X-band ESR determination of Dzyaloshinsky-Moriya interaction in the two-dimensional $SrCu_2(BO_3)_2$ system

Andrej Zorko* and Denis Arčon
Institute "Jožef Stefan," Jamova 39, 1000 Ljubljana, Slovenia

Hans van Tol and Louis Claude Brunel
National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310

Hiroshi Kageyama
Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan
(Received 4 November 2003; revised manuscript received 11 February 2004; published 20 May 2004)

X-band ESR measurements on a single crystal of $SrCu_2(BO_3)_2$ system in a temperature range between 10 K and 580 K are presented. The temperature and angular dependence of rather broad ESR spectra can be explained by the inclusion of antisymmetric Dzyaloshinsky-Moriya (DM) interaction. However, the well-accepted picture of only out-of-plane interdimer DM vectors is not sufficient to explain the observed angular dependence. In order to account for the experimental linewidth anisotropy we additionally include sizable in-plane components of interdimer as well as intradimer DM interaction. We also emphasize that in addition to static buckling of crystal planes a recently introduced dynamical mechanism allowing for instantaneous DM interaction should be important and estimate the "average" size of intradimer DM vectors $D_\perp = 3.6 \pm 0.5$ K. Moreover, the linewidth at an arbitrary temperature can be divided into two contributions; namely, the first part arising from spin dynamics governed by the spin Hamiltonian of the system and the second part due to significant spin-phonon coupling. The nature of the latter mechanism is attributed to phonon-modulation of the antisymmetric interaction, which is responsible for the observed linear increase of the linewidth at high temperatures.

DOI: 10.1103/PhysRevB.69.174420 PACS number(s): 75.30.Gw, 75.50.Mm, 76.30.−v

I. INTRODUCTION

Low-dimensional quantum spin systems have been intensively studied over past years, both from the experimental as well as the theoretical point of view as they provide a reach variety of physical phenomena. Quantum spin fluctuations as well as magnetic anisotropy often play a crucial role in determining the ground state and low-lying magnetic excitations of these systems. In this manner a nonmagnetic singlet ground state with a spin gap to the first magnetically excited state is a result of competing exchange interactions or significant frustration present in the system.

Among only a few two-dimensional (2D) spin-gap systems is recently discovered $SrCu_2(BO_3)_2$ with a special orthogonal network of Cu^{2+} dimers formed out of localized $S=\frac{1}{2}$ spins (see Fig. 1).[1] Most of the magnetic properties of this system are well described by the Hamiltonian of the so called 2D orthogonal dimer model,[2] which takes into account antiferromagnetic exchange interaction J of each spin with its nearest neighbor (nn) as well as antiferromagnetic exchange coupling J' to four next-nearest neighbors (nnn), i.e., $H_{ex}=J\Sigma_{\langle ij\rangle}\mathbf{S}_i\cdot\mathbf{S}_j+J'\Sigma_{\{lm\}}\mathbf{S}_l\cdot\mathbf{S}_m$. Here the sums run over pairs of spins. Although various sets of exchange parameters have been reported,[2–4] the values[4] $J=85$ K and $J'=0.63J$ reproduce the temperature dependence of the magnetic susceptibility most accurately. At higher temperatures the interlayer exchange coupling $J''=0.09J$ has to be included to account for the experimental susceptibility.[4]

The ground state of the 2D orthogonal dimer model defined by H_{ex} is exactly solvable. It is simply a product of singlets on each dimer up to a critical ratio of exchange constants $(J'/J)_c=0.68$.[5] The experimentally determined values of isotropic exchange constants place $SrCu_2(BO_3)_2$ compound to the extreme vicinity of the phase boundary between the dimer phase and magnetically ordered phase. The singlet state remains the ground state of the system even when interlayer exchange J'' is taken into account.[6]

Within the orthogonal dimer model the lowest-lying mag-

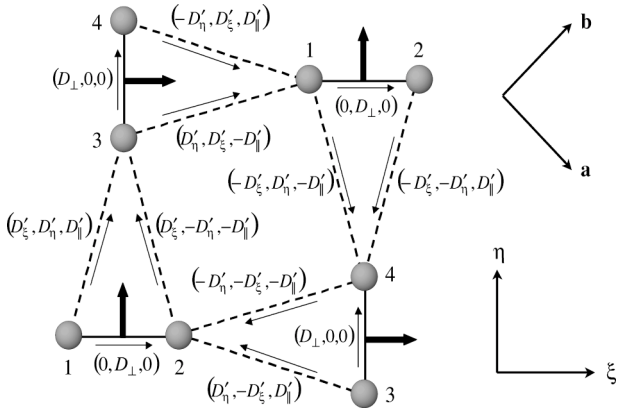

FIG. 1. The 2D network of Cu^{2+} ions with full lines representing the nn (J) and dashed lines the nnn (J') exchange coupling. The interdimer **D** and intradimer **D′** DM interactions are also presented with the thin arrows representing the orientation of corresponding bonds for DM interaction. Thick arrows are the nn DM vectors.

netically excited state is a single triplet excitation present on one of the dimers with the spin gap significantly suppressed with respect to the intradimer exchange J.[2] Experimentally, the first direct observation of the spin gap $\Delta = 35$ K was made by high-field ESR experiments.[7] Since then its existence has been confirmed by various spectroscopic methods.[8–10] So far, the picture of the low-lying magnetic excitations in $SrCu_2(BO_3)_2$ seems to be rather consistent. There are, however, still missing details. For instance, the observed anisotropic behavior of the single triplet excitation strongly depending on the direction of applied external magnetic field could not be explained with the oversimplified isotropic Hamiltonian H_{ex}. To explain this fine structure one needs to include the magnetic anisotropy into the spin Hamiltonian. Cépas *et al.*[11] introduced anisotropic terms in the form of antisymmetric Dzyaloshinsky-Moriya (DM) exchange interaction. Neglecting a small buckling of the $CuBO_3$ plane,[12] and using symmetry arguments[13] the proposed form $H_{DM} = \Sigma_{\{ij\}} \pm D'_{\parallel} \mathbf{e}_c \cdot \mathbf{S}_i \times \mathbf{S}_j$ takes into account only *nnn* interactions $\mathbf{D}'$ with the interdimer Dzyaloshinsky-Moriya vector of a magnitude $D'_{\parallel} = 2.1$ K pointing in the crystal **c**-direction, i.e., perpendicular to 2D Cu^{2+} plane (Fig. 1). On the other hand, the *nn* (intradimer) DM interaction **D** is set to zero due to the center of inversion positioned at the middle of each dimer bond. However, the presence of a sizable intradimer DM interaction has been lately suggested by several experiments. Such interaction could explain recent intriguing findings including unusual NMR shifts on B sites and staggered magnetization,[14] the relative intensities of singlet-triplet transitions observed in recent high-field ESR measurements[15] as well as the temperature dependence of the specific heat at low temperatures and in high magnetic fields (above 27 T).[16]

Moreover, though the *nnn* DM interaction reproduces the observed splitting of the single triplet excitation quite nicely and is of the expected amplitude,[12] $D'_{\parallel} \approx \Delta g/g \cdot J' \approx 6$ K, it cannot alone satisfactorily explain the observation of singlet-triplet transitions in the high-field ESR[7] and far-infrared absorption experiments.[9] These transitions are in principle allowed since the interdimer DM interaction mixes a finite amount of excited states into the ground singlet state. However, due to the symmetry of the system, the abovementioned DM terms still yield vanishing intensities of conventional magnetic dipole transitions between the ground state and the excited states.[17] Very recently, a mechanism of electric dipole transitions between the ground and the low-lying excited states has been proposed to be responsible for the observation of these ''forbidden'' transitions in the $SrCu_2(BO_3)_2$ system.[17,18] The authors explained the occurrence of infrared-active modes corresponding to magnons as well as the dependence of the relative intensities on the external magnetic field[9] by introducing a novel concept of dynamical DM interaction. In this picture, phonons induce instantaneous DM terms, which are otherwise forbidden by the symmetry of the crystal. Nevertheless strong experimental evidence for the dynamic DM interaction including the determination of its size is still missing.

In order to determine the major magnetic anisotropy interactions in $SrCu_2(BO_3)_2$ we performed a detailed single crystal X-band electron spin resonance (ESR) study in the temperature range between 10 K and 580 K, focusing in particular on the temperature and angular dependence of the ESR linewidth. We have chosen the ESR technique since ESR absorption spectra are intimately related to spin anisotropy present in the system. Conducting the experiment on a single crystal enabled us to determine the direction of the intradimer DM vectors in addition to the interdimer ones. For the first time we also present a quantitative estimation of the intradimer DM interaction in low magnetic fields. Our results give strong support to the new mechanism of the dynamical DM interaction[17,18] as will be discussed in the following sections and can explain a number of other experiments indicating the presence of *nn* DM interaction in the $SrCu_2(BO_3)_2$ system.

II. EXPERIMENTAL

Experiments were performed on a single crystal of $SrCu_2(BO_3)_2$ compound of a size $5 \times 2 \times 2$ mm^3, which was grown by the traveling solvent floating zone (TSFZ) method.[19] Its purity was verified by bulk susceptibility measurements down to 2 K while the orientation of crystal axes was determined from Laue x-ray back-reflection. X-band ESR measurements were performed on the commercial Bruker E580 FT/CW spectrometer at the Larmor frequency of $\nu_L \sim 9.5$ GHz. The measurements in the temperature range between 10 K and the room temperature were conducted using an Oxford-cryogenics liquid-helium-flow cryostat while measurements at temperatures between the room temperature and 580 K required a use of a high-temperature controller with preheated-nitrogen-flow cryostat. High-field ESR spectra on a powdered sample of $SrCu_2(BO_3)_2$ at the frequency of $\nu_L = 93.2$ GHz were recorded on a home build spectrometer working in a transition mode. The same high-purity polycrystalline sample was used for this measurement as in our previous X-band ESR report.[20]

III. THEORETICAL BACKGROUND

In the case of a large isotropic exchange interaction one can divide the Hamiltonian of a spin system in an external magnetic field into two parts $H = H_0 + H'$, where H_0 contains only the Zeeman interaction H_Z and isotropic exchange coupling H_{ex}, while all the spin anisotropy terms are contained in H' and can be treated as a perturbation. In general, at temperatures well above the characteristic Zeeman splitting ($k_B T \gg g\mu_B B_0$) the ESR absorption profile is formally given by the Fourier transform of the relaxation function $\varphi(t) = \langle \tilde{M}^+(t) M^-(0) \rangle / \langle M^+ M^- \rangle$, reflecting fluctuations of transverse magnetization operator $M^+ = g\mu_B \Sigma_i S_i^+$ in interaction representation averaged over ensemble.[21] At high temperatures ($T \gg J$) the Kubo-Tomita approach[21] to magnetic resonance is justified and well established. When the isotropic exchange interaction, which determines typical spin correlation time $\tau_c \sim \hbar/k_B J$, is large compared to the observed ESR peak-to-peak linewidth ΔB_{pp} ($k_B J \gg g\mu_B \Delta B_{pp}$) and spin diffusion is ineffective, the ESR absorption spectrum

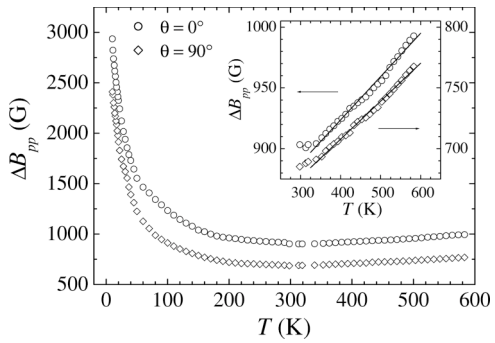

FIG. 2. Temperature dependence of the linewidth of the X-band ESR spectra of $SrCu_2(BO_3)_2$ single crystal for $\mathbf{B}_0 \| \mathbf{c}$ (circles) and $\mathbf{B}_0 \perp \mathbf{c}$ (diamonds). Inset shows the high-T linearly increasing behavior.

has a Lorentzian profile with a peak-to-peak linewidth[22]

$$\Delta B_{pp} \approx C \frac{k_B}{g\mu_B} \left(\frac{M_2^3}{M_4} \right)^{1/2}. \tag{1}$$

The second and the fourth moment of the resonance spectrum are given by expressions

$$M_2 = \langle [H', S^+][S^-, H'] \rangle / \langle S^+ S^- \rangle,$$
$$M_4 = \langle [H - H_Z, [H', S^+]][H - H_Z, [H', S^-]] \rangle / \langle S^+ S^- \rangle. \tag{2}$$

The constant C appearing in Eq. (1), however, is not rigorously determined. Since the second and forth moments of a pure Lorentzian line diverge, one is forced to carry out further approximations. The usually considered cut-off Lorentzian with a cut-off field at an arbitrary position yields a constant $C = \pi/3$. On the other hand, a more realistic lineshape given by the Lorentzian function multiplied by the exponential function of the form[22] $\exp[-|B - B_0|g\mu_B/k_B J]$ produces a constant of $C = 2\pi/\sqrt{6}$. It has to be emphasized that the exchange coupling in the $SrCu_2(BO_3)_2$ system is few orders of magnitude larger than the corresponding external magnetic field in X-band ESR experiments, which means that no deviations from Lorentzian lineshape are expected to be observable despite the multiplication with the exponential function.

On the other hand, spin diffusion may be important in low-dimensional systems at higher temperatures. In this case significant deviations from Lorentzian profiles and additional line broadening are observed.[23]

IV. RESULTS

Lorentzian shape of very broad X-Band ESR absorption lines measured in a single crystal of $SrCu_2(BO_3)_2$ has already been reported earlier.[24] The lineshape remains Lorentzian even at 580 K, proving that spin diffusion is negligible. The temperature dependence of the linewidth shows a broad minimum around room temperature (RT) for external magnetic field $\mathbf{B}_0$ parallel and perpendicular to the crystal anisotropy **c**-axis as shown in Fig. 2.

The increase of the linewidth below RT is significant in both directions and reflects the evolution of spin correlations

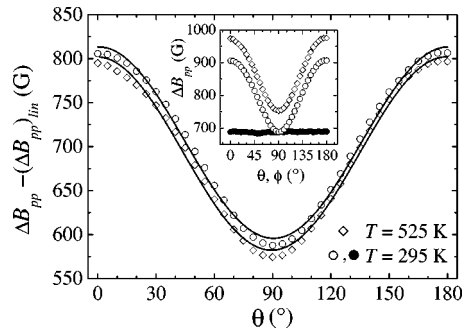

FIG. 3. X-band ESR anisotropy of $SrCu_2(BO_3)_2$ single crystal at 525 K (diamonds) and 295 K (circles) with the high-T linear part subtracted. The solid lines correspond to angular dependence predicted by Eq. (4) with $D'_{\|} = 2.4$ K and $D_{\perp} = 4.0$ K. The inset shows "raw" linewidth anisotropy in the crystal ac-plane (open symbols) at 525 K (diamonds) and 295 K (circles) and in the ab-plane at 295 K (full circles).

present in the investigated system. On the other hand, above RT the linewidth exhibits at first site rather surprising linear behavior with a slope almost independent on the angle θ between the external field $\mathbf{B}_0$ and crystal **c**-axis, i.e., the slope equals 0.355 ± 0.01 G/K for $\theta = 0°$ and 0.325 ± 0.01 G/K for $\theta = 90°$ (inset to Fig. 2). The unusual high-T increase has already been discussed on the qualitative grounds.[24] Its origin was proposed to arise from spin-orbit coupling giving rise to an additional line-broadening mechanism. However, in the present paper also a quantitative description is given on the basis of a phonon modulation of the Dzyaloshinsky-Moriya interaction. We shall come back to this linear contribution to the ESR linewidth later. For the moment, let us subtract this part from the measured linewidths and focus on the angular dependence.

Angular dependence of the linewidth at 295 K and 525 K is shown in the inset to Fig. 3. It is significant in the crystal ac-plane (dependence on the polar angle θ) while there is almost no angular dependence with respect to the azimuthal angle ϕ (ab-plane). The θ-dependence of the linewidth at both temperatures can be qualitatively described by an equation of the form $A + B(1 + \cos^2\theta)$. We use such a form rather than $A' + B' \cos^2\theta$ because of the characteristic linewidth anisotropy expected for the nnn DM interaction as it will be revealed in the next section. The experimentally determined values of the parameters are $A = 378 \pm 5$ G, $B = 218 \pm 5$ G for $T = 295$ K and $A = 362 \pm 5$ G, $B = 220 \pm 5$ G for $T = 525$ K when the high-temperature linear contribution is subtracted. As the high-T increasing part of the linewidth has more or less the same slope for $\theta = 0°$ and $\theta = 90°$ the same set of parameters A and B corresponds to the linewidth anisotropy for temperatures above approximately 340 K (see inset to Fig. 2).

Due to the large exchange coupling one expects a strong exchange narrowing of the ESR line. Therefore, only few spin-anisotropy interactions are expected to account for experimental linewidths. Major anisotropy contributions to the linewidth have already been evaluated in our previous report,[24] where the DM interaction was shown to play by far the biggest role. In fact, among the major magnetic aniso-

tropy interactions expected for a spin $S=\frac{1}{2}$ system, namely, the dipolar interaction, the hyperfine coupling, the symmetric anisotropic exchange and the antisymmetric DM interaction, the latter interaction is the only one giving linewidths of the correct order of magnitude.

V. ANALYSIS AND DISCUSSION

A. Linewidth anisotropy

Exploring the originally proposed picture of only interdimer DM interactions with corresponding DM vectors parallel to crystal **c**-axis proposed by Cépas *et al.*,[11] the angular dependence of the linewidth is expected to be of the form (see the Appendix)

$$\Delta B_{pp} \approx \frac{2\pi}{\sqrt{6}} \frac{k_B}{g\mu_B} \frac{D_{\parallel}'^2}{\sqrt{6(3J^2+3J'^2-2JJ')}}(1+\cos^2\theta). \tag{3}$$

The above equation possesses no ϕ-dependence, which is in excellent agreement with the experiment (Fig. 3). On the other hand, the θ-dependence of the form $B(1+cos^2\theta)$ is predicted. However, the experimental results presented in Fig. 3 differ from this prediction in one important detail. Namely, there is an additional constant parameter A, which has to be included to yield a satisfactory fit, even though the high-temperature linearly increasing part is subtracted from the ''raw'' data. We emphasize once again that the parameter A is of the same order of magnitude as parameter B. Therefore, the magnetic anisotropy introducing the additional A term should be substantial and cannot be simply ignored. This raises a fundamental question about the origin of this supplementary contribution to the linewidth. Symmetric anisotropy interaction, which should give the second largest contribution to the linewidth, can be safely dismissed from the possible causes of the observed discrepancy for at least two reasons. It is more than an order of magnitude too small and it yet again yields angular dependence of the form $(1+\cos^2\theta)$.[24]

We have already proposed in our initial report[24] that the observed angular dependence of the linewidth originates from additional magnetic-anisotropy terms of Dzyaloshinsky-Moriya type that should be included in the spin Hamiltonian. As already emphasized, when treating the $CuBO_3$ crystal planesas ideally planar only the interdimer DM interactions with vectors perpendicular to this plane are allowed for symmetry reasons.[11] On the other hand, a finite buckling of these planes has been reported below the displacive, second order structural phase transition occurring at $T_s=395$ K.[12] Bending of neighboring CuO_4 plaquettes allows for finite in-plane components of interdimer DM interaction $D_{\perp}'$ as well as for in-plane intradimer coupling $D_{\perp}$. Moreover, the direction of DM vectors of the latter interaction is well defined, due to the fact that a mirror plane perpendicular to crystal ab-plane containing a dimer still exists. The nn DM vectors thus have to point perpendicularly to the direction of the dimer (Fig. 1). The interdimer $D_{\perp}'$ coupling has recently been proposed to be responsible for the fine structure of the single triplet excitation at wave vector $Q=(1.5,0,0)$ observed in high-resolution inelastic neutron scattering experiments.[25] It has been estimated to be of the order of 35% of $D_{\parallel}'$ in the $J'=0$ limit. Since the ESR linewidth is proportional to the square of the amplitude of DM vector, the in-plane component of the nnn DM interaction yields smaller corrections to the linewidth. For this reason it can be neglected in the first approximation.

Taking into account the additional intradimer DM interaction $D_{\perp}$, the angular dependence of the ESR linewidth is given by the following expression (see the Appendix),

$$\Delta B_{pp} \approx \frac{2\pi}{\sqrt{6}} \frac{k_B}{g\mu_B} \left(\frac{(8D_{\parallel}'^2+3D_{\perp}^2+(8D_{\parallel}'^2-D_{\perp}^2)\cos^2\theta)^3}{96(32D_{\parallel}'^2J_1^2+3D_{\perp}^2J_2^2+(32D_{\parallel}'^2J_1^2-D_{\perp}^2J_2^2)\cos^2\theta)} \right)^{1/2}, \tag{4}$$

with $J_1^2=3J^2+3J'^2-2JJ'$ and $J_2^2=13J^2+6J'^2$. Due to the fact that dimers form an orthogonal network, the linewidth remains ϕ-independent, which is, as already stressed, in accordance with the experiment. The derived equation fits the observed linewidth anisotropy rather well, as shown in Fig. 3. The parameters obtained for 525 K are $D_{\parallel}'=2.4\pm0.1$ K and $D_{\perp}=4.0\pm0.1$ K. At 295 K the parameters are only slightly bigger, i.e., by approximately 0.1 K. Moreover, the high-T parameters seem to be valid for all temperatures above approximately 340 K as the linewidth simply increases with similar slope for all directions above this temperature. The $D_{\parallel}'=2.4$ K term is in good agreement with the previous estimation of the interdimer DM interaction determining the fine splitting of triplet excitations.[11]

We stress that the inclusion of a finite in-plane interdimer DM interaction $D_{\perp}'$ (Fig. 1) slightly modifies the value of $D_{\perp}$. If the DM interaction between nnn spins 1 and 3 is of the form $\mathbf{D}_{13}=(D_{\xi}',D_{\eta}',D_{\parallel}')$, the four symmetry operators of the $SrCu_2(BO_3)_2$ space group ($I\bar{4}2m$) below $T_s=395$ K, namely, the mirror planes ($m_1\ x,x,z$ and $m_2\ x,\bar{x},z$) and the fourfold rotoinversion axes ($\bar{4}^-0,1/2,z;0,1/2,1/4$ and $\bar{4}^+1/2,0,z;1/2,0,1/4$), determine all the remaining nnn DM vectors as indicated in Fig. 1. The resulting linewidth is qualitatively unchanged as well as the size of $D_{\parallel}'$ term. However, the in-plane components of nn and nnn DM interaction are coupled. Taking the latter from high-resolution inelastic neutron scattering results[25] to amount for $D_{\xi}'^2+D_{\eta}'^2=D_{\perp}'^2 \approx 0.1D_{\parallel}'^2$, our fit gives a smaller value of the former interaction at 525 K, i.e., $D_{\perp}=3.6$ K. However, since there is a

certain ambiguity about the size of $D'_\perp$ as it has been estimated only in the $J'=0$ limit, at this stage we can only make an estimation that the intradimer DM interaction is of the order of $D_\perp = 3.6 \pm 0.5$ K.

B. Nature of the in-plane DM interaction

The value of the *nn* DM interaction $D_\perp = 3.6$ K seems to be unexpectedly high at first glance. This interaction has been disregarded until very recently,[14–16] although it should be considerable due to finite buckling of $CuBO_3$ planes. At room temperature where the bending angle[12] of CuO_4 plaquettes with respect to **c**-axis is $\alpha = 4°$ it is of the order of $D_\perp = \sqrt{2} \sin\alpha(\Delta g/g)J \approx 1$ K.[26] We note, however, that this interaction is expected to vanish at temperatures above $T_s = 395$ K, i.e., at temperatures where the buckling disappears. Surprisingly, the ESR linewidth anisotropy is not affected by this structural phase transition at all.

A credible explanation of this puzzle is obtained if dynamical effects are taken into account.[17,18] In this picture lattice vibrations instantaneously break local symmetry, allowing for additional in-plane terms of DM interaction. However, there are requirements to be fulfilled before including this mechanism into the interpretation of our X-band ESR results. First of all, dynamical effects can be observed when the characteristic phonon frequency is small compared to characteristic exchange frequency $\omega_e \sim k_B J/\hbar$ determining the spin correlation time τ_c. Since optical phonons are needed to produce required lattice distortions, significant softening of a particular normal mode should be present. Second, the mean square displacements of ions, participating in the aforementioned lattice motion, from their equilibrium positions should be large enough to break the local symmetry significantly. It seems that both conditions are fulfilled in the $SrCu_2(BO_3)_2$ system.

Of our particular interest is the observation of a soft mode detected by the Raman scattering experiment.[26] The Raman shift of this optical mode amounts to 62 cm^{-1} (89 K) at $T = 15$ K and progressively softens by 44 cm^{-1} just below $T_s = 395$ K. It causes in-phase motion of almost all ions within the primitive cell (with the exception of Sr^{2+} ions), preferably along the crystal **c**-direction. The symmetry of this soft mode is also consistent with the observed anomalous anharmonicity of lattice properties, namely, a flattening of the local potentials of ions and a significant enhancement of their mean square displacements in the crystal **c**-direction, both phenomena progressively getting larger when approaching the transition to high-T phase.[12] For instance, the U_{33} principal components of the displacement tensor of Cu ions and O1 ions connecting them yield enhanced vibration amplitudes in the crystal **c**-direction in the high-T phase, which are virtually the same as static displacements (0.25 Å for Cu ions and 0.33 Å for O1 ions) of these ions at 100 K.[12] Such lattice vibrations break the local symmetry in a very similar way as it is broken in the low-T phase by finite buckling since the distortions are quasi-static on the time-scale of spin correlation time τ_c. Therefore, it is not surprising that the ESR linewidth anisotropy does not change qualitatively above RT despite crossing the structural phase transition. We propose that the origin of *nn* DM interaction $D_\perp = 3.6$ K is a combination of static, i.e., buckling of $CuBO_3$ planes, and dynamical mechanism and evolves progressively into a dynamical source with increasing temperature. The obtained parameter is thus an ''averaged'' value since the displacements are time dependent. Our experimental findings strongly support the new picture of dynamical DM interaction.[17,18]

By introducing additional anisotropic terms of DM type to the spin Hamiltonian of the system, one has to consider carefully whether the observed fine structure of triplet excitations can be theoretically reproduced. In fact, it has been shown using the finite temperature Lanczos (FTL) method on a finite-size Shastry-Sutherland lattice that the splitting remains primarily given by the out-of-plane interdimer DM interaction.[27]

C. High-temperature linewidth behavior

Next we focus on the high-T linearly increasing part of the ESR linewidth. For a pure spin Hamiltonian ESR linewidths are normally expected to approach a constant value for temperatures $T \gg J$. However, several mechanisms can lead to a temperature dependent ESR linewidth at such temperatures including spin diffusion, static spin correlations and spin-phonon coupling. Although the spin diffusion mechanism may become significant at higher temperatures, the measured Lorentzian ESR lineshape speaks strongly against it.[24] Second, the effect of static spin correlations (i.e., short-range order) on the linewidth can be observed in low-dimensional magnetic systems even up to temperatures of the order of $T \sim 10J$.[28] Following the original paper of Soos *et al.*,[29] the temperature-dependent second moment due to the DM interaction can be calculated

$$M_2^{DM} = \frac{S(S+1)}{3N}\Bigg\{ \sum_{(ij)} ((D_{ij}^x)^2 + (D_{ij}^y)^2 + 2(D_{ij}^z)^2)(1 - C_{ij}) + \sum_{\substack{(ij) \\ k \neq i,j}} (D_{ij}^x D_{ik}^x + D_{ij}^y D_{ik}^y + 2 D_{ij}^z D_{ik}^z) C_{jk} + \sum_{(ij)} \sum_{\substack{(kl) \\ k,l \neq i,j}} (D_{ij}^x D_{kl}^x + D_{ij}^y D_{kl}^y + 2 D_{ij}^z D_{kl}^z) \times (C_{ik} C_{jl} - C_{il} C_{jk}) \Bigg\} \frac{\chi_C}{\chi(T)}. \quad (5)$$

The temperature dependence due to static spin correlations is hidden in the ratio between Curie susceptibility χ_c and the measured susceptibility $\chi(T)$ as well as in functions C_{ij} reflecting two-site static spin correlation between spins at sites i and j. Each of the three sums in Eq. (5) yields its own characteristic temperature behavior, with the first one approaching the infinite-temperature second moment and the last two going to zero when increasing the temperature. It is highly unlikely that the two-site correlation function C_{ij} would evolve with temperature in such a way to produce angular-independent line broadening as observed in current investigation. Another reason allowing us to dismiss static

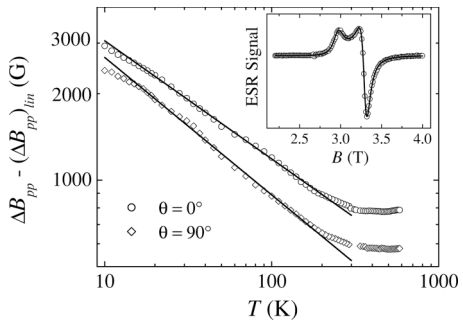

FIG. 4. Log-to-log plot of the linewidth of X-band ESR spectra from $SrCu_2(BO_3)_2$ single crystal with the high-T contribution subtracted for $\mathbf{B}_0 \| \mathbf{c}$ (circles) and $\mathbf{B}_0 \perp \mathbf{c}$ (diamonds). Full lines represent fits to an equation of the form $\Delta B = A/(T - T^*)^p$. The inset shows a high-field ESR spectrum of powdered $SrCu_2(BO_3)_2$ sample at RT (circles) and a fit to anisotropic Lorentzian powder distribution (full line).

spin correlations as the origin of the observed broadening is almost ideal linear dependence in a rather broad temperature range, i.e., between $3.5J$ and $7J$. In such a broad region one would expect significant bending of the linewidth curves towards the infinite temperature value if the broadening was due to short-range order effects.[28]

Therefore, the spin-phonon coupling should be the main broadening mechanism at high temperatures. The significance of such coupling has been highlighted from the dramatic softening of elastic constants both with temperature and applied magnetic field.[30] Spin-phonon interaction causes lifetime broadening effects. As the increase of the linewidth is linear, normal direct phonon processes should be involved. In particular, the observed line broadening can be either due to the usual spin-lattice relaxation between Zeeman split low-lying excited states or a reflection of transitions between the ground state and these states induced by a phonon modulation of antisymmetric Dzyaloshinsky-Moriya interaction.[31] For the former mechanism a strong field-dependent behavior is typical while no field dependence is expected in the latter case.[31] In the inset to Fig. 4 a high-field spectrum of a powdered sample, recorded at a frequency of 93.2 GHz at RT, is shown. As it can be seen, it is nicely fitted with a Lorentzian function for powder spectra yielding anisotropic linewidths of $\Delta B_{pp}^a = \Delta B_{pp}^b = 699 \pm 10$ G and $\Delta B_{pp}^c = 890 \pm 10$ G. These parameters are virtually the same as the single-crystal X-band values $\Delta B_{pp}^{\theta=90°} = 690 \pm 5$ G and $\Delta B_{pp}^{\theta=0°} = 907 \pm 5$ G. Since the linear contribution to the linewidth at RT is of the order of 100 G and is the same at two resonance fields differing by almost a factor of 10, we propose that the spin-lattice contribution to the linewidth is due to fluctuating DM interaction.

Making a rather crude approximation while neglecting correlation effects between a pair of interacting spins and their neighbors, the linewidth is determined by phonon-induced transitions between a singlet state and triplet states of a two spin system. Since J is two orders of magnitude larger than characteristic Zeeman energy and the phonon density scales as ω^2 in the Debye approximation, it is not surprising for the modulated-DM interaction effect to dominate over phonon-induced Zeeman transition within $S=1$ multiplet. In a simple picture of uncorrelated dimers the finite-lifetime contribution to the linewidth is given by the equation[22]

$$\Delta B_{pp}^{lin} \approx \frac{8z}{9\sqrt{3}} \frac{k_B^4}{g\mu_B} \frac{(\lambda R)^2 D^2 J^2}{\rho \hbar^3} \left\langle \frac{1}{c_t^5} + \frac{2}{3} \frac{1}{c_l^5} \right\rangle_{\Omega} k_B T. \quad (6)$$

Taking the number of independent pairs as $z=1$, $\lambda R = 10$ with the nearest-neighbor distance R and $dJ/dr = -\lambda J$,[32] $\rho = 4.1$ kg/dm^3,[33] an approximate average velocity[30] $c = 4600$ m/s in place of the complicated angular average and the above estimated intradimer DM interaction $D = D_\perp = 3.6$ K, we can calculate the slope of the linearly increasing part to be of the order of 0.14 G/K. This result is in a reasonable agreement with the experimentally observed slope 0.34 G/K, bearing in mind that the mean velocity, which is burdened with the biggest uncertainty, is taken to the power of 5. Moreover, Eq. (6) is strictly valid only in a crude approximation of independent dimers. Since interactions with other neighbors in general shorten the lifetime of a spin in a certain energy level, the slope is expected to be larger in the real system than the value our estimation produces. The fair agreement of this line-broadening mechanism with the experiment once again justifies the introduction of intradimer DM interaction.

D. Low-temperature linewidth behavior

At the end let us give a brief discussion on the temperature dependence of the ESR linewidth below RT. Figure 4 shows a log-log plot of the linewidth without the high-temperature linear part. The spin-phonon contribution to the linewidth at low temperatures becomes insignificant, which justifies the subtraction of the linear term instead of a term proportional to the actual number of phonons.

The evolution of the low-temperature part of the linewidth with temperature yields a linear dependence in the log-log plot to a reasonably good approximation in a rather broad temperature range between 15 K and 150 K. Solid lines correspond to a fit to the function $\Delta B = A/(T - T^*)^p$, characteristic of critical broadening effects. The obtained values for the exponent are $p = 0.41 \pm 0.01$ for $\theta = 0°$ and $p = 0.47 \pm 0.01$ for $\theta = 90°$, while the value of the characteristic temperature T^* is within the experimental error very close to zero. We have reported similar observations on the linewidth behavior in powder samples.[20] Such critical behavior typically occurs near phase-transition temperatures with induced long-range order in the low-temperature phase. In the case of the investigated system it is probably due to critical enhancement of antiferromagnetic fluctuations and thus a fingerprint of the importance of quantum criticality effects in the $SrCu_2(BO_3)_2$ system, as the system is believed to be situated in the extreme vicinity of the quantum borderline between the nonmagnetic and magnetically ordered ground state. However, the observed temperature interval (15 K to 150 K), in which this theory seems to be consistent, is surprisingly broad. In this respect, the results of our investigation call for a comprehensive theoretical evaluation of the temperature

evolution of the ESR spectra in the $SrCu_2(BO_3)_2$ system at lower temperatures. Such theory would also have to account for the observed small deviations from ''linear'' dependence below 15 K.

VI. CONCLUSIONS

In summary, a comprehensive X-band ESR study on a single crystal of a highly frustrated $SrCu_2(BO_3)_2$ system has been given in a broad temperature range between 10 K and 580 K. The anisotropy of the rather broad linewidth shed some important additional light on the spin anisotropy of the investigated systems. Previously proposed out-of-plane interdimer DM interaction as the dominant anisotropic contribution cannot adequately account for the experimental angular dependence. In addition to this interaction $D'_{\parallel}=2.4\pm0.1$ K one has to incorporate also sizable in-plane DM components. Taking the value of the in-plane *nnn* DM vector $D'_{\perp}\approx 0.35D'_{\parallel}$, as suggested by recent inelastic neutron scattering experiments, allowed us to evaluate for the first time also the intradimer DM interaction, $D_{\perp}=3.6\pm0.5$ K, which is believed to be partially responsible for many anomalous findings including staggered magnetization, high-field ESR-active transitions, and temperature dependence of the specific heat. Moreover, as in the high-T phase (above 395 K) the in-plane components of DM interaction are prohibited by symmetry; an explanation of the nature of these terms based on a novel dynamical DM interaction has been given. Taking into account the presence of a soft mode with a particular symmetry we emphasized that lattice distortions are quasistatic on the time-scale of the spin correlation time and that dominant ion displacements take place along crystal **c**-direction. Second, the observed anisotropic linewidth shows a peculiar temperature dependence, which can be decomposed into two contributions. The high-temperature linear contribution is arising from the interplay between spin and lattice degrees of freedom and has been attributed to the induced transitions between energy levels due to phonon-modulation of the *nn* Dzyaloshinsky-Moriya interaction. On the other hand, the low-temperature part exhibits critical-broadening-like behavior, which could be a consequence of enhanced antiferromagnetic correlations.

ACKNOWLEDGMENTS

It is a pleasure to thank Dr. A. Lappas for stimulating discussions on the magnetic properties of $SrCu_2(BO_3)_2$. HK thanks the Yamada Science Foundation (Japan) for supporting his work in low-dimensional systems and the MECSST (Japan) through Grant-in-Aid for Scientific Research No. 40302640.

APPENDIX

In low-dimensional spin systems with significant g-shifts and large isotropic exchange coupling the antisymmetric Dzyaloshinsky-Moriya interaction is often the dominant spin anisotropy contribution. In this case the second and the forth moments of the absorption line are given in the high-temperature limit (neglecting static spin correlations) by components of DM vectors in the laboratory frame as[22]

$$M_2^{DM}=\frac{S(S+1)}{3N}\sum_{(ij)}\left((D_{ij}^x)^2+(D_{ij}^y)^2+2(D_{ij}^z)^2\right),$$

$$M_4^{DM}=\frac{S^2(S+1)^2}{N}\left\{\frac{2}{3}\sum_{(ij)}J_{ij}^2\left((D_{ij}^x)^2+(D_{ij}^y)^2+2(D_{ij}^z)^2\right)\right.$$

$$+\frac{1}{18}\sum_{(ijk)}\left((F_{ijk}^x)^2+(F_{ijk}^y)^2+2(F_{ijk}^z)^2+(F_{jki}^x)^2\right.$$

$$\left.\left.+(F_{jki}^y)^2+2(F_{jki}^z)^2+(F_{kij}^x)^2+(F_{kij}^y)^2+2(F_{kij}^z)^2\right)\right\}, \tag{A1}$$

where the three-site term sums over functions $F_{ijk}^{\alpha}=J_{ij}(D_{ik}^{\alpha}-D_{jk}^{\alpha})+J_{ik}(D_{ij}^{\alpha}+D_{jk}^{\alpha})$. The expected ESR linewidth anisotropy is then obtained by transforming the DM vectors from the laboratory frame to the crystal frame

$$D_{ij}^x=D_{ij}^a\cos\theta\cos\varphi+D_{ij}^b\cos\theta\sin\varphi-D_{ij}^c\sin\theta,$$

$$D_{ij}^y=-D_{ij}^a\sin\varphi+D_{ij}^b\cos\varphi, \tag{A2}$$

$$D_{ij}^x=D_{ij}^a\sin\theta\cos\varphi+D_{ij}^b\sin\theta\sin\varphi+D_{ij}^c\cos\theta.$$

We denote an arbitrary orientation of applied constant magnetic field (z-direction in the laboratory frame) with the polar angle θ and the azimuthal angle ϕ in the crystal frame of $SrCu_2(BO_3)_2$ system with **c**-axis as the polar axis. Using the equations (1), (A1) and (A2) with the DM-vectors pattern shown in Fig. 1 we derive the expression for the angular dependence of the ESR linewidth in the $SrCu_2(BO_3)_2$ system for the case when only out-of-plane *nnn* DM interaction $\mathbf{D}'$ is present and the case which also takes into account the in-plane *nn* DM coupling **D**:

(1) $\mathbf{D}'=(0,0,D'_{\parallel}),\mathbf{D}=0$:

$$\Delta B_{pp}\approx\frac{2\pi}{\sqrt{6}}\frac{k_B}{g\mu_B}\frac{D_{\parallel}'^2}{\sqrt{6(3J^2+3J'^2-2JJ')}}(1+\cos^2\theta), \tag{A3}$$

(2) $\mathbf{D}'=(0,0,D'_{\parallel}),\mathbf{D}=(D_{\perp},0,0)$ or $\mathbf{D}=(0,D_{\perp},0)$:

$$\Delta B_{pp}\approx\frac{2\pi}{\sqrt{6}}\frac{k_B}{g\mu_B}\left(\frac{(8D_{\parallel}'^2+3D_{\perp}^2+(8D_{\parallel}'^2-D_{\perp}^2)\cos^2\theta)^3}{96(32D_{\parallel}'^2J_1^2+3D_{\perp}^2J_2^2+(32D_{\parallel}'^2J_1^2-D_{\perp}^2J_2^2)\cos^2\theta)}\right)^{1/2}, \tag{A4}$$

where $J_1^2=3J^2+3J'^2-2JJ'$ and $J_2^2=13J^2+6J'^2$.

*Author to whom correspondence should be addressed. Email address: andrej.zorko@ijs.si
[1] H. Kageyama *et al.*, Phys. Rev. Lett. **82**, 3168 (1999).
[2] S. Miyahara and K. Ueda, Phys. Rev. Lett. **82**, 3701 (1999).
[3] C. Knetter, A. Bühler, E. Müller-Hartmann, and G. S. Uhrig, Phys. Rev. Lett. **85**, 3958 (2000).
[4] S. Miyahara and K. Ueda, J. Phys. Soc. Jpn. **69**, 72 (2000).
[5] A. Koga and N. Kawakami, Phys. Rev. Lett. **84**, 4461 (2000).
[6] A. Koga, J. Phys. Soc. Jpn. **69**, 3509 (2000).
[7] H. Nojiri *et al.*, J. Phys. Soc. Jpn. **68**, 2906 (1999).
[8] H. Kageyama *et al.*, Phys. Rev. Lett. **84**, 5876 (2000).
[9] T. Rõõm *et al.*, Phys. Rev. B **61**, 14342 (2000).
[10] P. Lemmens *et al.*, Phys. Rev. Lett. **85**, 2605 (2000).
[11] O. Cépas *et al.*, Phys. Rev. Lett. **87**, 167205 (2001).
[12] K. Sparta *et al.*, Eur. Phys. J. B **19**, 507 (2001).
[13] T. Moriya, Phys. Rev. **120**, 91 (1960).
[14] S. Miyahara *et al.*, preprint.
[15] H. Nojiri, H. Kageyama, Y. Ueda, and M. Motokawa, J. Phys. Soc. Jpn. **72**, 3243 (2003).
[16] G. A. Jorge *et al.*, cond-mat/0309534v1 (unpublished).
[17] O. Cépas, T. Sakai, and T. Ziman, Prog. Theor. Phys. Suppl. **145**, 43 (2002).
[18] O. Cépas and T. Ziman, cond-mat/0401240v1 (unpublished).
[19] H. Kageyama *et al.*, J. Cryst. Growth **206**, 65 (1999).
[20] A. Zorko, D. Arčon, A. Lappas, and J. Giapintzakis, Phys. Rev. B **65**, 024417 (2001).
[21] R. Kubo and K. Tomita, J. Phys. Soc. Jpn. **9**, 888 (1954).
[22] T. G. Castner and M. S. Seehra, Phys. Rev. B **4**, 38 (1971).
[23] P. M. Richards, in *Local Properties at Phase Transitions*, edited by K. A. Müller (North-Holland, Amsterdam, 1976), p. 539.
[24] A. Zorko, D. Arčon, H. Kageyama, and A. Lappas, submitted to Appl. Mag. Res., cond-mat/0310178 (unpublished).
[25] K. Kakurai *et al.*, in *Quantum Properties of Low-Dimensional Antiferromagnets*, edited by A. Ajiro and J.-P. Boucher (Kyushu U. P., Fukuoka, 2002), p. 102.
[26] K.-Y. Choi *et al.*, Phys. Rev. B **68**, 104418 (2003).
[27] J. Bonča, S. El Shawish, and C. D. Batista, preprint.
[28] Z. G. Soos, K. T. McGregor, T. T. P. Cheung, and A. J. Silverstein, Phys. Rev. B **16**, 3036 (1977).
[29] Z. G. Soos, T. T. P. Cheung, and K. T. McGregor, Chem. Phys. Lett. **46**, 600 (1977).
[30] B. Wolf *et al.*, Phys. Rev. Lett. **86**, 4847 (2001).
[31] M. S. Seehra and T. C. Castner, Phys. Kondens. Mater. **7**, 185 (1968).
[32] D. Bloch, J. Phys. Chem. Solids **27**, 881 (1966).
[33] S. Zherlitsyn *et al.*, Phys. Rev. B **62**, R6097 (2000).