Soft Acoustic Modes in the Two-Dimensional Spin System $SrCu_2(BO_3)_2$

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$SrCu_2(BO_3)_2$ is a two-dimensional dimerized quantum spin system which is close to a quantum critical point. The sound velocity for the longitudinal and transverse acoustic modes shows strong spin-lattice effects. The shear c_{66} mode exhibits a pronounced softening of 4.5% as a function of temperature and softens more than 25% in fields up to 50 T. This huge effect occurs in the vicinity of the magnetization plateaus $m/m_0 = 1/4$ and $1/3$. We can analyze quantitatively the temperature dependence of all measured elastic modes c_{11}, c_{44}, and c_{66} with an exchange striction mechanism. The soft c_{66} mode with B_{2g} symmetry enables us to predict the possible symmetry of the condensed triplets in some plateaus.

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The physics of low-dimensional spin systems has a long history beginning with an analysis of the antiferromagnetically coupled spin chain by Bethe in 1931. In recent years many new effects were found especially for one-dimensional spin systems. Many studies deal with the energy gap between the nonmagnetic ground state and the first excited state, e.g., in antiferromagnetic Heisenberg chains with integer spin or dimerized spin $1/2$ systems. An external magnetic field can also produce spin gaps, which are seen as quantization steps in the magnetization curve. Recently Oshikawa *et al.* [1] gave the condition for the occurrence of magnetization plateaus in a spin chain: $n(S - m) =$ integer, where n is the period of the spin ground state, S is the spin, and m is the magnetization per magnetic ion. But also in the two-dimensional system $SrCu_2(BO_3)_2$ magnetization plateaus were observed. Of particular importance is the study of two-dimensional spin systems, mainly because of its relevance to high temperature superconductivity. Very few examples of 2D spin systems are known up to now.

$SrCu_2(BO_3)_2$ is a two-dimensional coupled dimer system with remarkable properties. This tetragonal compound consists of alternately stacked $CuBO_3$ and Sr layers. Within the $CuBO_3$ plane, the Cu^{2+}-Cu^{2+} dimers are orthogonally connected, giving rise to an exact orthogonal dimer ground state [2] (see Fig. 1) according to the Shastry-Sutherland model [3]. In the magnetic field $SrCu_2(BO_3)_2$ exhibits plateaus in the magnetization at $1/8$, $1/4$, and $1/3$ of the saturation magnetization [4]. Furthermore, it is close to a quantum critical point (QCP) for the exchange parameters $J = 100$ K, $J' = 68$ K [2,5] (for a definition of J, J', see Fig. 1). In zero magnetic field the singlet-triplet splitting is $\Delta \cong 35$ K deduced from neutron scattering (with negligible dispersion) [6], from ESR [7], and from Raman scattering [8].

Recently there have been several theoretical papers investigating the quantum critical point for such a system. Apart from the dimer singlet ground state for approximately $J'/J < 0.7$ and the possible magnetic ground state for $J'/J > 0.7$ various papers discussed the possibility of intermediate phases such as helical spin arrangements [9], plaquette singlet phase [10], or second order phase transitions with nontrivial critical exponents [11]. Further developments give quantitative calculations for excited states [12] in zero magnetic field.

We want to make several important points in this Letter. As we show below very dramatic sound velocity phenomena have been discovered both as a function of temperature and high magnetic field indicating that the dimer system as shown in Fig. 1 is very sensitive to specific ionic displacements. Therefore, care has to be taken in applying the theoretical results for the QCP to the case of $SrCu_2(BO_3)_2$ because the lattice degrees of freedom have not been taken into account up to now. Other important features which we

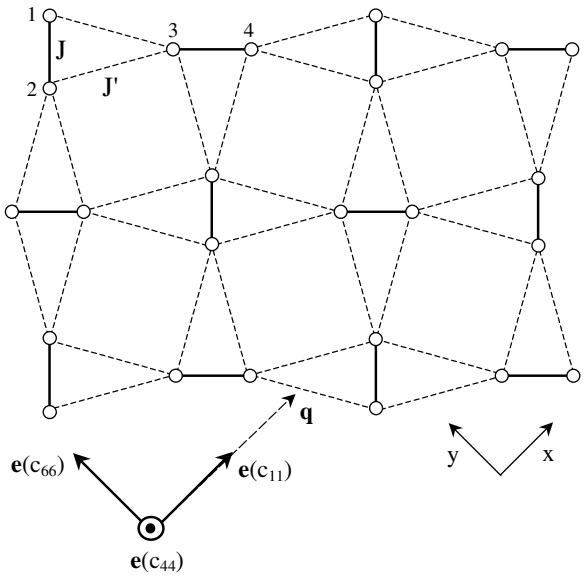

FIG. 1. Geometric arrangement of the dimers and of the different elastic modes. Here $\mathbf{q}$ is the ultrasound wave vector; $\mathbf{e}(c_{ii})$ is the polarization for the different acoustic c_{ii} modes. In the case of the c_{44} mode the polarization is parallel to the z direction.

outline below deal with a quantitative description of the temperature dependence of the elastic constants. Finally the dramatic softening of some symmetry elastic constants in high magnetic fields enables us to predict the symmetry of the ground state for the various plateaus.

Recently we have established with ultrasonic experiments a new spectroscopic tool suitable for pulsed high magnetic fields. In a series of papers [13–15] we have shown that with ultrasonic velocity and attenuation we can investigate soft magnetic modes, magnetoacoustic quantum oscillations, and different phase transitions in pulsed fields up to 50 T. This technique can be complementary to ESR in pulsed fields [16] because it covers the low frequency region. The longitudinal mode c_{11} was used previously to investigate the softening of the magnetic excitations in $SrCu_2(BO_3)_2$ [15]. This was possible through the resonant coupling of the sound wave and the soft magnetic excitations between the magnetic plateaus.

The sample has a size of about $3.9 \times 4 \times 1$ mm^3. Two opposite surfaces normal to the [100] crystallographic direction were polished for the ultrasonic experiments. We used resonance quartz transducers with the fundamental frequency of 10 MHz glued by liquid polymer (Thiokol-32) in the case of a transverse sound excitation. A broad frequency band piezoelectric film glued on the sample with a two component epoxy was used for the excitation of the longitudinal sound waves. The experimental setup is described in Ref. [14].

In Fig. 2 we show our main results obtained at 1.5 K, the relative elastic constant changes as a function of applied pulsed fields $B \parallel a$ up to 50 T for the elastic modes c_{11}, c_{44}, and c_{66}. All three modes propagate in the [100] direction with the polarization vectors $\mathbf{e}$ along [100] for the longitudinal c_{11} mode, along [001] out of the tetragonal plane for the shear c_{44} mode, and along [010] for the shear c_{66} mode as indicated in Fig. 1. Clearly the in-plane mode c_{66} shows a dramatic softening with increasing field between the plateaus of more than 25% compared to 2.5% for c_{11} and no softening at all for c_{44}. For c_{66} and c_{11} we notice sharp spikes at the corresponding field values where the magnetization changes from one plateau to the next one, i.e., at 27, 36, and 43 T for $B \parallel a$.

What is the reason for the dramatic softening of c_{66} and what makes the big differences in the different modes? As for the c_{11} investigated before in detail [15], we show that exchange striction effects are responsible for these phenomena. This exchange striction coupling arises from the strain dependence of the exchange interaction [18]:

$$E_{exs} = \sum_{ij} [J(\boldsymbol{\delta} + \mathbf{u}_i - \mathbf{u}_j) - J(\boldsymbol{\delta})]\mathbf{S}_i \cdot \mathbf{S}_j . \quad (1)$$

Here $\boldsymbol{\delta} = \mathbf{R}_i - \mathbf{R}_j$ measures the distance between two magnetic ions and $\mathbf{u}_i$ is the displacement vector for the ion $\mathbf{R}_i$. With a sound wave given by $\mathbf{u} = U\mathbf{e}\exp[i(\mathbf{q}\cdot\mathbf{r} - \omega t)]$, where $\mathbf{e}$ is the polarization vector, U is the amplitude, ω is the frequency of the sound wave, the exchange striction term reads

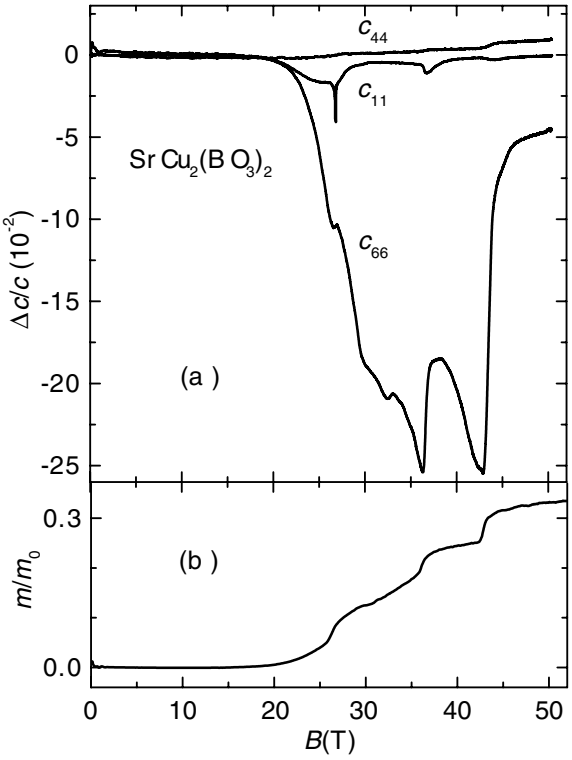

FIG. 2. Relative change of the elastic constant c_{ij} (a) as a function of high magnetic field in $SrCu_2(BO_3)_2$ at $T = 1.5$ K. Magnetic field direction was $B \parallel [100]$. The ultrasonic frequency was 10 MHz (c_{44} and c_{66} modes) and 86 MHz (c_{11} mode). Also shown is the magnetization (b) for $B \parallel [100]$ from Ref. [17].

$$E_{exs} = \sum_i U(dJ/d\boldsymbol{\delta} \cdot \mathbf{e})(\mathbf{q} \cdot \boldsymbol{\delta})(\mathbf{S}_i \cdot \mathbf{S}_{i+\delta}) e_i^{i(\mathbf{q}\cdot\mathbf{R} - \omega t)}. \quad (2)$$

Here we have expanded the exponential to first order because $q\delta \ll 1$ for sound waves of 100 MHz. Usually Eq. (2) tells us [$(dJ/d\boldsymbol{\delta} \cdot \mathbf{e}) = 0$ or $(\mathbf{q} \cdot \boldsymbol{\delta}) = 0$] that shear waves propagating along symmetry directions do not couple with this mechanism whereas longitudinal waves do. However, with Eq. (2) and the geometry of Fig. 1 it is evident that the c_{66} mode can couple to the spin system via Eq. (2), whereas c_{44} can couple only in higher order. Explicit calculations give for example the distance between the magnetic ions $\overline{12}$ in Fig. 1. It is given by the following expressions:

$$c_{11} \text{ and } c_{66} \text{ modes: } \overline{12} \cong \sqrt{2}\,a[1 + \tfrac{d}{2a}],$$
$$c_{44} \text{ mode: } \overline{12} \cong \sqrt{2}\,a[1 + \tfrac{d^2}{4a^2}],$$

where $\sqrt{2}\,a$ is the undisturbed distance and d is proportional to the amplitude U.

It is seen that the c_{11} and c_{66} modes couple linearly in the strain or amplitude U to the spin system whereas c_{44} couples only quadratically in the strain. These considerations explain the absence of any essential field dependent effect for c_{44}. They explain also the temperature dependence of the various elastic modes shown in Fig. 3.

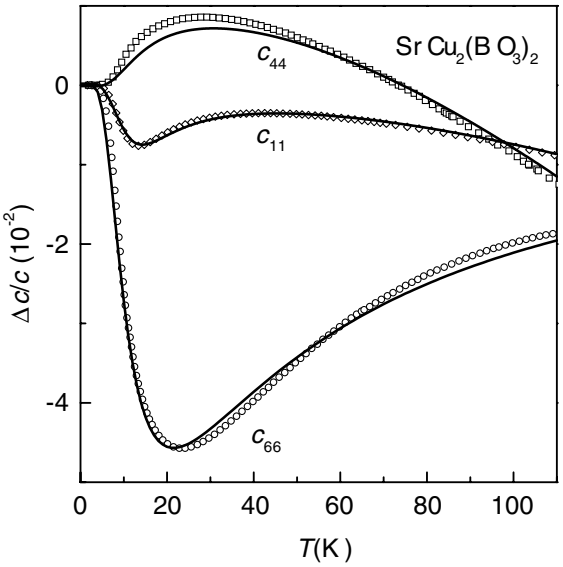

FIG. 3. Temperature dependences of the elastic constants c_{ij} in $SrCu_2(BO_3)_2$ (symbols) and fit (solid line) made in assumption of exchange striction coupling (see text for details). The ultrasonic frequencies were 10 MHz (c_{44} mode), 47 MHz (c_{66} mode), and 98 MHz (c_{11} mode).

Figure 3 gives $c_{ij}(T)$ for c_{11}, c_{44}, and c_{66} acoustic modes. Plotted is the temperature dependence of relative change normalized by the c_{ij} value at $T = 1.5$ K: $[c_{ij}(T) - c_{ij}(1.5\ \mathrm{K})]/c_{ij}(1.5\ \mathrm{K})$. The absolute values of $c_{ij}(1.5\ \mathrm{K})$ are given in Table I. The temperature dependence of the c_{11} mode was already discussed together with the magnetic susceptibility χ_m before [15]. A RPA-molecular field expression for χ_m and c_{11} could explain the temperature dependence quantitatively. For the c_{11} and c_{66} modes the expressions read

$$c_{ii}(T) = c_{ii}^{o}(T) - G_1^2 N \chi_{str}\,, \tag{3}$$

where $\chi_{str} = \chi_s/(1 - K\chi_s)$. K is the strength of the $(q = 0)$ dimer-dimer interaction, χ_s is the strain susceptibility of a single dimer, N is the density of dimers, and $G_1 = |\partial\Delta_1/\partial\varepsilon|$ is a single dimer coupling constant as explained in Ref. [15]. For the c_{11} mode we have to consider only the singlet and the first excited triplet state we take $\Delta_1 \cong 30$ K [15]. For the c_{66} mode we have to include the next higher triplet state at $\Delta_2 = 58$ K [6] because c_{66} couples very strongly to this level. This explains the higher minimum position compared to c_{11}. In addition the softening of the c_{66} mode begins at temperatures higher as for the c_{11} mode (see Fig. 3). χ_s for c_{11} was given in Ref. [15] and χ_s for c_{66} reads

$$\chi_s = -\frac{1}{G_1^2}\frac{d^2F}{d\varepsilon^2} = \frac{kT}{Z^2}\left\{Z\frac{d^2Z}{d\varepsilon^2} - \left(\frac{dZ}{d\varepsilon}\right)^2\right\}, \tag{4}$$

where $Z = 1 + 3\exp(-\Delta_1/kT) + 3\exp(-\Delta_2/kT)$. The fit of Eq. (3) to the experimental results in Fig. 3 is rather good for c_{11} and c_{66}. In order to show our original experimental results we did not subtract temperature background from our experimental data. Instead we found this background, using empirical equations [19], and added it to the exchange striction fit [see Eqs. (3) and (4)]. No background was added for the c_{66} mode fit because of the very large (in comparison to the background) softening of this mode. It turns out that the effective interaction K is ferrodistortive for c_{11} ($K = 23$ K) and antiferrodistortive for c_{66} ($K = -19$ K). The coupling constant $G_2 = |\partial\Delta_2/\partial\varepsilon|$ is 2.9 times larger than G_1 (see Table I).

For c_{44} we know from above that the coupling is of higher order in the strain. Therefore instead of a coupling $(1/J)\partial J/\partial\varepsilon = (1/\Delta)\partial\Delta/\partial\varepsilon$ we have a higher order coupling constant $(1/J)\partial^2 J/\partial\varepsilon^2 = (1/\Delta)\partial^2\Delta/\partial\varepsilon^2$ and we get

$$c_{44} = c_{44}^0 + \frac{3N}{Z}\frac{\partial^2\Delta_1}{\partial\varepsilon^2}\exp\left(\frac{-\Delta_1}{kT}\right). \tag{5}$$

This expression gives again a good fit to the experimental results as seen from Fig. 3 with a value of the coupling constant $\partial^2\Delta_1/\partial\varepsilon^2 = 1680$ K. In summary, we conclude that the anomalous temperature dependence of the elastic constants is adequately described with this exchange striction coupling. Now we return to Fig. 2, the high field effects on c_{ij}. Again we can argue that c_{44} should not couple to the magnetic excitation in lowest order as discussed above. Experimentally it does not show any magnetic field dependence except for a small hardening between each plateau of 0.1%. On the other hand Eq. (2) shows that one can have a resonant interaction between phonons and magnetic excitations because of the special geometry of $\mathbf{q}$ and $\mathbf{B}$. In the presence of high magnetic fields $\mathbf{B} = (B_x, 0, 0)$ we get $\mathbf{S}_i\mathbf{S}_j = S_i^x S_j^x + S_i^y S_j^y + S_i^z S_j^z = (\langle S\rangle + \delta S_i^x)(\langle S\rangle + \delta S_j^x) + \delta S_i^y \delta S_j^y + \delta S_i^z \delta S_j^z$. Therefore we can have bilinear phonon-magnon coupling for the c_{66} and c_{11} modes such as $\delta S^x \varepsilon_{ii}$ or $H \sim g(a_q^+ b_q + a_q b_q^+)$ with a, a^+, b, b^+ magnon and phonon operators. Such a resonant interaction close to the crossover leads to coupled phonon-magnon modes of the form [18]

$$(\omega - \omega_m)(\omega - vq) = g^2, \tag{6}$$

where g is proportional to the coupling constant, v is the sound velocity, and q is the wave number. $\omega_m = \gamma|B - B_c|$ is the magnetic excitation mode which follows a linear field dependence up to 27 T as shown by ESR measurements [5]. Magnetic excitations in higher fields have not been observed yet. From Eq. (6) we get for the

TABLE I. Values of some elastic constants c_{ij} in $SrCu_2(BO_3)_2$ [15] at $T = 1.5$ K and some exchange striction coupling constants.

c_{ij}	(10^{11} erg/cm^3)	K (K)	G_1 (K)	G_2 (K)	$\frac{\partial^2\Delta_1}{\partial\varepsilon^2}$ (K)
c_{11}	25.8	23	970	⋯	⋯
c_{66}	8.2	−19	1300	3770	⋯
c_{44}	0.96	⋯	⋯	⋯	1680

relative velocity change

$$\frac{\Delta v}{v} = \frac{\omega_m/\omega_0 + 1}{2} - \sqrt{\frac{(\omega_m/\omega_0 - 1)^2}{4} + \left(\frac{g}{\omega_0}\right)^2} - 1. \quad (7)$$

Here ω_0 is the acoustic frequency. Equation (7) can only qualitatively describe the sound velocity as a function of the magnetic field for the c_{11} and c_{66} modes.

The difference between the effects of the c_{11} and c_{66} modes which amount to an order of magnitude must be explained by a detailed microscopic consideration of the exchange striction coupling constant in the two cases. Simple length change effects give the same magnitude for the two modes as outlined above. Angular dependences of the exchange and other factors have to be taken into account for a full description of such a coupling. Such a calculation has not yet been performed.

We can try to describe the huge difference between c_{11} and c_{66} in another way in analogy to the soft mode concepts. We explain it similarly to the recently discussed charge ordering phenomena and the sound wave-charge fluctuation coupling [20,21]. In these cases the symmetry of the corresponding elastic constant (c_{44} for Yb_4As_3 and c_{66} for NaV_2O_5) predicts the symmetry of the frozen charge order (body diagonal for Yb_4As_3 and zigzag structure for NaV_2O_5). Likewise in our case of $SrCu_2(BO_3)_2$ we can argue that the soft c_{66} mode predicts the symmetry of the resonantly coupled magnetic excitation and consequently of the triplet condensation for the corresponding plateaus as calculated theoretically [2]. Taking the data of Fig. 2 we predict especially for the plateaus 1/4 (above $B = 36$ T) and 1/3 (above 43 T) a B_{2g}-type symmetry arrangement. Calculations of such an arrangement are given in Ref. [2] for the square unit cell. The hard core boson model gives rather an arrangement of B_{1g} symmetry for the 1/4 plateau. The plateau for 1/8 should give a mixture of B_{1g} and B_{2g} symmetry.

We have shown that the exchange striction coupling can account quantitatively for the temperature dependence of the three acoustic modes; it can also explain the absence of a magnetic field effect for c_{44} and for the resonant coupling of the sound wave with the magnetic excitations for the c_{11} and c_{66} modes. There are other possibilities such as a single ion magnetoelastic coupling. But for $S = 1/2$ spin the quadrupolar matrix elements are zero and therefore this coupling should give only small effects.

In summary, we have given evidence for a very dramatic spin-lattice coupling in the two-dimensional dimer substance $SrCu_2(BO_3)_2$. The in-plane shear mode exhibits a very strong softening at magnetic field values between the magnetization plateaus, but also as a function of temperature. This means that the Cu^{2+}-Cu^{2+} dimers are very strain dependent especially for the ε_{xy} strain. Any theory describing the magnetism of this system has to include the spin phonon coupling. This has to be done for describing the magnetic excitations, the general phase diagram, and especially for parameter choices which include the quantum critical point.

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