Spin-triplet excitons in the $S=\frac{1}{2}$ gapped antiferromagnet $BaCuSi_2O_6$: Electron paramagnetic resonance studies

S. A. Zvyagin,[1] J. Wosnitza,[1] J. Krzystek,[2] R. Stern,[3] M. Jaime,[4] Y. Sasago,[5] and K. Uchinokura[6]
[1]*Dresden High Magnetic Field Laboratory (HLD), Forschungszentrum Rossendorf, Postfach 510119, D-01314 Dresden, Germany*
[2]*National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310, USA*
[3]*National Institute of Chemical Physics and Biophysics, 12618 Tallinn, Estonia*
[4]*National High Magnetic Field Laboratory, Los Alamos National Laboratory, MS-E536, Los Alamos, New Mexico 87545, USA*
[5]*Central Research Laboratory, Hitachi Ltd., Higashi-Koigakubo, Kokubunji-shi, Tokyo 185-8601, Japan*
[6]*RIKEN, Wako 351-0198, Japan*

(Received 20 December 2005; revised manuscript received 21 February 2006; published 29 March 2006)

$BaCuSi_2O_6$, a $S=\frac{1}{2}$ quantum antiferromagnet with a double-layer structure of Cu^{2+} ions in a distorted planar-rectangular coordination and with a dimerized spin singlet ground state, has been studied by means of the electron paramagnetic resonance technique. It is argued that multiple absorptions observed at low temperatures are intimately related to a thermally activated spin-triplet exciton superstructure, which appears to be a characteristic feature of low-dimensional anisotropic spin-$\frac{1}{2}$ systems with the dimerized spin-singlet ground state. We showed that analysis of the angular dependence of exciton modes could be used for accurate estimation of anisotropy parameters in $BaCuSi_2O_6$; the procedure can be applied for a large number of $S=\frac{1}{2}$ quantum antiferromagnets. In addition, the temperature dependence of EPR intensity and linewidth in $BaCuSi_2O_6$ has been studied and discussed.

DOI: 10.1103/PhysRevB.73.094446 PACS number(s): 75.40.Gb, 76.30.−v, 75.10.Jm

Electron paramagnetic resonance (EPR) is known as an extremely powerful tool for probing the magnetic excitation spectrum in exchange-coupled spin systems. A new theoretical approach for calculating low-temperature EPR parameters of $S=\frac{1}{2}$ AFM chains, which is based on bosonization and the standard Feynman–Dyson self-energy formalism, has been recently developed by Oshikawa and Affleck.[1] The theory allows a precise calculation of the EPR parameters (such as linewidth and g factor shift) and their dependence on temperature and magnetic field for uniform $S=\frac{1}{2}$ antiferromagnetic chains and chains with staggered g factor and the Dzyaloshinskii–Moriya interaction (so-called sine-Gordon spin chains). The predictions were found in excellent agreement with experimental results.[2]

In this paper we continue studying EPR properties of low-dimensional (low-D) quantum spin systems. $BaCuSi_2O_6$ (barium copper cyclosilicate, also known as Han Purple Pigment[3]) can be regarded as an almost ideal realization of the $S=\frac{1}{2}$ system of weakly interacting spin dimers with the spin-singlet ground state and gapped excitation spectrum.[4] By application of an external magnetic field the gap can be closed, creating a gas of *interacting* bosonic spin-triplet excitations (triplons). In $BaCuSi_2O_6$ this phenomenon can be effectively described in terms of the field-induced Bose–Einstein condensation of triplons.[3,5] Here, we focus on another interesting phenomenon associated with interacting excited triplets but in the low-field quantum-disordered state, employing temperature as a tuning parameter. We argue, that a fine structure observed in low-temperature EPR spectra of $BaCuSi_2O_6$ is a fingerprint of triplet excitations (excitons), which are mobile at low temperatures and getting localized when temperature is increased. We show that anisotropy can be regarded as one of the main sources of the low-temperature EPR linewidth broadening in low-dimensional spin-$\frac{1}{2}$ systems with the dimerized spin-singlet ground state.

$BaCuSi_2O_6$ crystallizes in the tetragonal noncentrosymmetric space group $I\bar{4}m2$ ($Z=4$, $a=7.042$ Å, $c=11.133$ Å).[6] Magnetic Cu^{2+} ions are arranged in layers with the c axis perpendicular to the layers (Fig. 1). Within each layer Cu^{2+} ions form a weakly distorted planar-rectangular-coordination structure of $S=\frac{1}{2}$ sites (the O-Cu-O angle corresponding to bonds along the rectangular diagonal direction, 177.8°,[7] deviates from that for an ideal planar configuration). The Cu^{2+} ions from two neighboring layers are coupled with each other, forming a two-dimensional (2D) dimer structure. The intradimer distance is relatively small, 2.743 Å, while the distance between dimers is 7.042 Å. The Cu bilayers are structurally separated from each other by planes of Ba^{2+} ions. The quasi-2D nature of the interdimer interactions in $BaCuSi_2O_6$ has been confirmed by means of inelastic neutron scattering,[4] yielding $J_1\sim 51$ K and $J_2\sim 2.2$ K at tem-

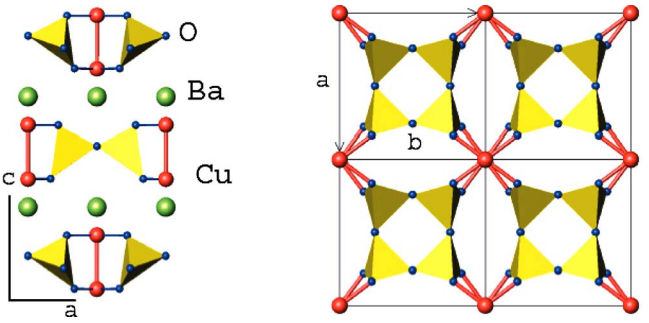

FIG. 1. (Color online) Schematic views of the room-temperature crystal structure of $BaCuSi_2O_6$, composed of SiO_4 tetrahedra (Si atoms are located in tetrahedron centers), CuO_4 distorted squares, and Ba atoms. The Cu^{2+} ions in the $Cu_2Si_4O_{12}$ layers form a quasi-two-dimensional system of weakly interacting dimers.

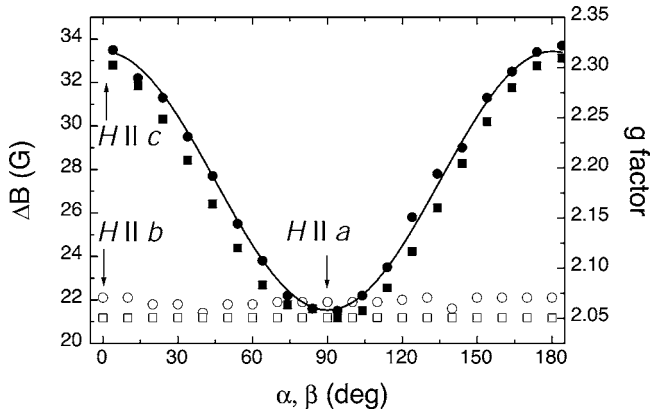

FIG. 2. Room-temperature angular dependence of the g factor and the peak-to-peak EPR linewidth in $BaCuSi_2O_6$, ΔB, in the *ac* plane (close squares and circles, respectively), and in the *ab* plane (open squares and circles, respectively). The line is a fit of the angular dependence of the EPR linewidth in the *ac* plane.

perature $T=3.5$ K (where J_1 and J_2 are intra- and interdimer exchange coupling constants, respectively).

Single-crystalline samples used in this work were prepared by the floating-zone technique as described in Ref. 3. The experiments were performed using a Bruker Elexys E680 spectrometer at the *X*-band frequency (9.39 GHz), in a configuration $h_\omega \| H$ (where h_ω is a magnetic component of microwave field and H is an applied magnetic field).

A well-defined single EPR line has been observed in $BaCuSi_2O_6$ at room temperature. In Fig. 2, the angular dependences of the g factor and peak-to-peak EPR linewidth, ΔB, of this absorption in the *ac* plane, and in the *ab* plane, are shown. The line in Fig. 2 corresponds to a fit of the angular dependence of the EPR linewidth in the *ac* plane using the standard formula[8]

$$\Delta B/\Delta B_\perp = 1 + c\cos^2\alpha, \tag{1}$$

corresponding to the weakly distorted planar-rectangular-coordination structure of Cu^{2+} ions in $BaCuSi_2O_6$ (where ΔB is the peak-to-peak linewidth and $c \sim 0.55$). Both the linewidth and g factor are anisotropic within the *ac* plane with a maximum along the c axis ($\Delta B_\| = 33.5 \pm 0.5$ G, $g_\| = 2.306 \pm 0.003$), while being minimal and isotropic in the *ab* plane ($\Delta B_\perp = 21.7 \pm 0.5$ G, $g_\perp = 2.050 \pm 0.003$). Since $g_\| \neq 2$ and $g_\| > g_\perp$ the orbital singlet state $d_{x^2-y^2}$ can be identified as the ground state, with electron-density maxima located in the basal *ab* plane.[9] Such a configuration suggests the absence of direct orbital overlaps between Cu sites from neighboring layers, revealing a strong superexchange mediating the Cu-Cu intradimer coupling.

In contrast, a very rich EPR spectrum has been observed in $BaCuSi_2O_6$ at low temperatures (Fig. 3). Below 9 K the central line is split into four components labeled C1-4, which are clearly a sign of the hyperfine structure due to the $I=3/2$ nuclear spin of unpaired Cu^{2+} sites,[9–11] caused by defects. A difference between resonance fields of absorptions B2 and B1 corresponds to a splitting between $T_z=0$ and $T_z=\pm 1$ excited states (Fig. 3, inset). The absorption F (not shown in Fig. 3, but plotted in Fig. 4) is the so-called "half-field" resonance and corresponds to transitions between $T_z=-1$ and $T_z=+1$ levels. Since $\Delta M_S=2$, these transitions are nominally forbidden, but become allowed by symmetry in certain situations, e.g., when wave functions from neighboring spin levels are mixed.[9]

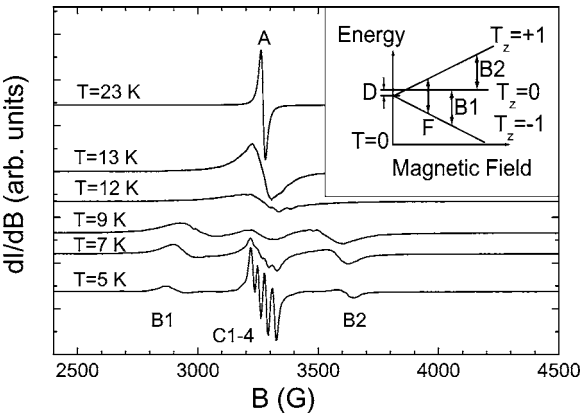

FIG. 3. The evolution of the low-temperature EPR spectra of $BaCuSi_2O_6$; the magnetic field is applied along the *a* axis. Note that points at lower temperatures are taken with an increased amplification rate. The lines A, B1 and B2 correspond to spin-triplet excitons. The hyperfine structure C1-4 is related to interactions within unpaired doublet Cu^{2+} sites, caused by defects. The line F (Fig. 4) is outside the shown field range. The inset shows a schematic view of the energy-level diagram for dimerized $S=\frac{1}{2}$ systems in the tetragonal configuration.

Studying the angular dependence of the lines B1 and B2 allows an approximate estimate of the anisotropy parameter D using the expression

$$B = B_0 \pm \frac{1}{2}\frac{D}{g\mu_B}\left(3\frac{g_\|^2}{g^2}\cos^2\Theta - 1\right), \tag{2}$$

where $g^2 = g_\|^2\cos^2\Theta + g_\perp^2\sin^2\Theta$.[9] In our calculations we used the approach developed by Baranowski *et al.*,[12] which allows for a more accurate estimate of the zero-field splitting parameters for a fully anisotropic g tensor and for every orientation of the field B. Results of the simulation are shown

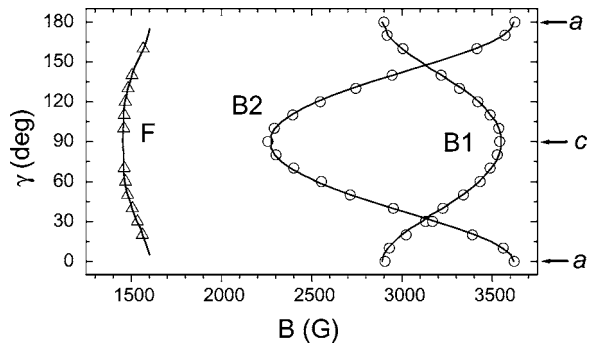

FIG. 4. Angular dependence of the EPR spectrum in $BaCuSi_2O_6$ in the *ac* plane, taken at a temperature of 6 K; γ is the angle between the direction of the applied field and the *a* axis. Triangles and circles correspond to experimental data, while lines correspond to stimulation results.

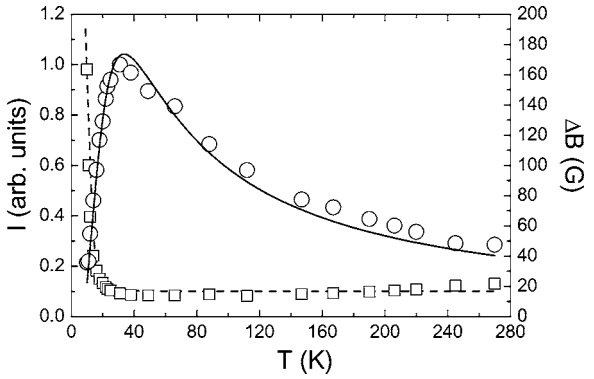

FIG. 5. Temperature dependencies of the integrated EPR intensity I (circles) and peak-to-peak linewidth ΔB (squares), measured with magnetic field H parallel to the a axis at temperatures down to 10 K. The solid line is a fit using the isolated-dimer model with an energy gap $\Delta=53$ K. The dashed line is a guide for the eye.

in Fig. 4 by lines. The best fit yields $g_{\perp}=2.05$, $g_{\parallel}=2.31$ for the g factor, and $D=0.1$ K. Interestingly, the g factors obtained from low-temperature data simulations are consistent with those obtained from room-temperature experiments.

Upon warming up, the transitions B1 and B2 move towards each other and merge (Fig. 3), so that only one absorption line A can be resolved at temperatures higher than $\sim$12 K. Spin-triplet excitations contribute to the EPR intensity, resulting in a pronounced peak in the temperature dependence at $\sim$40 K (Fig. 5, circles). Since the interdimer exchange interaction in $BaCuSi_2O_6$ is significantly weaker than the intradimer coupling ($J_2 \ll J_1$), the isolated-dimer model (which is characterized by a simple singlet-triplet energy scheme with a flat dispersion of the triplet excitations) is used to fit the EPR data. The Boltzmann distribution is included to analyze the temperature dependence of the EPR signal and to determine the singlet-triplet energy gap Δ. Normally, the EPR intensity is determined by a difference between populations of the lowest excited states, and at sufficiently low temperatures ($T \ll \Delta$) should be proportional to the number of thermally activated triplet states. Thus, for the integrated absorption (and assuming a temperature independent size of the energy gap) we can write $I(T) \sim \{\exp[(-\Delta + g\mu_B B)/k_B T] - \exp[(-\Delta - g\mu_B B)/k_B T]\}/Z$, where μ_B is the Bohr magneton, k_B is the Boltzmann constant, Z is the partition function for the singlet-triplet energy scheme, and Δ is the singlet-triplet gap. The best fit of the experimental data yields the mean energy gap of $\Delta=53$ K, which is in excellent agreement with the data obtained from the neutron scattering.[4]

Since their relevancy to the understanding EPR properties of $BaCuSi_2O_6$, let us now discuss results of neutron scattering measurements[4] in more detail. It was observed that at low temperatures the interdimer coupling results in a relatively small but yet pronounced dispersion of triplet excitations along the layer direction. The physical picture of the dispersion of magnetic excitations in $BaCuSi_2O_6$ can be associated with single-dimer (local) excitations "hopping" from one site to another within the Cu^{2+} bilayers. The delocalized, "excitonic" nature of spin-triplet excitations has been revealed, for instance, in some organic charge-transfer salts with spin-singlet ground state.[13] It was shown that the exciton motion can be particularly prominent in low-D materials: it is very fast along one crystallographic direction and slow along other directions [one-dimensional (1D) propagation], or very fast within one crystallographic plane (2D propagation). The growing number of excitons causes pronounced changes in the dispersion of magnetic excitations in $BaCuSi_2O_6$. As follows from neutron-scattering measurements,[4] at $T\sim 50$ K the bandwidth along the in-plane direction is significantly reduced compared to that at 3.5 K, so that the dispersion of the triplet excitation becomes almost flat at high temperatures. Qualitatively the observed behavior can be described as following: at high temperatures excitons cannot freely hop from one site to another (since most of the sites are already occupied), so that the dimer excitations have to reside on their own sites. Thus, triplets get localized, which manifests itself in the suppression of the excitation dispersion at high temperatures.

Let us now discuss the EPR results. As we saw above, the fine structure observed in the low-temperature regime can be nicely reproduced taking into account an anisotropy parameter $D=0.1$ K, characterizing the splitting of the excited triplet. Upon warming up, the two peaks in the fine structure are getting closer to each other. At $T\sim 12$ K (depending on the orientation, i.e., the original splitting of the two lines) the fine structure cannot be resolved any more, and a single line is observed. Upon further temperature increase, the EPR line is getting narrower (Fig. 5) until the linewidth becomes almost constant at temperatures higher than $T\sim 20$ K. All these phenomena are textbook examples of the temperature-activated exchange processes taking place between the particular dimers excited to the triplet state. As described, e.g., in Ref. 14, in the slow-exchange regime (exchange frequency $\nu \ll g\mu_B|B2-B1|$) the two lines corresponding to the individual $\Delta M_S=1$ transitions get broadened upon raising the temperature, and start moving towards each other, while in the fast exchange regime ($g\mu_B|B2-B1| \ll \nu$) the single averaged line gets narrowed with increasing temperature.[15]

The nature of the exchange cannot be easily discerned from the EPR-detected effects alone. There are two possibilities, which can be termed "static exchange" and "motional exchange." In the first case the triplet excitations are immobile, while in the second case they move in plane, "bumping" into each other with a frequency dependent on the concentration of the excited dimers. Combining the EPR observations with those obtained from neutron scattering one can clearly decide that it is the motional exchange that takes place in the system up to about 20 K. Above that point (which can be regarded as the "motional-static exchange" crossover) most of the dimers are already excited into the triplet state, and the excitons become immobilized. In such a case, the "static exchange" takes over, which is clearly not thermally activated.

The angular dependence of the EPR linewidth in the fast exchange regime requires some consideration. If the anisotropy of the EPR spectrum as shown in Fig. 2 was related entirely to the underlying fine structure, then the linewidth minima should appear at the two crossover points in the slow-exchange spectra—as shown in Fig. 4, i.e., approximately 30° from the a axis. Since this is not the case, with

the linewidth minimum appearing along the *a* axis, and the linewidth following Eq. (1), it means that the reasons for the linewidth anisotropy at higher temperatures must be more complex. It is known that the EPR linewidth in low-D spin systems can be affected by several factors, including symmetric anisotropic term (anisotropic exchange and/or dipole-dipole interactions) and the Dzyaloshinskii–Moriya interaction (for most recent discussion, see, for instance, Ref. 16), which can significantly influence the angular dependence of the EPR linewidth at low temperatures. Analysis of all these parameters in connection with the temperature dependence of the EPR properties in $BaCuSi_2O_6$ can be a rather complex and challenging problem. It would be very interesting to study theoretically a contribution of excitons to the EPR linewidth, whose concentration and mobility are temperature dependent.

As shown, studying the angular dependence of exciton modes in $BaCuSi_2O_6$ by means of a such high-resolution spectroscopy technique as EPR, allowed the accurate determination of the anisotropy parameter *D*. The described procedure might be of particular importance for studying a generic phase diagram predicted for anisotropic $S=\frac{1}{2}$ quantum chains (see, for instance, Ref. 17), and can be applied for a large number of $S=\frac{1}{2}$ quantum antiferromagnets with the dimerized spin singlet ground state. A low-temperature fine structure similar to that in $BaCuSi_2O_6$, has been recently observed in the $S=\frac{1}{2}$ dimer spin system $VOHPO_4\cdot\frac{1}{2}H_2O$ (Ref. 18). A multiple-peak EPR fine structure, caused by a rather complex topology of magnetic interactions (there are at least two nonequal positions of Cu^{2+} ions) has been also observed[19] in the quasi-2D gapped spin system β-$Sr_2Cu(BO_3)_2$ (Ref. 20). In both cases the linewidth exhibited a temperature dependence, similar to that in $BaCuSi_2O_6$. We suggest that the anisotropy effects revealed in $BaCuSi_2O_6$, can be also relevant to the low-temperature EPR line broadening observed in the low-D spin antiferromagnets $CuGeO_3$ (Ref. 21) and α'-NaV_2O_5 (Ref. 22).

In conclusion, resonance properties of $BaCuSi_2O_6$, a quasi-2D gapped antiferromagnet with the dimerized spin singlet ground state, has been studied by means of *X*-band EPR technique. We argued that multiple absorptions observed in low-temperature EPR spectra were intimately related to a thermally activated spin-triplet exciton superstructure. We demonstrated that the analysis of the angular dependence of exciton modes could be used as a powerful tool for accurate estimation of zero-field splittings within triplet states (and corresponding anisotropy parameters) in gapped $S=\frac{1}{2}$ quantum antiferromagnets with the dimerized spin-singlet ground state. We hope that our experimental findings will stimulate a theoretical interest, which would make not only qualitative, but also quantitative interpretation of the temperature dependence of EPR parameters in $BaCuSi_2O_6$ and related materials possible.

The authors express their sincere thanks to A. K. Kolezhuk, V. Kataev and G. Teitel'baum for fruitful discussions. A. Ozarowski is acknowledged for providing a spectral simulation program. The work was supported by the Saxon Ministry of Science and the Fine Arts (SMWK) and the Federal Ministry of Education and Research (BMBF) of Germany. A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by NSF Cooperative Agreement No. DMR-0084173, by the State of Florida, and by the DOE. S.A.Z. and R.S. acknowledge the support from the NHMFL through the Visiting Scientist Program Nos. 1368 and 1314, respectively. R.S. was supported by the Estonian Science Foundation.

[1] M. Oshikawa and I. Affleck, Phys. Rev. Lett. **82**, 5136 (1999); Phys. Rev. B **65**, 134410 (2002).
[2] S. A. Zvyagin, A. K. Kolezhuk, J. Krzystek, and R. Feyerherm, Phys. Rev. Lett. **95**, 017207 (2005).
[3] M. Jaime, V. F. Correa, N. Harrison, C. D. Batista, N. Kawashima, Y. Kazuma, G. A. Jorge, R. Stern, I. Heinmaa, S. A. Zvyagin, Y. Sasago, and K. Uchinokura, Phys. Rev. Lett. **93**, 087203 (2004).
[4] Y. Sasago, K. Uchinokura, A. Zheludev, and G. Shirane, Phys. Rev. B **55**, 8357 (1997).
[5] S. E. Sebastian, P. A. Sharma, M. Jaime, N. Harrison, V. Correa, L. Balicas, N. Kawashima, C. D. Batista, and I. R. Fisher, Phys. Rev. B **72**, 100404(R) (2005).
[6] L. W. Finger, R. M. Hazen, and R. J. Henley, Am. Mineral. **74**, 925 (1989).
[7] K. Sparta and G. Roth, Acta Crystallogr., Sect. B: Struct. Sci. **60**, 491 (2004).
[8] A. Bencini and D. Gatteschi, in *EPR of Exchange Coupled Systems* (Springer, Berlin, 1990).
[9] A. Abragam and B. Bleaney, in *Electron Paramagnetic Resonance of Transition Ions* (Dover, New York, 1970).
[10] T. C. Ensign, T.-T. Chang, and A. H. Kahn, Phys. Rev. **188**, 703 (1969).
[11] R. W. Reynolds, L. A. Boatner, M. M. Abraham, and Y. Chen, Phys. Rev. B **10**, 3802 (1974).
[12] J. Baranowski, T. Cukierda, B. Jezowska-Trzebiatowska, and H. Kozlowski, Chem. Phys. Lett. **39**, 606 (1976).
[13] J. Krzystek, J. U. von Schütz, G. Ahlgren, J. Hellberg, S. Söderholm, and G. Olovsson, J. Phys. (Paris) **47**, 1021 (1986); J. Krzystek and J. U. von Schütz, *Advances in Chemical Physics*, v. LXXXVI, 167–329, edited by I. Prigogine and S. A. Rice (Wiley, New York, 1993), Vol. LXXXVI, pp. 167–329.
[14] A. Carrington and A. D. McLachlan, *Introduction to Magnetic Resonance* (Harper and Row, New York, 1967).
[15] The actual exchange frequency can be calculated in both temperature regimes. The reference to the relevant formulas is: A. M. Ponte Goncalves, Chem. Phys. **19**, 397 (1977) A more fundamental reference to the exchange phenomena is: P. W. Anderson and P. R. Weiss, Rev. Mod. Phys. **25**, 269 (1953).
[16] J. Choukroun, J.-L. Richard, and A. Stepanov, Phys. Rev. Lett. **87**, 127207 (2001).
[17] K. Nomura and K. Okamoto, J. Phys. A **27**, 5773 (1994); R. D. Somma and A. A. Aligia, Phys. Rev. B **64**, 024410 (2001).
[18] J. Cao, J. T. Haraldsen, S. Brown, J. L. Musfeldt, J. R. Thompson,

S. Zvyagin, J. Krzystek, M.-H. Whangbo, S. E. Nagler, and C. C. Torardi, Phys. Rev. B **72**, 214421 (2005).
[19] S. Zvyagin (unpublished).
[20] S. E. Sebastian, D. Yin, P. Tanedo, G. A. Jorge, N. Harrison, M. Jaime, Y. Mozharivskyj, G. Miller, J. Krzystek, S. A. Zvyagin, and I. R. Fisher, Phys. Rev. B **71**, 212405 (2005).
[21] R. M. Eremina, M. V. Eremin, V. N. Glazkov, H. A. von Nidda, and A. Loidl, Phys. Rev. B **68**, 014417 (2003).
[22] M. Lohmann, H. A. Krug von Nidda, M. V. Eremin, A. Loidl, G. Obermeier, and S. Horn, Phys. Rev. Lett. **85**, 1742 (2000).