

Thermal Conductivity and Heat Capacity of $\text{SrCu}_2(\text{BO}_3)_2$: A Quasi- Two-Dimensional Metal Oxide Compound with a Spin Gap

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The thermal conductivity and heat capacity of $\text{SrCu}_2(\text{BO}_3)_2$, a quasi-two-dimensional metal oxide compound with a spin gap, were studied at low temperatures. In the temperature interval $0.4 < T < 3.2$ K, the thermal conductivity of a single crystal sample in the ab plane varies according to the power law $\kappa \propto T^{2.73}$. As the temperature increases further, a deep minimum is observed in the region of $T_{\min} \approx 9.8$ K. This behavior is explained by the scattering of phonons—the major heat carriers—on the fluctuations of the spin subsystem. © 2001 MAIK “Nauka/Interperiodica”.

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In the past decade, a number of low-dimensional quantum-mechanical systems were discovered which, when cooled down to low temperatures, exhibit the appearance of a spin gap separating the nonmagnetic ground state from the spectrum of spin excitations. The formation of a spin gap in such concentrated magnetic systems is manifested by their unusual low-temperature magnetic properties, whereby the samples behave as nonmagnetic substances rather than exhibit ferro- or antiferromagnetic ordering. The ground state of these compounds is a spin singlet representing an isolated configuration of spins in which the projection of their total magnetic moment onto any direction is zero. Whether a given system reaches a ground state with or without the spin gap, depends on the mutual arrangement and magnitude of the spin magnetic moments, as well as on the magnitudes and hierarchy of the exchange interaction constants.

Recently, the group of substances with a spin gap, containing compounds such as spin-peierls CuGeO_3 [1], spin ladder SrCu_2O_3 [2], plaquette type system CaV_4O_9 [3], and charge-ordered system NaV_2O_5 [4], expanded to include a low-dimensional magnetic compound $\text{SrCu}_2(\text{BO}_3)_2$ [5]. The new member in close to high-temperature superconductors of the cuprate group: $\text{SrCu}_2(\text{BO}_3)_2$ possesses a layer structure, exhibits a pseudo-spin-gap behavior, and shows the ability to

antiferromagnetic ordering upon a small change in the parameters.

$\text{SrCu}_2(\text{BO}_3)_2$ possesses a tetragonal unit cell with the room-temperature lattice constants $a = b = 8.995$ Å, $c = 6.649$ Å. The structure of this compound comprises slightly corrugated ab planes formed by CuBO_3 , which are separated by layers of nonmagnetic Sr^{2+} ions along the c axis. As is seen in Fig. 1, the ab plane contains rectangular planar CuO_4 complexes linked by triangular BO_3 groups. All Cu^{2+} ions possess the spin 1/2 and occupy crystallographically equivalent positions. The nearest-neighbor Cu^{2+} ions form magnetic dimers, while triangular BO_3 complexes link these dimers so as to form an orthogonal network.

At present, $\text{SrCu}_2(\text{BO}_3)_2$ is the only known substance to which the quantum-mechanical Shastry–Sutherland model [6] can be applied. This theory allows the ground state of an orthogonal dimer network to be exactly calculated. Depending on the ratio of exchange integrals in (J) and between (J') dimers, a system occurs either in the antiferromagnetic ground state (for $J'/J > 0.70$) or in the state with localized magnetic dimers (for $J'/J < 0.70$). At $J'/J = 0.70$, the ground state of an orthogonal dimer network is the spin fluid. According to [7], the exchange integrals in $\text{SrCu}_2(\text{BO}_3)_2$ are $J' = 68$ K and $J = 100$ K, which corre-

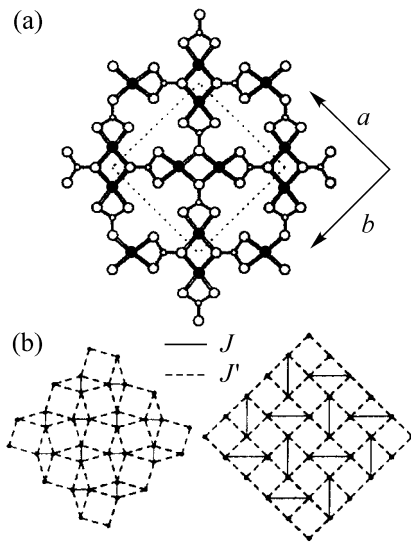


Fig. 1. Schematic diagrams showing the (a) crystal and (b) magnetic structures of $\text{SrCu}_2(\text{BO}_3)_2$ in the ab plane: (●) Cu^{2+} ions; (○) B^{3+} ions; (○) O^{2-} ions.

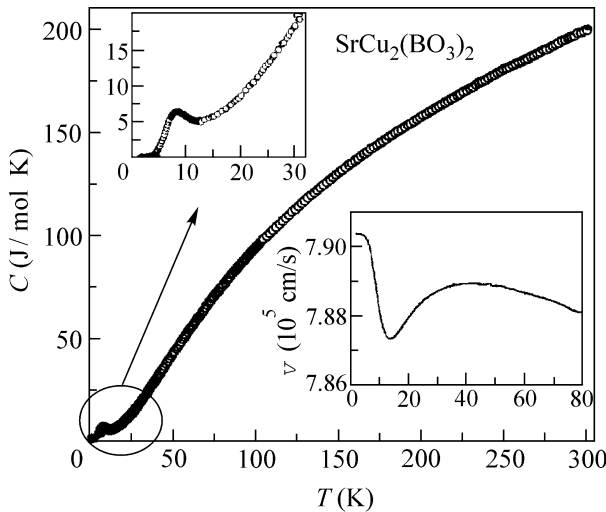


Fig. 2. The temperature dependence of heat capacity in $\text{SrCu}_2(\text{BO}_3)_2$. The bottom inset shows the temperature dependence of the longitudinal sound velocity in the [100] direction (data from [13]).

sponds to the case of localized dimers in the ground state at an exchange integral ratio $J'/J = 0.68$ close to the critical value. The spin gap width $\hbar\omega_0/k_B$ in $\text{SrCu}_2(\text{BO}_3)_2$ amounts to 34 K [5, 7, 9].

A sample of $\text{SrCu}_2(\text{BO}_3)_2$ studied in our experiments was cut to size $6 \times 1.6 \times 0.4$ mm from a single crystal ingot grown by the floating zone technique [10]. The thermal conductivity $\kappa(T)$ of the single crystal sample was studied in a broad range of temperatures from 0.4 to 300 K by the method of stationary thermal flux in the [100] direction (in the ab plane). The heat capacity

$C(T)$ of pressed powder samples was studied in the range from 1.6 to 300 K with the aid of a quasi-adiabatic microcalorimeter. The errors of determination of the κ and C values at low temperatures were about 10%.

Figure 2 shows the temperature dependence of the heat capacity of $\text{SrCu}_2(\text{BO}_3)_2$. Against a monotonic buildup of the heat capacity with increasing temperature, the curve exhibits a clearly pronounced maximum at $T \approx 8.3$ K related to the formation of a spin excitation spectrum [11, 12]. The inset in Fig. 2 shows a temperature dependence of the longitudinal sound velocity v in the [100] direction (reproduced from [13]). As is seen, there is a minimum at $T \approx 13.3$ on the background of $v(T)$ decreasing with the increase in the sample temperature.

Figure 3 shows the temperature variation of the thermal conductivity of $\text{SrCu}_2(\text{BO}_3)_2$. At lowest temperatures, the curve obeys the power law $\kappa \propto T^{2.73}$; as the temperature grows, the κ value passes through a maximum at $T \approx 3.7$ K, then drops to show a minimum at $T \approx 9.8$ K, and increases again with a maximum at $T \approx 47$ K. A maximum value of the thermal conductivity of $\text{SrCu}_2(\text{BO}_3)_2$ at $T \approx 3.7$ K amounts to $\kappa = 28$ W/(m K). A difference in the temperatures at which the features were observed in the curves of $\kappa(T)$, $C(T)$, and $v(T)$ can be related to the fact that the ground state in $\text{SrCu}_2(\text{BO}_3)_2$ is attained without clearly pronounced phase transition at a certain temperature.

The involved temperature variation of the thermal conductivity exhibiting the alternation of maxima and minima is probably a general characteristic of the systems with spin gaps. The $\kappa(T)$ curves with two peaks were previously reported for many low-dimensional compounds, although different interpretations were given in various particular cases. In CuGeO_3 , the high-temperature peak in the thermal conductivity was explained by the magnon mechanism, and the low-temperature peak, by the phonon mechanism of the heat transfer [14]. The double peak observed in the thermal conductivity of $\text{SrCu}_2(\text{BO}_3)_2$ was interpreted in terms of the magnon propagation over spin chains and ladders [15]. In NaV_2O_5 , both peaks in $\kappa(T)$ were attributed to the phonon heat transfer [16].

In our opinion, a more justified interpretation on the $\kappa(T)$ behavior in the case of $\text{SrCu}_2(\text{BO}_3)_2$ is based on the phonon heat transfer mechanism. According to the neutron scattering data [9], the spin excitations virtually do not spread over the lattice and, hence, cannot participate in the heat transfer. The minimum of $\kappa(T)$ at $T_{\min} \approx 9.8$ K is probably indicative of a strong phonon coupling to the spin subsystem.

We have analyzed the temperature variation of the thermal conductivity within the framework of a simple

Debye lattice thermal conductivity model [17], in which

$$\kappa(T) = \frac{k_B}{2\pi^2 v_s} \left(\frac{k_B}{\hbar}\right)^3 T^3 \int_0^{T_D/T} \frac{x^4 e^x \tau(x, T)}{(e^x - 1)^2} dx.$$

Here, $x = \hbar\omega/k_B T$, ω is the phonon frequency, $\tau^{-1} = \sum_i \tau_i^{-1}$ is the total phonon relaxation rate in various scattering processes, $T_D \approx 450$ is the Debye temperature [13], and v_s is the polarization-averaged sound velocity ($v_s \approx 4.5 \times 10^5$ cm/s [13]).

A satisfactory description of the low-temperature thermal conductivity is obtained with an allowance for the phonon scattering at the sample boundaries ($\tau_b^{-1} = v_s/l_C$), dislocations ($\tau_d^{-1} = A_d\omega$), point defects ($\tau_{pd}^{-1} = A_{pd}\omega^4$), in the three-phonon processes ($\tau_{3ph}^{-1} = A_{3ph}\omega^2 T^3$), and on the spin subsystem fluctuations ($\tau_{flu}^{-1} = A_{flu}\omega^4 T^2 C_s$) [18, 19]. The Casimir length $l_C = 1.12S^{1/2}$ (S is the sample cross section area) determined from the sample geometry was 0.84 mm. In the above relaxation terms, A_i are the fitting parameters and C_s is the heat capacity of the spin subsystem determined by subtracting the phonon contribution from the experimental profile (see the inset in Fig. 3).

The parameters of scattering on dislocations and point defects were determined from a power-law approximation of the low-temperature ($0.4 < T < 3.2$ K) branch of the thermal conductivity, where $\kappa \propto T^{2.73}$. Deviation of the $\kappa(T)$ value from the cubic law expected in the boundary scattering regime can be related to a significant phonon scattering on dislocations. Since the thermal conductivity at high temperatures is determined by the phonon scattering on the spin density fluctuations, which hinders reliable estimation of the parameters of the three-phonon scattering process, our selection for A_{3ph} is rather arbitrary.

The solid curve in Fig. 3 shows the approximation of the temperature dependence of the thermal conductivity in $\text{SrCu}_2(\text{BO}_3)_2$ calculated with an allowance of all the aforementioned scattering processes. The dashed curve represents the $\kappa(T)$ variation determined with neglect of the phonon scattering on the spin subsystem fluctuations. As is seen, the phonon scattering on the spin density fluctuations decreases the thermal conductivity by almost two orders of magnitude at temperature in the region of minimum in the $\kappa(T)$ curve. The so large depression of the phonon thermal conductivity probably indicates that the entire spectrum of thermal phonons is involved in interaction with the spin subsystem. This conclusion is confirmed by the results of ultrasonic measurements showing that the low-fre-

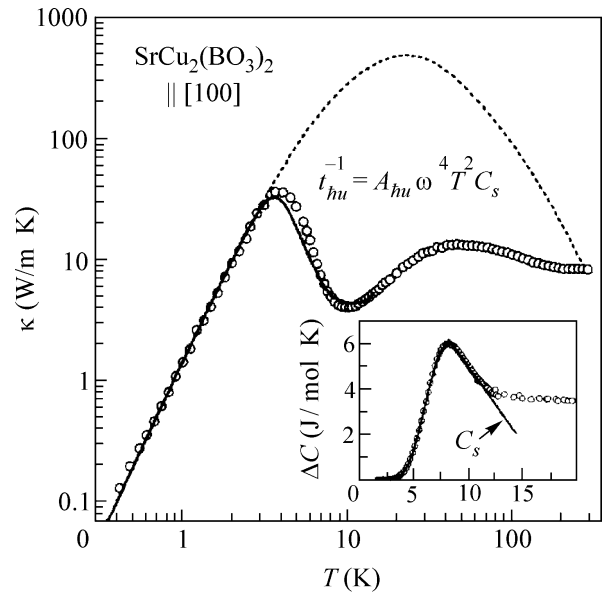


Fig. 3. The temperature dependence of the heat capacity of a $\text{SrCu}_2(\text{BO}_3)_2$ single crystal in the [100] direction. Open circles represent the experimental data, solid curve shows the results of calculations with an allowance of the phonon scattering on the spin subsystem fluctuations, dashed curve corresponds to the calculation ignoring the spin-phonon interaction. The inset illustrates determination of the heat capacity C_s of the spin subsystem (see the text).

quency acoustic phonons actually participate in the interaction [13].

Recently, the minimum observed in the temperature dependence of the thermal conductivity in $\text{SrCu}_2(\text{BO}_3)_2$ was given an alternative interpretation based on the resonance scattering of phonons in a two-level system of magnetic excitations [12]. In our opinion, this explanation should be taken with care since the resonance scattering can be effective only within a certain narrow part of the phonon spectrum.

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REFERENCES

1. M. Hase, I. Terasaki, and K. Uchinokura, *Phys. Rev. Lett.* **70**, 3651 (1993).
2. M. Azuma, Z. Hiroi, M. Takano, *et al.*, *Phys. Rev. Lett.* **73**, 3463 (1994).
3. S. Taniguchi, T. Nishikawa, Y. Yasui, *et al.*, *J. Phys. Soc. Jpn.* **64**, 2758 (1995).
4. M. Isobe and Y. Ueda, *J. Phys. Soc. Jpn.* **65**, 1178 (1996).
5. H. Kageyama, K. Yoshimura, R. Stern, *et al.*, *Phys. Rev. Lett.* **82**, 3168 (1999).

6. B. S. Shastry and B. Sutherland, *Physica B (Amsterdam)* **108**, 1069 (1981).
7. S. Miyahara and K. Ueda, *Phys. Rev. Lett.* **82**, 3701 (1999).
8. H. Kageyama, *J. Phys. Soc. Jpn.* **68**, 1821 (1999).
9. H. Kageyama, M. Nishi, N. Aso, *et al.*, *Phys. Rev. Lett.* **84**, 5876 (2000).
10. H. Kageyama, K. Onizuka, Y. Ueda, *et al.*, *J. Cryst. Growth* **206**, 65 (1999).
11. H. Kageyama, K. Onizuka, Y. Ueda, *et al.*, *Zh. Éksp. Teor. Fiz.* **117**, 145 (2000) [*JETP* **90**, 129 (2000)].
12. M. Hofmann, H. Kierspel, T. Lorenz, *et al.*, *cond-mat/0103012* (2001).
13. S. Zherlitsyn, S. Schmidt, B. Wolf, *et al.*, *Phys. Rev. B* **62**, R6097 (2000).
14. Y. Ando, J. Takeya, D. L. Sisson, *et al.*, *Phys. Rev. B* **58**, R2913 (1998).
15. A. V. Sologubenko, K. Gianno, H. R. Ott, *et al.*, *Phys. Rev. Lett.* **84**, 2741 (2000).
16. A. N. Vasil'ev, V. V. Pryadun, D. I. Khomskii, *et al.*, *Phys. Rev. Lett.* **81**, 1949 (1998).
17. R. Berman, *Thermal Conduction in Solids* (Clarendon Press, Oxford, 1976; Mir, Moscow, 1979).
18. K. Kawasaki, *Prog. Theor. Phys.* **29**, 801 (1963).
19. H. Stern, *J. Phys. Chem. Solids* **26**, 153 (1965).

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