Spin dynamics in $S=\frac{1}{2}$ chains with next-nearest-neighbor exchange interactions

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Low-energy magnetic excitations in the $S=\frac{1}{2}$ chain compound $[(C_6H_9N_2)CuCl_3]CuCl_3$ [known as (6MAP)$CuCl_3$] are probed by means of tunable-frequency electron spin resonance. Two modes with asymmetric (with respect to the $h\nu=g\mu_B B$ line) frequency-field dependences are resolved, illuminating the striking incompatibility with a simple uniform $S=\frac{1}{2}$ Heisenberg chain model. The unusual ESR spectrum is explained in terms of the recently developed theory for $S=\frac{1}{2}$ chains, suggesting the important role of next-nearest-neighbor interactions in this compound. Our conclusion is supported by model calculations for the magnetic susceptibility of (6MAP)$CuCl_3$, revealing a good qualitative agreement with experiment.

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A $S=\frac{1}{2}$ Heisenberg antiferromagnetic (AF) chain is one of the paradigms in modern quantum many-body physics. The most important feature of this model is its integrability by means of the famous Bethe ansatz.[1] However, as revealed theoretically and experimentally, the uniform spin chains are unstable with respect to any perturbation, breaking the chain uniformity. Such instability gives rise to a rich variety of strongly correlated spin states and quantum phase transitions, making these objects an attractive ground for testing various theoretical concepts experimentally. A competition between nearest-neighbor (NN) and next-nearest-neighbor (NNN) interactions, as well as the presence of magnetic anisotropy, can fundamentally modify the ground-state properties of quantum spin chains resulting in a large diversity of complex magnetic structures.[2–6] The experimental determination of these interactions often is a challenging task. For that, magnetic and thermodynamic measurements (magnetization, magnetic susceptibility, and specific heat) are very helpful but do not give a detailed picture of magnetic interactions. Inelastic neutron scattering is a more suitable tool but it has certain serious limitations (including, for instance, requirements on the sample size and chemical composition of the material). That is why the search for new approaches (both theoretical and experimental) that are helpful in clarifying the microscopic structure of magnetic interactions appears to be of particular importance.

Electron spin resonance (ESR) is traditionally recognized as one of the most sensitive techniques for probing magnetic excitations in spin systems with collective ground states (see, for instance, Refs. 7–10). Here, we present ESR studies of the low-energy excitation spectrum in the $S=\frac{1}{2}$ chain system $(C_6H_9N_2)CuCl_3$ [hereafter (6MAP)$CuCl_3$]. Two gapped modes with asymmetric (with respect to the $h\nu=g\mu_B B$ line) resonance positions have been observed in the low-temperature ESR spectrum, reflecting the discrepancy with the simple $S=\frac{1}{2}$ Heisenberg AF chain model, employed for this compound previously.[11] Our data are interpreted in the frame of the recently developed mean-fieldlike theory for $S=\frac{1}{2}$ chains,[12] strongly suggesting a multiplication of the magnetic unit cell and the presence of NNN interactions in this compound.

(6MAP)$CuCl_3$ crystallizes in the orthorhombic structure belonging to the space group *Pnma* with lattice constants $a=11.4$ Å, $b=6.6$ Å, and $c=12.8$ Å (determined at room temperature).[11] The number of formula units per unit cell is $Z=4$. The compound is built up from well-isolated, doubly bridged linear chains of Cu^{2+} ions (Fig. 1). There are two types of crystallographically similar chains running along the b axis. Each copper ion has a square-pyramidal coordination geometry, with the axial bond substantially longer than the basal ones, and with the direction of the axial bond alternating along the chain axis b. The Cu-Cl-Cu bridging angle is well above 90°, which defines the AF nature of the NN exchange interactions [$J/k_B \approx 110$ K (Refs. 11 and 13)]. Using the formula for the Néel temperature T_N from Ref. 14 and assuming $T_N < 100$ mK (as evident from muon spin-relaxation experiments[15]), the interchain interaction J'/k_B is estimated to be less than 40 mK, suggesting $J'/J < 4 \times 10^{-4}$ and indicating an almost perfect one-dimensional nature of the magnetic correlations in (6MAP)$CuCl_3$. However, below about 15 K a deviation from the behavior expected for a $S=\frac{1}{2}$ uniform Heisenberg AF chain appears,[11,13,16] i.e., the low-temperature magnetic susceptibility shows a pronounced

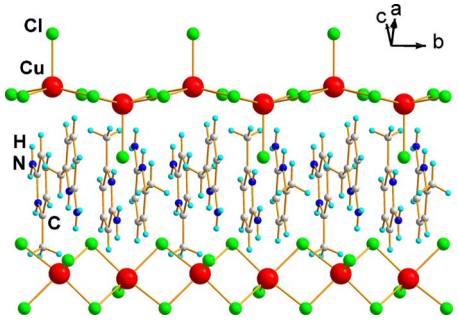

FIG. 1. (Color online) Crystal structure of (6MAP)$CuCl_3$.

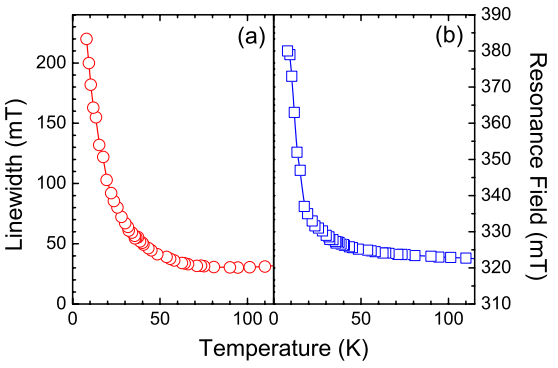

FIG. 2. (Color online) (a) Temperature dependence of the linewidth and (b) resonance field measured at a frequency of 9.4 GHz. Lines are guides to the eye.

low-temperature upturn. Very often, in spin-chain compounds such a low-temperature tail in magnetic susceptibility originates from the broken-chain effects and/or defects, overshadowing the intrinsic low-temperature susceptibility behavior (which is of particular importance when describing the ground state of spin chain materials). To get a deeper insight into the ground state in (6MAP)$CuCl_3$ we decided to probe the low-temperature excitation spectrum in this compound by use of ESR measurements.

Experiments have been performed at the Dresden High Magnetic Field Laboratory (Hochfeld Magnetlabor Dresden, HLD) using an X-band spectrometer (Bruker ELEXSYS E500) at a fixed frequency of 9.4 GHz and a tunable-frequency ESR spectrometer (similar to that described in Ref. 17). High-quality single-crystalline (6MAP)$CuCl_3$ samples with a typical size of $1.5\times1.5\times4$ mm^3 were used. The magnetic field was applied along the b axis. The magnetization measurements have been performed by use of a "Quantum Design" Physical Property Measurement System (PPMS).

A single ESR line (with $g=2.06$ measured at 20 K) was observed at temperatures above 5 K. It was shown theoretically,[18] that the ESR response of an ideal uniform Heisenberg spin chain with magnetically isotropic interactions should reveal a single peak in the ESR absorption with zero linewidth[19] and with the position of the resonance proportional to the applied magnetic field. Spin-spin correlations would yield a shift of the resonance position and a broadening of the ESR line *only* in the presence of magnetic anisotropy. The temperature dependence of ESR linewidth and field measured at frequency 9.4 GHz down to 7 K is shown in Fig. 2, confirming unambiguously the incompatibility of the observed ESR behavior with the simple uniform $S=\frac{1}{2}$ Heisenberg chain model. The low-temperature upturn of the linewidth, seen in Fig. 2, can only be explained by the presence of relevant perturbations (from the viewpoint of renormalization group) of the critical Heisenberg chain [for instance, the multiplication of unit cell, caused by symmetric (exchange) or asymmetric (Dzyaloshinskii-Moriya) spin-spin interactions, or the g-tensor alternation].[18]

To study the frequency-field dependence of the magnetic excitations in (6MAP)$CuCl_3$, further experiments were performed using the high-field (up to 16 T) tunable-frequency ESR spectrometer. Below ~5 K, a second resonance mode (the mode B, Fig. 3) appears. The frequency-field diagram of the magnetic excitations in (6MAP)$CuCl_3$ obtained at 1.4 K is shown in Fig. 4. The resonance absorptions in the studied frequency-field range have a linear field dependence with $g\approx2$. Linear extrapolations of the frequency-field dependences of the ESR modes A and B to zero field yield the resonance-field shifts $\Delta_A=15.9$ GHz (0.76 K) and $\Delta_B=-59$ GHz (−2.83 K), respectively. The observation of two gapped modes clearly indicates the incompatibility with the simple uniform magnetically isotropic $S=\frac{1}{2}$ Heisenberg AF model, suggesting the presence of additional interactions in this compound.

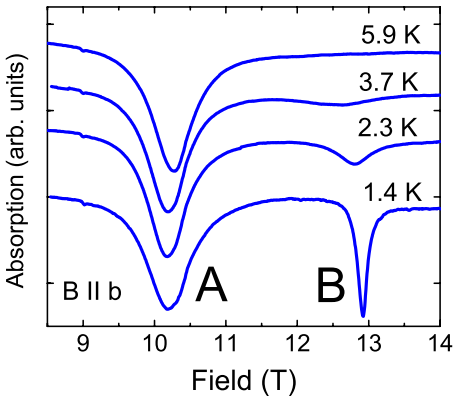

FIG. 3. (Color online) ESR spectra of (6MAP)$CuCl_3$ obtained at a frequency of 300 GHz for different temperatures.

Recently, the dynamical mean-fieldlike theory for the ESR in $S=\frac{1}{2}$ chains with NN and NNN interactions (zigzag spin ladders) has been developed.[12] It was shown that in the case of an alternation of NN interactions, two ESR modes at the frequencies $h\nu_{1,2}=|g\mu_B B+\Delta_{1,2}|$ should emerge, where

$$\Delta_{1,2}=\frac{1}{2}\{(J_1+J_2+A_1+A_2)R_+ \pm [(J_1+J_2-2A_N)^2R_+^2 + (A_1+A_2-2A_N)(2J_1+2J_2-2A_N+A_1+A_2)R_-^2]^{1/2}\}. \quad (1)$$

Here B is the value of the applied magnetic field, μ_B is

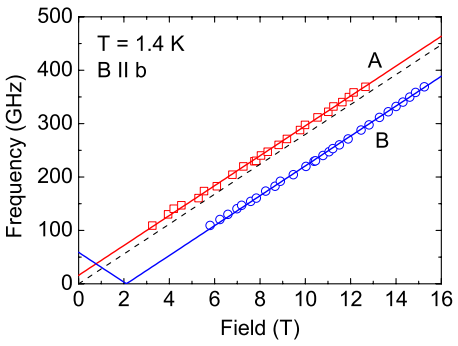

FIG. 4. (Color online) Field dependence of the magnetic-excitation frequencies in (6MAP)$CuCl_3$ at $T=1.4$ K. Symbols denote experimental data while solid lines correspond to theoretical results (see text for details). The dashed line denotes $h\nu=g\mu_B B$ for $g=2$ (where h is the Planck constant, ν is the excitation frequency, μ_B is Bohr's magneton, and B is the magnetic field).

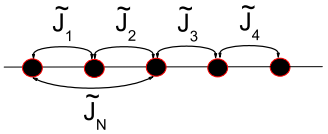

FIG. 5. (Color online) A schematic view of a spin-chain structure with four nearest-neighbor ($\tilde{J}_{1,2,3,4}$) and one next-nearest-neighbor ($\tilde{J}_N$) interactions proposed for (6MAP)$CuCl_3$ (see text for details).

Bohr's magneton, J_1 and J_2 are spin-spin isotropic interactions along the chain, A_1 and A_2 denote the magnetic anisotropy, while A_N is the magnetically anisotropic NNN interaction. $R_{\pm}=\langle S^z_{0,1}\rangle \pm \langle S^z_{0,2}\rangle$ are the sum and the difference of average values of the projections of the magnetic moments of two magnetic centers (in the absence of the oscillating microwave field), respectively. Importantly, depending on the sign and strength of NN and NNN interactions, the theory predicts different frequency-field diagrams of magnetic excitations which can be observed using ESR. ESR experiments on the frustrated $S=\frac{1}{2}$ quasi-one-dimensional systems In_2VO_5,[20] Li_2ZrCuO_4,[21] and on the asymmetric spin-ladder compound IPA-$CuCl_3$ (Ref. 22) revealed qualitative agreement with the theoretical predictions.

Contrary to uniform $S=\frac{1}{2}$ Heisenberg AF chains the combined effect of alternation and magnetic anisotropy is predicted to manifest itself in the opening of a gap in the ESR spectrum. Most importantly, the presence of the AF NN and large enough NNN interactions $[A_N[\langle S^z_{0,1}\rangle^2+\langle S^z_{0,2}\rangle^2]>(A_1+A_2)\langle S^z_{0,1}\rangle\langle S^z_{0,2}\rangle]$ should result in asymmetric (with respect to $h\nu=g\mu_B B$) frequency-field dependences of ESR peaks (Fig. 4 in Ref. 12). This proposed frequency-field dependence is consistent with our observations in (6MAP)$CuCl_3$, strongly suggesting the presence of an NNN interaction and alternation in this compound. Hydrogen position disorder in the amino groups linking the Cu chains[11] can be regarded as the origin of the proposed alternation[23] (see discussion below).

The presence of additional interactions responsible for the energy-gap opening in the low-energy ESR spectrum should manifest itself also in a peculiar behavior of the magnetic susceptibility at temperatures $T\sim\Delta_{1,2}/k_B$. On the other hand, the observation of a broad maximum in the susceptibility of (6MAP)$CuCl_3$ at $T\sim 70$ K implies the presence of short-range-order spin correlations at this energy scale. Hence, additional magnetic eigenstates with energies much larger than the gaps, observed in the ESR experiments, need to be included. To describe both the magnetic susceptibility and the ESR data, a minimal model has to include four magnetic sublattices. Different values of exchange couplings (defined as $\tilde{J}_{1,2,3,4}$, Fig. 5) between neighboring sites along the chain would yield the multiplication of the magnetic unit cell and as a consequence four ESR modes in the excitation spectrum.

Since no integrable four-center Heisenberg AF spin model for (6MAP)$CuCl_3$ is available, the simplified four-center XY spin-chain model[23,24] is applied to illustrate the proposed scenario. The exceptional usefulness of this model is determined by its solvability. The dispersion laws of the four excitation branches, A, B, C, and D, are shown in Fig. 6. The

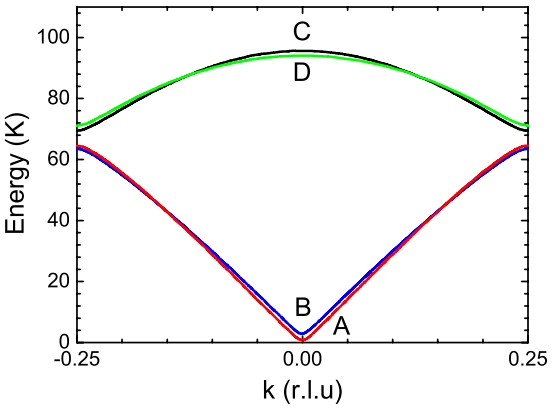

FIG. 6. (Color online) Dispersion relations of magnetic excitations at $B=0$, determined by use of a four-center spin-chain model.

best agreement between the ESR data and calculations was obtained using the parameters $\tilde{J}_1/k_B=\tilde{J}_3/k_B=105$ K, $\tilde{J}_2/k_B=110$ K, $\tilde{J}_4/k_B=96$ K, and $\tilde{J}_N/k_B=0.8$ K for the alternating NN ($\tilde{J}_{1-4}$) and NNN ($\tilde{J}_N$) interactions, respectively. The theory predicts also the existence of two higher energy ESR transitions (modes C and D).

In Fig. 7, we show the temperature dependence of the magnetic susceptibility (down to 1.8 K) together with the calculation results (based on the four-center chain model, Fig. 5) using the obtained parameters. As follows from the model, the presence of low-energy ESR gaps observed in our experiments should determine the low-T part of the magnetic susceptibility while the high-energy branches (and the related gaps) are responsible for the high-T magnetic susceptibility dependence. The main features of the calculated susceptibility behavior (low-temperature maximum, a pronounced dip at $T\approx 13$ K, and a broad maximum at $T\approx 70$ K) are consistent with the experimental data, suggesting the validity of the four-center spin-chain model with NNN interaction. Detailed theoretical studies of the four-center AF spin chain with NN and NNN interactions (unfor-

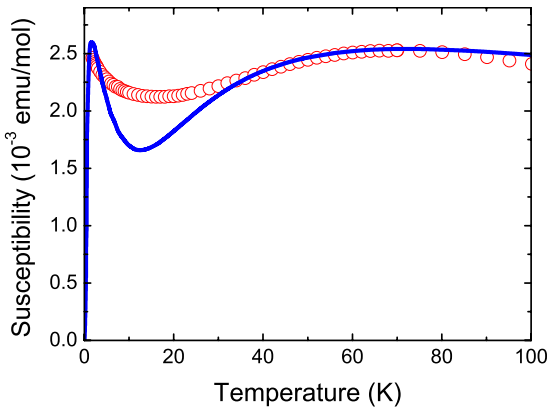

FIG. 7. (Color online) Temperature dependence of the magnetic susceptibility of (6MAP)$CuCl_3$ with a magnetic field of 0.1 T applied along the b axis. Experimental data are shown by symbols while the solid line corresponds to results of calculations for the four-center model with the same set of parameters as in Fig. 6 (see the text for details).

tunately, not available now) are necessary to precisely determine relevant characteristics (exchange integrals, magnetic anisotropy, etc.) of the studied compound.

There are two previously known compounds with an alternating $S=\frac{1}{2}$ Heisenberg chain structure, that are structurally uniform at room temperature: Cu(4-methylpyridine)$_2$Cl$_2$[$CuCl_2(mepy)_2$] (Ref. 25) and Cu(N-methylimidazole)$_2$Br$_2$[$CuBr_2(midz)_2$].[26] The alternation parameter (ratio of weaker to stronger interactions strength was found to be 0.6(1) for $CuCl_2(mepy)_2$ and 0.4(1) for $CuBr_2(midz)_2$. Although due to the tendency of these materials to twin in neither case the methyl hydrogen atoms could be located, the uniform nature of the chains at room temperature is verified. Studies of the dielectric constants of the two compounds clearly revealed anomalies near 50 K for $CuCl_2(mepy)_2$ (Ref. 27) and at 50 and 105 K for $CuBr_2(midz)_2$.[28] These data were interpreted as freezing of the methyl-group rotations which could induce slight twisting of the copper octahedra so as to produce an alternating variation of the exchange pathways. We are not aware of any low-temperature structural study that confirms this hypothesis. Nevertheless, magnetic studies of these materials[29,30] revealed the characteristic maximum in the magnetic susceptibility as well as a gapped ground state [similar to that observed in (6MAP) $CuCl_3$].

While the methyl groups in (6MAP) $CuCl_3$ are ordered at room temperature, the hydrogen atoms of the amino groups are disordered,[11] leaving open the possibility that the observed magnetic behavior arises from a similar freezing transition. A potential signature of the proposed scenario is a pronounced field-independent maximum in the specific heat at $\sim$2.3 K,[16] which would correspond to a low-temperature Schottky anomaly due to the hydrogen position order. Low-temperature structural studies of (6MAP) $CuCl_3$ are planned. It is notable that the variations in the exchange strengths in (6MAP) $CuCl_3$ are much smaller than those observed in $CuCl_2(mepy)_2$ and $CuBr_2(midz)_2$.

To summarize, employing the recently developed theory for ESR in alternating spin chains the asymmetric double-peak ESR structure observed in (6MAP) $CuCl_3$ is interpreted as a signature of NNN interactions. The proposed four-center spin-chain model consistently describes both the observed ESR spectrum and the magnetic susceptibility. Hence, based on the proposed model our study has demonstrated the potential feasibility of using ESR to probe NNN interactions in alternating spin chains with high resolution (available for ESR). Our approach can be of particular importance for understanding the nature of the ground-state and low-temperature magnetic properties of a wide range of spin-chain systems with competing NN and NNN exchange interactions (including zigzag spin ladders). Our observations call for systematic low-temperature structural and neutron-scattering studies of (6MAP) $CuCl_3$, which would allow to verify the proposed model.

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[1] H. A. Bethe, Z. Phys. **71**, 205 (1931).
[2] See, e.g., A. A. Zvyagin, *Finite Size Effects in Correlated Electron Models: Exact Results* (Imperial College Press, London, 2005), and references therein.
[3] P. Pincus, Solid State Commun. **9**, 1971 (1971); M. C. Cross and D. S. Fisher, Phys. Rev. B **19**, 402 (1979).
[4] F. D. M. Haldane, Phys. Rev. B **25**, 4925 (1982); K. Okamoto and K. Nomura, Phys. Lett. A **169**, 433 (1992).
[5] S.-L. Drechsler, O. Volkova, A. N. Vasiliev, N. Tristan, J. Richter, M. Schmitt, H. Rosner, J. Màlek, R. Klingeler, A. A. Zvyagin, and B. Büchner, Phys. Rev. Lett. **98**, 077202 (2007).
[6] C. N. Yang and C. P. Yang, Phys. Rev. **150**, 327 (1966); A. A. Zvyagin, J. Phys.: Condens. Matter **3**, 3865 (1991); Zh. Eksp. Teor. Fiz. **98**, 1396 (1990).
[7] A. K. Hassan, L. A. Pardi, G. B. Martins, G. Cao, and L.-C. Brunel, Phys. Rev. Lett. **80**, 1984 (1998).
[8] K. Katsumata, J. Phys.: Condens. Matter **12**, R589 (2000).
[9] S. Hill, R. S. Edwards, N. Aliaga-Alcalde, and G. Christou, Science **302**, 1015 (2003).
[10] S. A. Zvyagin, A. K. Kolezhuk, J. Krzystek, and R. Feyerherm, Phys. Rev. Lett. **93**, 027201 (2004).
[11] U. Geiser, R. M. Gaura, R. D. Willet, and D. X. West, Inorg. Chem. **25**, 4203 (1986).
[12] A. A. Zvyagin, Phys. Rev. B **79**, 064422 (2009).
[13] Y. Liu, J. E. Drumheller, and R. D. Willett, Phys. Rev. B **52**, 15327 (1995).
[14] C. Yasuda, S. Todo, K. Hukushima, F. Alet, M. Keller, M. Troyer, and H. Takayama, Phys. Rev. Lett. **94**, 217201 (2005).
[15] S. Blundell *et al.* (unpublished).
[16] M. Ozerov, E. Čižmár, J. Wosnitza, S. A. Zvyagin, F. Xiao, C. P. Landee, M. M. Turnbull, J. Phys.: Conf. Ser. **150**, 042159 (2009).
[17] S. A. Zvyagin, J. Krzystek, P. H. M. van Loosdrecht, G. Dhalenne, and A. Revcolevschi, Physica B **346-347**, 1 (2004).
[18] M. Oshikawa and I. Affleck, Phys. Rev. Lett. **82**, 5136 (1999); A. A. Zvyagin, Phys. Rev. B **63**, 172409 (2001); M. Oshikawa and I. Affleck, *ibid.* **65**, 134410 (2002).
[19] In the absence of spin-lattice and electron-nuclear couplings, i.e., caused by the electron spin-spin interactions only.
[20] A. Möller, T. Taetz, N. Hollmann, J. A. Mydosh, V. Kataev,

M. Yehia, E. Vavilova, and B. Büchner, Phys. Rev. B **76**, 134411 (2007).

[21] E. Vavilova, A. S. Moskvin, A. Arango, A. Sotnikov, S. L. Drechsler, R. Klingeler, O. Volkova, A. Vasiliev, V. Kataev, and B. Büchner, EPL **88**, 27001 (2009).

[22] H. Manaka and I. Yamada, Phys. Rev. B **62**, 14279 (2000).

[23] Such an alternation can be caused, for instance, by different magnetic interactions along the chain as result of a spin-Peierls transition. However, a thorough search for possible superstructures by synchrotron x-ray diffraction, carried out at the MAGS beamline at HZB, gave no indication for a crystallographic/structural anomaly (which would suggest a spin-Peierls transition) down to 1.5 K.

[24] A. A. Zvyagin, Phys. Lett. A **158**, 333 (1991).

[25] W. E. Marsh, W. J. Valente, and D. J. Hodgson, Inorg. Chim. Acta **51**, 49 (1981).

[26] J. A. C. van Ooijen, J. Reedijk, and A. L. Spek, J. Chem. Soc. Dalton Trans. **1979**, 1183.

[27] J. W. Hall, W. E. Marsh, R. R. Weller, and W. E. Hatfield, Inorg. Chem. **20**, 1033 (1981).

[28] A. J. Wolthuis, W. J. Huiskamp, L. J. de Jongh, and J. Reedijk, Physica B&C **133**, 161 (1985).

[29] J. H. Smit, L. J. De Jongh, J. A. C. van Ooijen, J. Reedijk, and J. C. Bonner, Physica B **97**, 229 (1979).

[30] H. J. M. de Groot, L. J. de Jongh, R. D. Willett, and J. Reedijk, J. Appl. Phys. **53**, 8038 (1982).