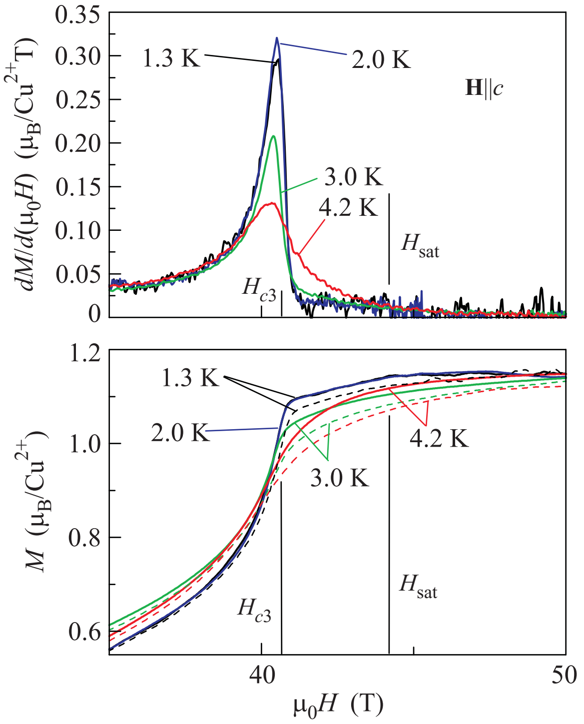

Fig.3. dM/dH, $M(H)$ curves measured with a pulse field technique for **H**$\|c$. The dashed and solid lines correspond to the magnetization curves for field ascending and descending processes, respectively

Our measurements make clear that the field at the large peak of dM/dH is not the saturation field $H_{\rm sat}$ as supposed before, but marks a transition into a new high field phase.

	H_{c1}, T (1.9 K)	H_{c2}, T (1.3 K)	H_{c3}, T (1.3 K)	$H_{\rm sat}$, T (1.3 K)
H$\|a$	2.5	7.6$\pm$0.2	47.9$\pm$0.2	52.8$\pm$0.3
H$\|b$	3.1	7.6$\pm$0.2	47.2$\pm$0.2	52.1$\pm$0.3
H$\|c$	–	6.7$\pm$0.2	40.5$\pm$0.2	44.4$\pm$0.3
Theory Ref.[13] ($T = 0$)	–	–	44.5	47.1

For the analysis, we use the model Hamiltonian:

$$\hat{\mathcal{H}} = \sum[J_1(\boldsymbol{S}_{i,j}\cdot\boldsymbol{S}_{i,j+1}) + \boldsymbol{S}_{i,j}\cdot\boldsymbol{J}_1^a\cdot\boldsymbol{S}_{i,j+1}] + \\ + \sum[J_2(\boldsymbol{S}_{i,j}\cdot\boldsymbol{S}_{i,j+2}) + \boldsymbol{S}_{i,j}\cdot\boldsymbol{J}_2^a\cdot\boldsymbol{S}_{i,j+2}] + \\ + \sum[J_3(\boldsymbol{S}_{i,j}\cdot\boldsymbol{S}_{i+1,j+1}) + J_3(\boldsymbol{S}_{i+1,j+1}\cdot\boldsymbol{S}_{i,j})] + \\ + \sum\mu_B\boldsymbol{H}\cdot\boldsymbol{g}\cdot\boldsymbol{S}_{i,j}, \quad (1)$$

where $g_{aa} = 2.070$, $g_{bb} = 2.095$, and $g_{cc} = 2.313$ are the diagonal components of g-tensor, $J_1/k_{\rm B} = -18.5$ K, $J_2/k_{\rm B} = 44$ K, $J_3/k_{\rm B} = -4.3$ K and $J^a_{1aa}/k_{\rm B} = 0.16$ K,

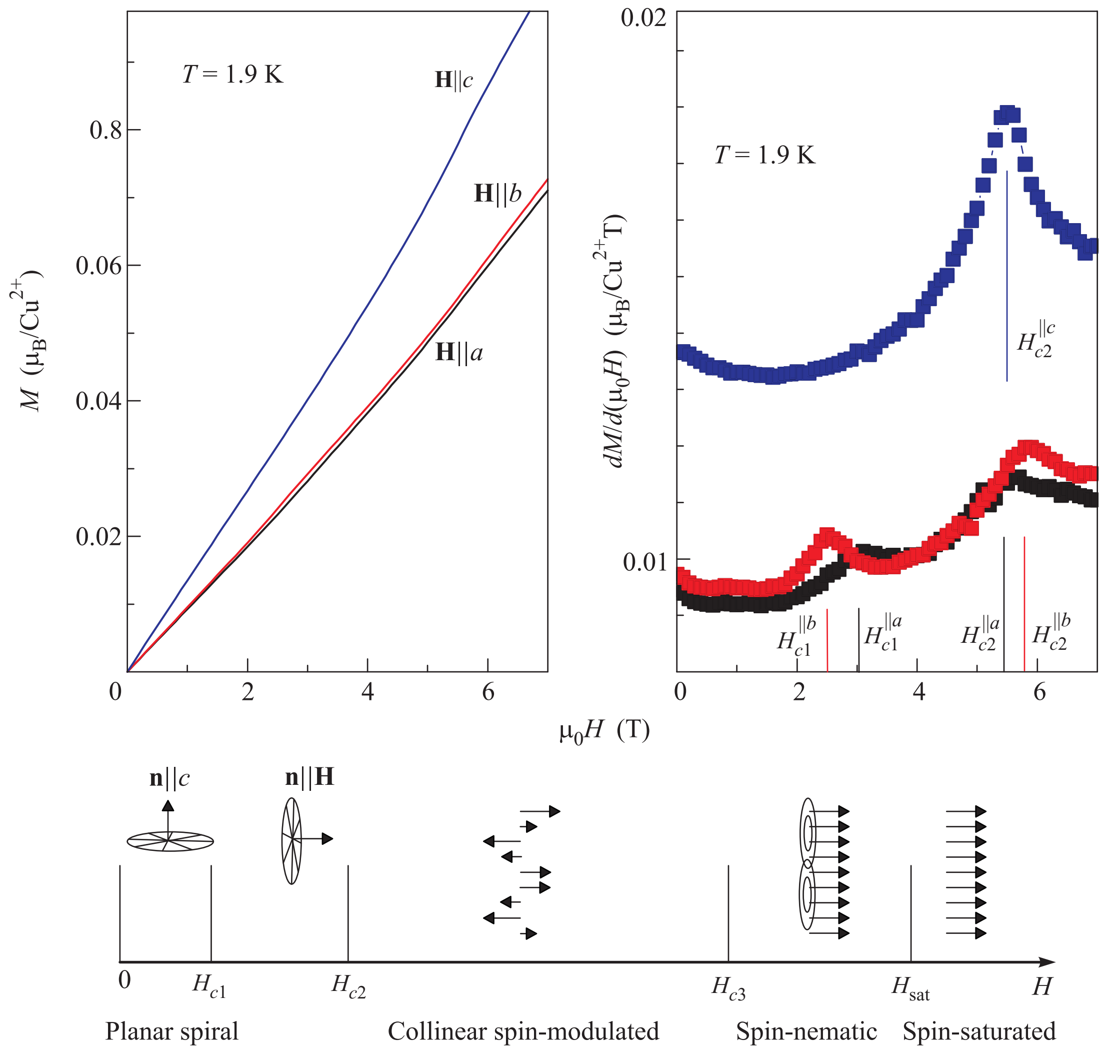

Fig.4. Upper panel: the low field magnetization curves $M(H)$ (left) and their field derivatives (right) for three field directions and at T=1.9 K. Lower panel: the scheme of expected magnetic phases in $LiCuVO_4$ at $T < 2$ K. $\mathbf{n}$ – is a unit vector normal to the spin plane

$J^a_{1bb}/k_B = -0.02$ K, and $J^a_{1cc}/k_B = -1.75$ K, $J^a_{2cc}/k_B = -0.2$ K are the diagonal components of $\boldsymbol{J}^a_1$ and $\boldsymbol{J}^a_2$-tensors. The remaining components of tensors are proposed to be small. The summation is over exchange bonds marked in Fig.1. The components of $\boldsymbol{g}$ and $\boldsymbol{J}^a_1$ tensors are obtained from ESR experiments [22], $J_{1,2,3}$ – from the neutron scattering study [15] and J_{2cc} – from the gap of the low–frequency antiferromagnetic resonance mode [16]. The saturation fields $H^{a,b,c}_{\rm sat}$ may be evaluated roughly in the classical 1D approximation as $H^i_{\rm sat}$=$4J_2S(1 + J_1/4J_2)^2/g_i\mu_B$ (i=a, b, and c) [23, 13]: $\mu_0H^a_{\rm sat}$=50 T, $\mu_0H^b_{\rm sat}$=50 T, and $\mu_0H^c_{\rm sat}$=45 T. These values are in good agreement with our experiment.

Our observations clearly indicate that the field H_{c3} is different from the saturation field. The field and magnetization intervals, corresponding to the newly found magnetic phase, can be compared with theoretical calculations performed in different models for a nematic phase. A numerical investigation of a frustrated chain was carried out [9] using a model with anisotropic exchange interactions J^a_{1cc}, J^a_{2cc}, at the condition J^a_{1cc}/J_1=J^a_{2cc}/J_2. Three phases were predicted for a system with exchange parameters J_1, J_2, and J^a_{1cc} of $LiCuVO_4$. In low fields, there is a quadrupolar spin density wave phase, having the same nearest spin correlation as the spin modulated phase observed in the experiment. A quadrupolar spin nematic phase should occur in a range below $H_{\rm sat}$. Then, a saturated phase appears above $H_{\rm sat}$. This work predicts a nematic phase in the interval of magnetization between $M_{\rm sat} - \Delta M$ and $M_{\rm sat}$. The value of ΔM is predicted to be 20–30% of $M_{\rm sat}$. The experimental value of ΔM in $LiCuVO_4$, however, is 5% of $M_{\rm sat}$. In low fields, a planar spiral is observed for $LiCuVO_4$ instead of a spin density wave predicted by the model. Note that the experimental $M(H)$ curves differ essentially from those obtained numerically for a 1D model [9]. For a usual 1D model, the fluctuation divergence of dM/dH takes place at $H_{\rm sat}$, whereas in the experiment the divergence is found at $H_{c3} < H_{\rm sat}$. Probably, this difference is caused by the 2D character of exchange links in $LiCuVO_4$.

A more adequate 2D model with exchange interactions J_1, J_2, J_3 was considered analytically in Ref. [13]. A phase transition from a spiral umbrella-like phase to a spin- nematic one was predicted at a critical field H_c. The field range of the nematic phase should reach $H_{\rm sat}$. For exchange parameters of $LiCuVO_4$, the saturation field is predicted to be 47.1 T, and the width of field range of nematic phase $H_{\rm sat}-H_c$=2.6 T, which is not far from the experimental value of $H_{\rm sat}$-H_{c3} (3.9 – 4.9 T). This theory presumes an isotropic g-factor of 2.0, which differs from the real values of $g_{a,b,c}$. Besides, the exchange parameters $J_{1,2,3}$ are known to have the accuracy of 12, 1.5 and 70%, correspondingly. This may be a reason of a considerable uncertainty in the estimation of H_c. Moreover, we compare the value of dM/dH in the high field phase with the theoretical prediction for the spin nematic phase. According to Ref. [13], dM/dH in the nematic state is approximately a half of the slope of the classical magnetization curve, which is $M_{\rm sat}/H_{\rm sat}$. As one can see in Fig.2, the value of dM/dH in the high field phase corresponds well to $\frac{1}{2}M_{\rm sat}/H_{\rm sat}$ indeed.

In conclusion, a new magnetic phase near the saturation field is observed in a quasi-1D $S = 1/2$ magnet with competing ferromagnetic NN and antiferromagnetic NNN exchange interactions $LiCuVO_4$. By comparison with theoretical studies of Refs.[1, 7 – 9, 13], this new phase must be a spin nematic one. This proposition is supported by reasonable agreement between the critical fields and dM/dH calculated analytically [13] in the 2D model and experimental ones.

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1. A. V. Chubukov, Phys. Rev. B **44**, 4693 (1991).
2. A. K. Kolezhuk, Phys. Rev. B **62**, 6057(R) (2000).
3. A. K. Kolezhuk and T. Vekua, Phys. Rev. B **72**, 094424 (2005).
4. D. V. Dmitriev and V. Yu. Krivnov, Phys. Rev. B **77**, 024401 (2008).
5. R. O. Kuzian and S.-L. Drechsler, Phys. Rev. B **75**, 024401 (2007).
6. H. T. Ueda and K. Totsuka, Phys. Rev. B **80**, 014417 (2009).
7. T. Hikihara, L. Kecke, T. Momoi, and A. Furusaki, Phys. Rev. B **78**, 144404 (2008).
8. J. Sudan, A. Lüscher, and A. M. Läuchli, Phys. Rev. B **80**, 140402(R) (2009).
9. F. Heidrich–Meisner, I. P. McCulloch, and A. K. Kolezhuk, Phys. Rev. B **80**, 144417 (2009).
10. A. F. Andreev and I. A. Grishchuk, Sov. Phys. JETP **60**, 267 (1984).
11. P. G. de Gennes, *Liquid crystals*, Clarendon Press, Oxford (1974).
12. M. Blume and Y. Y. Hsieh, J. Appl. Phys. **40**, 1249 (1969).
13. M. E. Zhitomirsky and H. Tsunetsugu, Europhys. Lett. **92**, 37001 (2010).
14. B. J. Gibson, R. K. Kremer, A. V. Prokofiev et al., Physica B **350**, e253 (2004).
15. M. Enderle, C. Mukherjee, B. Fäk et al., Europhys. Lett. **70**, 237 (2005).
16. N. Büttgen, H.-A. Krug von Nidda, L. E. Svistov et al., Phys. Rev. B **76**, 014440 (2007).
17. M. G. Banks, F. Heidrich-Meisner, A. Honnecker et al., J. Phys.: Condens. Matter **19**, 145227 (2007).
18. N. Büttgen, W. Kraetschmer, L. E. Svistov et al., Phys. Rev. B **81**, 052403 (2010).
19. A. V. Prokofiev, I. G. Vasilyeva, and W. Assmus, J. Crystal Growth **275**, e2009 (2005).
20. A. V. Prokofiev, I. G. Vasilyeva, V. N. Ikorskii et al., Sol. State Chem. **177**, 3131 (2004).
21. M. Hagiwara, S. Kimura, H. Yashiro et al., J. Phys. Conf. Ser. **51**, 647 (2006).
22. H.-A. Krug von Nidda, L. E. Svistov, M. V. Eremin et al., Phys. Rev. B **65**, 134445 (2002).
23. T. Nagamiya, K. Nagata, and Y. Kitano, Prog. Theor. Phys. **27**, 1253 (1962).