Quasi-one-dimensional S = 1/2 magnet Pb[Cu(SO₄)(OH)₂]: frustration due to competing in-chain exchange

M. Baran[1], **A. Jedrzejczak**[1], **H. Szymczak**[1], **V. Maltsev**[2], **G. Kamieniarz**[*3,4], **G. Szukowski**[3], **C. Loison**[5], **A. Ormeci**[5], **S.-L. Drechsler**[6], and **H. Rosner**[5]

[1] Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, 02-668 Warsaw, Poland
[2] Department of Geology, Moscow State University, 119899 Moscow, Russia
[3] Institute of Physics, A. Mickiewicz University, ul. Umultowska 85, 61-614 Poznan, Poland
[4] Max-Planck-Institut für Physik Komplexer Systeme, 01187 Dresden, Germany
[5] Max-Planck-Institut für Chemische Physik Fester Stoffe, 01187 Dresden, Germany
[6] Institut für Festkörpertheorie im IFW Dresden, 01171 Dresden, Germany

Zero-field susceptibility and specific heat of Pb[Cu(SO₄)(OH)₂] (linarite) single crystal were measured. In order to verify that linarite is a quasi-one-dimensional system with competing nearest-neighbour and next-nearest-neighbour in-chain exchange interaction ($J_1 \approx -30$ K, $J_2 \approx 15$ K), theoretical results based on electronic structure calculations within the LDA and a phenomenological modelling using the finite-temperature transfer-matrix method are taken into account. The possibility of various ground states is discussed in terms of the screened onsite repulsion U_s: commensurate Neel or spin-Peierls phases versus incommensurate spiral states with acute or obtuse pitch angles.

1 Introduction

Quantum effects in low-dimensional spin systems have attracted widespread and general interest. In spite of their simplicity, the quasi-1D spin systems involve rich physics and may exhibit energy gaps due to frustrated spin interactions. Although recent work on frustrated systems has been focused on the case when both nearest-neighbour (*nn*) and next-nearest-neighbor (*nnn*) interactions are antiferromagnetic (afm), a frustrated regime occurs also in the case of ferromagnetic (fm) *nn* and afm *nnn* exchange interactions [1–4].

The linarite crystal (Pb[Cu(SO₄) (OH)₂]) studied here represents an interesting case as it has also *s* = 1/2 spins arranged in isolated chains and at the same time it orders magnetically at low *T*. Such situation seems to be typical for a family of quasi-1D compounds with competing fm *nn* and afm *nnn* exchange.

In this paper the properties of the linarite single crystal are studied in LDA and estimates of exchange parameters and thermodynamic model calculations are performed to check this scenario suggested by an analysis of magnetic susceptibility and specific heat data.

2 Experiment

The space group symmetry of linarite is P2₁/m and the lattice parameters are *a* = 9.701(2) Å, *b* = 5.650(2) Å, *c* = 4.690(2) Å, *β* = 102.65(2)° [5]. The magnetically active Cu²⁺ ions (*s*=1/2) enter CuO₂

* Corresponding author: e-mail: gjk@amu.edu.pl, Phone: +48 61 8295 071, Fax: +48 61 8257 758

chains. Each of them is fourfold coordinated (Fig. 1). The oxygen surrounding, consisting of oxygen atoms O(4) and O(5) (the notation O(i) is introduced to distinguish different oxygen positions; i = 1–5), forms a flat tetragon close to the square. The distances from Cu to O(4) and O(5) are equal to 1.927 Å, and 1.976 Å, respectively. The O(4) and O(5) atoms in the CuO4 squares belong to the hydroxyl (OH) groups. In addition, two further oxygen atoms (O(3)) complete the coordination figure of a strongly distorted octahedron (with Cu-O(3) distances of about 2.539 Å). The CuO4 squares compose roof-shaped, staggered, Cu-O ribbons along the b-axis, with dihedral angle between each two neighbouring planes being equal to about 155º.
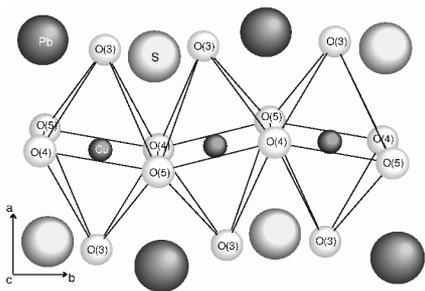

Fig. 1 Sketch of a buckled CuO$_2$ chain and its neighbourhood.

The magnetic properties of linarite were studied with a commercial SQUID magnetometer (Quantum Design, MPMS-5) in the temperature range 2–300 K and in magnetic fields up to 50 kOe. The temperature dependence of magnetic susceptibility, $\chi(T) = M(T)/H$, was measured in various magnetic fields applied both along the symmetry 2_1 axis (b-axis), i.e. along the Cu-O chains, as well as along the a and c-axes. As an example, the $\chi(T)$ dependence measured in H = 6 kOe (**H**||**b**) is shown in Fig. 2. $\chi(T)$ decreases rapidly below 5 K. At T < 3 K an anomaly was found in the $\chi(T)$ dependence which can be clearly seen in $d\chi/dT$ and $d(\chi T)/dT$ (the latter shown in the inset in Fig. 2), indicating a transition for $T \approx 2.7$ K.

Heat capacity measurements were carried out using the adiabatic heat pulse method. The data for T < 20 K are shown in Fig. 3. At $T \approx$ (2.83–2.86) K a sharp λ-like shaped anomaly was found. The specific heat, C, falls down very rapidly just below T_c but it is distinctly enhanced for $T > T_c$, suggesting a possible contribution of short-range magnetic ordering in the examined quasi-1D system. Far from the transition point in $C(T)$ curve the lattice contributio $C_L = \beta T^3 + \gamma T^5$ with $\beta = 3.4 \times 10^{-3}$ Jmol^{-1}K^{-4} and $\gamma = -3.8 \times 10^{-6}$ Jmol^{-1}K^{-6} prevails. From β a Debye temperature of about 185 K was found. However, in the temperature region up to 20 K only about 70% of the total entropy is attained which may occur for cuprates [6].
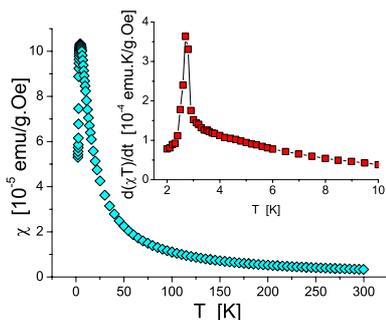

Fig. 2 Magnetic susceptibility $\lambda = M/H$ measured in H = 6 kOe directed along the b-axis, as a function of temperature (in the inset the $d(\chi T)/dT$ behavior in the low temperature region).
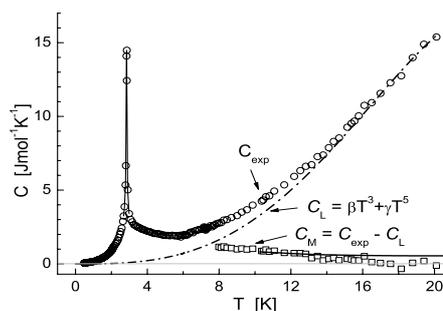

Fig. 3 Specific heat vs. temperature in zero magnetic field. The solid line presents the theoretical temperature dependence given in Ref. [6] for $|\alpha|$ =0.4 (recalculated for J_1 = 30 K).

3 Theory and discussion

The 1D spin-1/2 Heisenberg Hamiltonian with *nn* and *nnn* couplings is expressed by

$$\hat{H} = J_1 \sum_i (\hat{S}_i \hat{S}_{i+1} + \alpha \hat{S}_i \hat{S}_{i+2}) , \qquad (1)$$

where $\hat{S}_i$ is the spin-1/2 operator and $\alpha = J_2/J_1$ is a measure of frustration in the magnetic chain. For the model (1), the fits performed for our experimental data and $\alpha = 0$ failed so that we applied for the case $\alpha \neq 0$ a fitting based on the results of numerically exact quantum transfer-matrix method. Fitting the experimental susceptibility data for three crystallographic directions [7], the following exchange integrals were obtained: $J_1 = -30$ K, $J_2 = 15$ K (with about 10% uncertainty), i.e. the *nn* exchange is fm, while *nnn* interactions are afm. The corresponding *g* factors were found as follows: 2.00, 2.19, 2.30 for the crystallographic directions *a, b, c*, respectively [7]. A least-square fit of the susceptibility (χ_b) to the curie-Weiss law for temperatures above 150 K leads to a positive Weiss constant (of about 0.3 K for the linear fit and about 6 K for quadratic and cubic fits). Temperature dependence of the inverse of χ_a and χ_c deviates from the linear behaviour in the same region.

After subtracting the lattice contribution, also the magnetic part of the specific heat (Fig. 3) can be well reproduced by the theoretical curve [8] for $J_1 = -30$ K. Since $J_2/J_1 < -0.25$, an incommensurate ground state with the total spin $S_{tot} = 0$ [9] may appear so that the system deserves some attention.

First we present qualitative arguments. The *nn* superexchange part of J_1 (see Eq. (2)) can be realized through O(4) or O(5) $2p$ orbitals. This coupling is realized with 94.3° and/or 91.3° bending of Cu-O-Cu bonds, through O(4) and O(5), respectively. The nature of Cu-O-Cu couplings in linarite could be expected to be fm taking into account rather small deviation of the Cu-O-Cu angle γ from 90°. According to Goodenough-Kanamori-Anderson rule, the *nn* Cu-Cu coupling converts from afm to fm, as γ changes from 180° to 90° in accord with Mizuno *et al.* [9] concerning properties of edge-shared CuO$_2$ chains. For cuprates with CuO$_2$ chains the only known exception with $J_1 > 0$ occurs in CuGeO$_3$ for large $\gamma = 99°$ and strong crystal field [9]. In linarite, the bonds are nearly orthogonal ($\gamma = 91.3°$), such effect should be much less important. The *nnn* exchange (J_2) along *b* is realized through Cu-O(4,5)-O(4,5)-Cu paths.

In order to get more insight into the origin of the main exchange integrals, we have performed band structure calculations using the full-potential linear-muffin-tin orbital method (FPLMTO) [10]. The calculations based on the local density approximation (LDA or LSDA) were fully-relativistic (spin-orbit interaction treated variationally). For the exchange and correlation potentials the Perdew-Wang parametrization [11] was used. Basis functions, electron densities and potentials were expanded in spherical harmonics with a cut-off $l_{max} = 8$ inside non-overlapping muffin-tin spheres, and in Fourier series in the interstitial region. We employed double-κ basis functions for the semicore and the *d* states. The valence *s* and *p* states of all atoms but H were represented by a triple-κ basis.

The basis set consisted of the following states: (i) Pb: semicore $5s$, $5p$, $5d$, and $6s$, $6p$, $6d$; (ii) Cu: semicore $3s$, $3p$ and $4s$, $4p$, $3d$; (iii) S: semicore $2s$, $2p$ and $3s$, $3p$, $3d$; (iv) O: $2s$, $2p$, $3d$; (v) H: $1s$, $2p$. All these basis functions were included in the same energy panel and thus allowed to hybridize. For Brillouin zone integrations a special **k**-points method with a Gaussian broadening of width 10 mRyd was used. As the position of the hydrogen atoms could not be determined experimentally, we optimized them to minimize the total energy of the crystal using LSDA-DTF calculations with a basis-set of numerical atomic orbitals (see Table 1 for details of the pseudo-potentials). The lattice constant and all the atom positions were fixed to their experimental values [10], except for H. Optimized hydrogen Wyckoff positions, (0.136, –0.250, 0.392) and (0.124, 0.250, 0.070), were used to calculate a more accurate electronic structure with the FPLMTO scheme. We have checked that the density of states obtained with FPLMTO [10] and SIESTA [12] ere in good agreement.

element	reference	s	p	d	f	cc
Cu	atom	2.00	2.00	1.58	2.30	3.43
Pb (pseudo-core 4d)	PbII	2.20	2.90	3.55	2.90	1.50
O	atom	1.01	1.02	1.44	1.23	-
S	atom	1.50	1.59	1.74	1.94	-
H	atom	1.25	1.25	1.25	-	-

Table 1 Cutoff-radii and core-correction radii (in a$_B$) used to generate the non-con-serving pseudo-potentials with Trouiller-Martins scheme and Perdew-Wang functional [11].

The resulting sizable dispersion along *b* of the single band crossing the Fermi level is shown in Fig. 4. Ignoring weak interchain transfer, we fitted an extended tight-binding model including besides the nn and nnn parameters t_1 and t_2 also those related to the long-range transfer up to the third and fourth nearest neighbours t_3 and t_4, respectively.

In comparison with other edge-shared CuO_2 compounds, we arrived at somewhat enhanced nn transfer integral $t_1 = -130.5$ meV and at a reduced nnn transfer integral $t_2 = -79$ meV. Both effects are caused by the chain buckling . The small long-range terms $t_3 = -9$ meV and $t_4 = 1$ meV can be ignored as usual. Knowing t_i, we may estimate the corresponding exchange interactions, taking into account the usual superexchange *and* fm contributions (following from the direct fm Cu-O exchange and Hund's rule coupling on O sites) as

$$J_1 = \frac{4t_1^2}{U_s - V_{1s}} - J_{1s}^{fm}; \quad J_2 = \frac{4t_2^2}{U_s - V_{2s}} - J_{2s}^{fm}, \quad J_{is}^{fm} = J_{ib}^{fm} \frac{U_s}{U_b} e^{-r/\xi}, i = 1, 2, \quad (2)$$
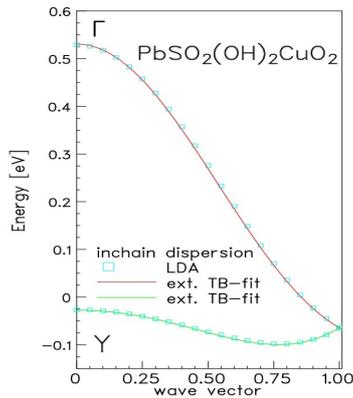
Fig. 4 Calculated and fitted (full lines) inchain dispersion along ΓY (the wave vector 1 corresponds to 0.5 Y = $(0,1,0)\pi/2b$).

where U_s, V_{1s}, V_{2s} denote screened onsite, nn and nnn intersite Coulomb interactions of an extended single-band Hubbard model, respectively, J_{is}^{fm} are fm contributions and r denotes the *Cu–Cu* distance. Adopting realistic values $U_s = 5$ eV, $V_{1s} = 1.5$ eV, $V_{2s} = 0.5$ eV, a bare Coulomb repulsion $U_b = 10$ eV and fm exchange contributions J_b^{fm} of 50 meV and 10.5 meV, respectively [13], we obtain for a screening length ξ of 25 Å the couplings $J_1 = -33.5$ K and $J_2 = 15.7$ K.

In conclusion, our exchange couplings following from electronic structure calculations performed within LDA are in qualitative accord with the values previously found from phenomenological modelling [7]. The latter explain the magnetic properties measured experimentally and we expect that linarite is a novel quasi-1D competing system which might exhibit helimagnetism with an acute pitch angle. Neutron and NMR studies would be helpful to check a helical phase as found in related edge-shared CuO_2 chain systems Li(Na)Cu_2O_2 [3], and $LiVCuO_4$ [4]. Note that our analysis is sensitive to the choice of the *U* value. For smaller (larger) U_s (V_{1s}) and smaller J_{1s}^{fm}, J_1 would be antiferromagnetic, allowing either obtuse helices, ordinary Nèel state, or a spin-Peierls phase, depending on the strength of the spin-phonon coupling.

References

[1] A. Gippius et al., Phys. Rev. B **70,** 020406(R) (2004).
[2] M. Hase et al., Phys. Rev. B **70**, 104426 (2004).
[3] L. Capogna et al., Phys. Rev. B **10**, 104402 (2005),
    S.-L. Drechsler et al., Europhys. Lett., in print.

[4] B. J. Gibson et al., Physica B **350**, 253 (2004).
[5] R. K. Eby and F. Hawthorne, Acta Cryst. B **49**, 28 (1993).
[6] M. Yamaguchi et al., J. Phys. Soc. Jpn. **65**, 2998 (1996).
[7] G. Kamieniarz et al., Comput. Phys. Commun. **147**, 716 (2002).
[8] T. Tonegawa and I. Harada, J. Phys. Soc. Jpn. **58**, 2902 (1989).
[9] Y. Mizuno et al., Phys. Rev. B **57**, 5326 (1998).
[10] K. Koepernik and H. Eschrig, Phys. Rev. B **59**, 1743 (1999).
[11] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
[12] J. M. Soler et al., J. Phys. C: Condens. Matter **14**, 2745 (2002).
[13] S.-L. Drechsler et al., J. Magn. Magn. Mater. **290/291**, 345 (2005).