

High-Pressure EPR Studies and an Explanation of the Atypical Temperature Dependence of the Weak Interdimer Exchange Coupling in $[\text{Co}(\text{en})_3]_2[\text{Cu}_2\text{Cl}_8]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ Crystals

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Received October 25, 1990

A merging effect of the EPR lines under hydrostatic pressure in $[\text{Co}(\text{en})_3]_2[\text{Cu}_2\text{Cl}_8]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ up to 450 MPa was observed. It was found that the weak interdimer superexchange coupling ($|J| = 0.0072 \text{ cm}^{-1}$ under normal conditions) decreases under pressure. The coupling simultaneously decreases on cooling. Both effects, although atypical, can be explained as being driven by the normal thermal lattice contraction of the crystal under the assumption that the effective $|J|$ -value is ferromagnetic ($J > 0$) with temperature- and pressure-dependent antiferromagnetic contributions that increase when the lattice shrinks. $J > 0$ is justified by an analysis of the exchange pathway between dimers. A general model of a competition between ferro- and antiferromagnetic contributions to the $|J|$ value is proposed, which shows that $(d|J|/dT) > 0$ suggests a ferromagnetic coupling whereas $(d|J|/dT) < 0$ suggests an antiferromagnetic coupling.

Introduction

A very weak exchange coupling ($|J| < 0.1 \text{ cm}^{-1}$) was measured by EPR in various copper(II) salts, and it was found to be temperature dependent.¹⁻¹⁹ Temperature variations of the coupling were also observed as a deviation between experimental and theoretical temperature behavior of the magnetic susceptibility of some copper(II) dimeric salts²⁰⁻²² and in neutron inelastic scattering experiments of chromium(III) dimers.²³ The temperature dependence seems to be driven by several mechanisms changing an efficiency of the superexchange transmission between paramagnetic ions. These mechanisms cause different $J(T)$ dependences with various dJ/dT signs.

In the majority of crystals, the $|J|$ value increases with a lowering of temperature. It is mainly due to a thermal lattice contraction (volume effect), which results in a shortening of intermolecular distances. A similar effect in $|J|$ value can be also expected at low temperatures as a result of a decrease in triplet state (triplet

excitons) density in a crystal with antiferromagnetic coupling. This is observed in TCNQ salt crystals.²⁴⁻²⁶

In a few crystals it was found, however, that the $|J|$ value decreases with the lowering of temperature in a manner similar to that observed for a chemical exchange rate in solutions. For single crystals, one can suppose that it is an atypical effect. It was observed in single crystals of $[\text{N}(n\text{-Bu})_4]_2[\text{Cu}(\text{mnt})]_2$ ⁵ and in $[\text{M}(\text{en})_3]_2[\text{Cu}_2\text{Cl}_8]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$).¹⁵ This effect can be due to lattice vibrations (dynamic effect). A decrease in vibrational amplitudes of atomic motions with lowering temperature is expected to reduce the overlap between atomic orbitals on a given superexchange pathway. A decrease of exchange coupling with temperature was observed also in copper(II) cryptates where it was suggested that it is related to the exchange elasticity effect.⁹

In general, one can expect that both the volume and dynamic effects contribute to the temperature dependence of an exchange integral. The two contributions can be separated when the high-pressure effect on $|J|$ value is known, as was discussed in $[\text{Cu}_2(\text{dien})_2\text{Cl}_2](\text{ClO}_4)_2$ with "normal" $|J|(T)$ dependence.²⁷ It can be done because hydrostatic pressure lower than 1 GPa has no significant influence on atomic vibrations; thus, a pure volume effect can be assumed. Thus, the $|J|$ value nearly linearly increases with pressure as observed by EPR in $[\text{Cu}_2(\text{dien})_2\text{Cl}_2](\text{ClO}_4)_2$ ²⁷ and by luminescence spectroscopy in binuclear chromium(III) complexes.²⁸⁻³⁰

In this paper, an effect of hydrostatic pressure on the EPR spectrum and on exchange coupling in $[\text{Co}(\text{en})_3]_2[\text{Cu}_2\text{Cl}_8]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ is described and an explanation of the atypical temperature variation of the exchange integral is proposed. To be sure that the atypical $|J|(T)$ behavior is not due to an anomalous thermal lattice expansion, we have measured by X-ray methods the temperature dependence of the unit cell parameters, which have shown no anomaly, a monotonic decrease in unit cell dimensions on cooling, and a small anisotropy of thermal expansion coefficients.³¹

The orthorhombic crystal of $[\text{Co}(\text{en})_3]_2[\text{Cu}_2\text{Cl}_8]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ($\text{en} = \text{ethylenediamine} = \text{N}_2\text{C}_2\text{H}_8$) consists of antiferromagnetically coupled bis(μ -chloro)-bridged dimers $[\text{Cu}_2\text{Cl}_8]^{4-}$ surrounded by diamagnetic complexes $[\text{Co}(\text{en})_3]^{3+}$, uncoordinated Cl^- , and H_2O .^{15,32} Intradimer exchange coupling results in singlet-triplet

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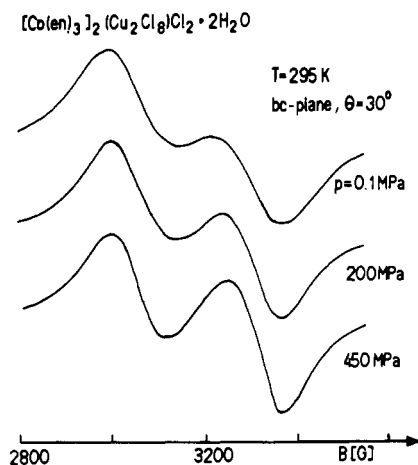


Figure 1. Pressure effect in the EPR spectrum of [Co(en)₃]₂[Cu₂Cl₈]Cl₂·2H₂O single crystal at room temperature.

splitting, $2J_0 = -14.6 \text{ cm}^{-1}$, which is temperature independent down to helium temperatures.^{15,33} Magnetically equivalent dimers are arranged in layers parallel to the (001) plane. The only chemical contact between layers is via a hydrogen bond (2.84 Å) between a water molecule in a layer and an ethylenediamine molecule in the neighboring layer.

EPR spectra indicate that the zero-field splitting (fine structure) and hyperfine structure are smeared out by interionic interactions with the former becoming resolved below 17 K.^{15,34} The single-crystal EPR spectrum consists of two resonance lines from magnetically nonequivalent sites, i.e., from dimers located in different layers. It allowed us to determine interdimer exchange coupling between the layers by an analysis of the merging effect between the two EPR lines.^{13,15} This coupling is isotropic and very weak, with the exchange integral $|J| = 0.0072 \text{ cm}^{-1}$ under normal conditions.

Experimental Section

A hydrostatic pressure effect (up to 450 MPa) on the EPR spectra was recorded at ambient temperature and at 153 K by using an X-band RADIOPAN SE/X-2542 spectrometer with a cylindrical corundum TE₁₁₂ resonator and 80-Hz magnetic modulation.³⁵ The resonator was coupled to the regular X-band wave guide by a matching corundum wedge and placed in a beryllium bronze pressure chamber, which was outside cooled by nitrogen vapor. A single-crystal sample was mounted into the resonator hole and surrounded by petroleum ether as a hydrostatic pressure transmitter.

Exchange Integral Determination from Merging Cu(II) EPR Lines

It is very easy to check if the two spin subsystems giving two (or more) distinct resonance lines in the single-crystal EPR spectrum are dynamically coupled or not. If the subsystems are not coupled, the total EPR spectrum can be reproduced by a computer simulation as a collection of overlapping symmetrical EPR lines. In the other case, the spectrum is disturbed by the onset of a merging effect, which appears when the jumps of spins between the spin subsystems produce line broadening comparable to the line splitting as a result of the lifetime shortening. The probability of jump can be identified as the exchange frequency, $\nu_{\text{ex}} = |J|/h$. In such a case, the simplest approach to describe the shape of a total EPR spectrum is a generalization of the Bloch equations, which are generally used in nuclear magnetic resonance³⁶ and for hyperfine structure of radical ESR spectra.³⁷ For

Cu(II) ions two additional facts have to be taken into account: (i) The line-width values are generally not identical for the component lines, which have, moreover, different angular line-width dependences. Fortunately the integral intensity of the lines is generally the same. (ii) The lines have different *g* factors, whereas the common *g* factor describes an NMR spectrum and resolved ESR hyperfine structures. The difference in the *g* factors is especially pronounced for Cu(II) ions due to their large spin-orbit coupling.

If a single crystal with two spin subsystems "A" and "B" gives a two-component EPR spectrum with *g* factors and half-widths g_A and g_B and Γ_A and Γ_B respectively, the shape $Y(B)$ of the first derivative of the absorption in a field-swept spectrometer can be described in the form²⁷

$$Y(B) = N\{[W_2 - 2(B - B_0)J](W_1^2 + W_2^2) - 4[(B - B_0)W_1 + (\Gamma_0 + J)W_2][(B - B_0)W_2 - (\Gamma_0 + 2J)W_1]\}/(W_1^2 + W_2^2)^2 \quad (1)$$

where

$$W_1 = (B - B_A)(B - B_B) - [\Gamma_A + 2Jg_B/(g_A + g_B)] \times [\Gamma_B + 2Jg_A/(g_A + g_B)] + 4J^2g_Ag_B/(g_A + g_B) \quad (1a)$$

$$W_2 = (B - B_A)[\Gamma_B + 2Jg_A/(g_A + g_B)] + (B - B_B)[\Gamma_A + 2Jg_B/(g_A + g_B)] \quad (1b)$$

and

$$\Gamma_0 = (\Gamma_A + \Gamma_B)/2 \quad B_0 = (B_A + B_B)/2 \quad (1c)$$

N is the amplitude normalization factor, and *J* is the exchange integral of the coupling between "A" and "B" assuming the Hamiltonian $H_{\text{ex}} = |J|S_1 \cdot S_2$. All parameters in eq 1 are given in gauss, and the relation between field and energy value of *J* is

$$J [G] = 10710(g_A + g_B)/(g_Ag_B)J [\text{cm}^{-1}] \quad (1d)$$

A computer fitting of eq 1 to an experimental two-component single-crystal EPR spectrum gives true line positions (*g* factors), peak-to-peak ΔB_{pp} line widths ($\Gamma = \sqrt{3}/2\Delta B_{\text{pp}}$), and an absolute value of the exchange integral $|J|$. Equation 1 is not sensitive to the sign of *J*; thus an observation of the merging effect does not allow one to distinguish between effects produced by ferro- or antiferromagnetic coupling. For real systems, eq 1 allows one to find the $|J|$ values in the range from 10^{-4} cm^{-1} for very narrow radical EPR lines up to about 0.1 cm^{-1} , with very high accuracy limited only by the noise in a recorded experimental spectrum.

It should be stressed that eq 1 can be used for a fitting of an experimental spectrum when the individual lines in the spectrum are Lorentzian. It is a prerequisite of the Bloch equation approach. This condition is very often fulfilled, especially when the hyperfine structure expected for Cu(II) is coalesced into a single line due to coupling between equivalent sites. To check if for a given crystal the lines are Lorentzian in shape, one should record EPR spectra in a crystal plane where only a single line is observed or along the crystal symmetry axes where the lines from nonequivalent sites superimpose and a merging effect does not operate. Along these directions, EPR lines are narrowest.

Results

Lately, we found¹⁵ that the interdimer exchange coupling in [Co(en)₃]₂[Cu₂Cl₈]Cl₂·2H₂O is isotropic; thus, the influence of the high pressure can be measured in any single-crystal orientation. We made the measurements in the crystal *bc* plane at about $\theta = 30^\circ$ where the splitting between the lines is maximal.

The pressure effect on the EPR spectrum at room temperature is shown in Figure 1. It is clearly seen that the resolution of the spectrum increases with pressure. It is due to a decrease in exchange coupling with simultaneous line narrowing without changing of *g* factors. The pressure dependence of $|J|$ and peak-to-peak linewidth ΔB_{pp} determined by using eq 1 are shown in Figures 2 and 3. The $|J|$ value decreases linearly with pressure

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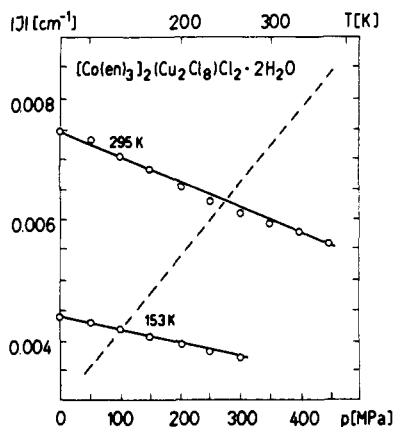


Figure 2. Pressure dependence of the interdimer exchange integral at room temperature and at 153 K. The broken line shows temperature dependence of the interdimer exchange integral.

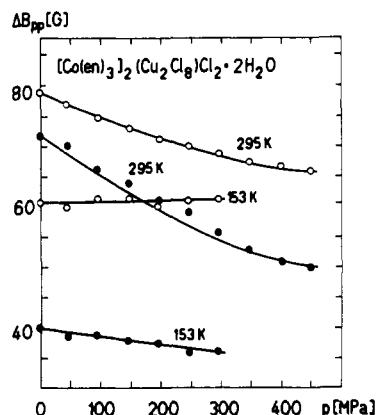


Figure 3. Peak-to-peak line-width pressure variations at 295 and 153 K for both components of the EPR spectrum. Solid circles represent the low-field line.

at both room and low temperatures (153 K) with coefficients $\partial|J|/\partial p = -4.4 \times 10^{-6} \text{ cm}^{-1}/\text{MPa}$ and $-2.3 \times 10^{-6} \text{ cm}^{-1}/\text{MPa}$ respectively. Thus an increase in pressure affects the $|J|$ value in the same way as a decrease in temperature (see dashed line in Figure 2).

We found a similar behavior for ΔB_{pp} values for both lines. Pressure narrows the lines at room temperature but has an insignificant effect at 153 K. It reflects the line-width temperature behavior. The lines narrow with lowering of the temperature, but at about 180 K the lines become practically temperature independent or even a broadening appears at some crystal orientations.¹⁵ The line-width value is determined in our crystal by unresolved zero-field splitting. The fine structure doublet is coalesced into a single line by a small exchange coupling between magnetically equivalent sites but becomes resolved below 15 K.³³ Thus the temperature and pressure line-width behaviors, we observed reflect variation in superexchange coupling between equivalent Cu(II) dimers. The problem of how a hydrostatic pressure affects the shape and width of EPR lines is generally not well recognized although a pressure effect was reported for ΔB_{pp} in $(\text{TMPD})\text{ClO}_4$,³⁸ $[\text{Cu}_2(\text{dien})_2\text{Cl}_2](\text{ClO}_4)_2$,²⁷ and CdCr_2Se_4 .⁹ We will not discuss this problem here.

Discussion

In our crystal, an increase of pressure affects the interdimer exchange coupling in the same way as a decrease of temperature. This is typical behavior when thermal expansion of a crystal lattice dominates over the lattice vibration effect in the temperature

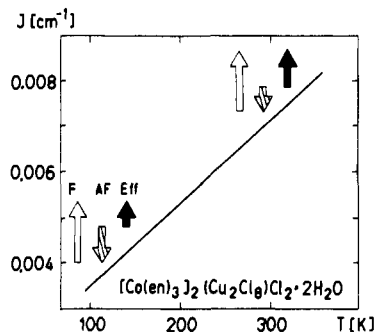


Figure 4. Temperature variation of the effective ferromagnetic inter-dimer exchange integral in $[\text{Co}(\text{en})_3]_2(\text{Cu}_2\text{Cl}_8)\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (solid arrows) and relative changes of the ferromagnetic F (open arrows) and antiferromagnetic AF (dashed arrows) contributions.

dependence of a physical parameter. In our case, we can write a simple thermodynamic relation (assuming J as the absolute number)

$$\left(\frac{\partial J}{\partial T}\right)_p = \left(\frac{\partial J}{\partial T}\right)_v - \frac{\alpha_v}{\beta_v} \left(\frac{\partial J}{\partial p}\right)_T \quad (2)$$

where the experimentally measured $(\partial J/\partial T)_p$ value is a sum of the dynamic (phonon) contribution $(\partial J/\partial T)_v$ and static (volume) contribution $(\partial J/\partial p)_T$, α_v is the volume thermal expansion coefficient, and β_v is volume compressibility coefficient. Equation 2 holds for isotropic crystals. Thus it is only a approximation in our crystal where α is an anisotropic quantity.³¹ Equation 2 shows that the volume effect in $(\partial J/\partial T)_p$ is enhanced by the coefficient α_v/β_v , which is negative, and $|\alpha_v/\beta_v| > 1$ for the crystals with a "normal" lattice behavior, i.e., when a thermal expansion is larger than a lattice compressibility. Unfortunately, the compressibility coefficients are not available for our crystal, and we can only evaluate roughly the dynamic term in eq 2. Taking $\alpha_v = 4.0 \times 10^{-5} \text{ K}^{-1}$,³¹ assuming typical $\beta_v \leq -\alpha_v/3$, and using experimental room-temperature data $(\partial J/\partial T)_p = 19 \times 10^{-6} \text{ cm}^{-1}/\text{K}$,¹⁵ and $(\partial J/\partial p)_T = 4.4 \times 10^{-6} \text{ cm}^{-1}/\text{MPa}$, we calculated $(\partial J/\partial T)_v \leq 5.8 \times 10^{-6} \text{ cm}^{-1}/\text{K}$. Thus the dynamic (phonon) contribution $(\partial J/\partial T)_v$ does not exceed 30% in the observed temperature variation of the interdimer exchange coupling $(\partial J/\partial T)_p$, which is therefore governed by the volume effect in our crystal.

It is a surprising conclusion. Although the $J(T)$ dependence is driven by the typical thermal lattice contraction, the $|J|$ value atypically decreases on cooling when interdimer distances decrease, instead of the expected increase in $|J|$ like in most of the crystals.

We claim that a temperature variation of exchange coupling is governed by a competition between different contributions having different temperature behavior. An effective exchange coupling that produces a level splitting measured by EPR spectroscopy can be expressed as the sum of two components: an antiferromagnetic, negative coupling J_{AF} and a positive ferromagnetic coupling J_F , which can be identified as Anderson's kinetic and potential exchanges, respectively. MO theories of superexchange introduced by Hoffmann et al.⁴⁰ and Kahn et al.⁴¹ show, that J_F is not sensitive to small structural changes whereas J_{AF} varies significantly. Thus, the $J_{\text{eff}}(T)$ dependence reflects the $J_{AF}(T)$ behavior, and the $|J_{AF}|$ value is expected to increase on cooling. However, the direction of change of $J_{\text{eff}} = J_F + J_{AF}$ depends on the relative values of J_F and J_{AF} contributions, which have opposite signs. When the ferromagnetic component dominates, an increase in $|J_{AF}|$ value on cooling will result in a decrease of the effective J_{eff} . It is just what we observe in our crystal (see Figure 4).

In the opposite situation, i.e. when the antiferromagnetic component dominates, which is more often the case, cooling of a crystal will result in an increase of the J_{eff} value, as is presented

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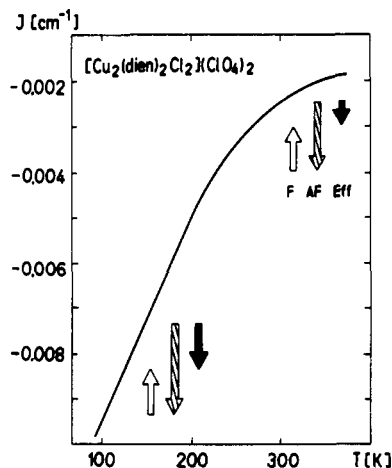


Figure 5. Temperature variation of the effective antiferromagnetic interdimer exchange integral in $[\text{Cu}_2(\text{dien})_2\text{Cl}_2](\text{ClO}_4)_2$ according to the data in ref 14. The arrow description is as in Figure 4.

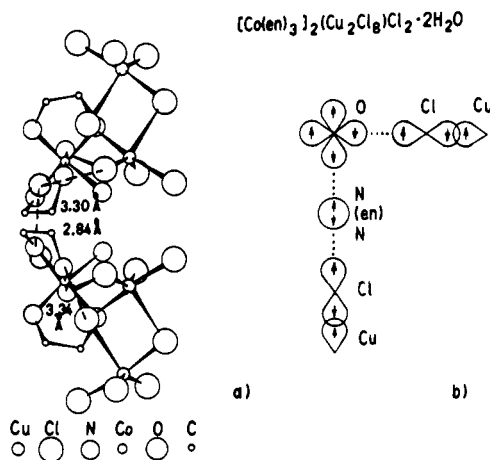


Figure 6. (a) Superexchange pathway (dashed line) between dimers located at a neighboring layer in the $[\text{Co}(\text{en})_3]_2(\text{Cu}_2\text{Cl}_8)\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ crystal. The total length of the pathway is about 18 Å. (b) Simplified picture of the pathway with the arrangement of spins (arrows) resulting in ferromagnetic coupling.

for $[\text{Cu}_2(\text{dien})_2\text{Cl}_2](\text{ClO}_4)_2$ in Figure 5.

Thus we conclude that exchange coupling between dimers located in different layers of the $[\text{Co}(\text{en})_3]_2(\text{Cu}_2\text{Cl}_8)\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ crystal is ferromagnetic. We can justify this conclusion by an analysis of the superexchange pathway between dimers using

Goodenough-Kanamori rules. There is only the single hydrogen bond between the layers; thus, it is easy to identify the superexchange pathway. This pathway is presented in Figure 6a. Unpaired electrons are localized on $d_{x^2-y^2}$ orbitals, which overlap with in-plane chlorine ions. Then an overlap between succeeding atomic orbitals goes through a hydrogen bond (3.30 Å) between Cl^- and the water molecule, via an interlayer hydrogen bond (2.84 Å) to the nitrogen atom of ethylenediamine molecule, and through this molecule and a $\text{N} \cdots \text{Cl}$ hydrogen bond (3.43 Å) to the $\text{Cu}(\text{II})$ ion of the neighboring dimer. This pathway is not a straight line, but can be sketched in a simplified way as is presented in Figure 6b. There is a single orthogonal point on the pathway at the H_2O molecule. Thus according to Goodenough-Kanamori rules, the resulting coupling between $\text{Cu}(\text{II})$ should be ferromagnetic as is shown by the spin arrangement in Figure 6b where spins located at atomic orbitals are represented by arrows. This supports our conclusion, which we have drawn from a discussion of the temperature and pressure effects.

Conclusions

We have shown in this paper that the decrease of the interdimer superexchange coupling on cooling in $[\text{Co}(\text{en})_3]_2(\text{Cu}_2\text{Cl}_8)\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ is not related to a decrease in amplitudes of atomic vibrations but is due to a crystal lattice contraction. The coupling is ferromagnetic and is reduced at low temperatures by an increase of the antiferromagnetic contribution, which is opposite in sign.

Generally, $|J|(T)$ dependence reflects a shift of the balance between ferro- and antiferromagnetic contributions with the latter being very sensitive to the geometry of a superexchange pathway. In most paramagnetic crystals with a weak exchange coupling studied so far, the $|J|$ value increases on cooling since in most crystals the antiferromagnetic coupling dominates. An opposite temperature $|J|$ value behavior is atypical since ferromagnetic coupling rarely appears.

Equation 1 allows us to determine the value of a weak exchange coupling from the EPR spectra, but the sign cannot be distinguished. The temperature and pressure variations of $|J|$ can, however, indicate if the coupling is ferro- or antiferromagnetic since the $\partial|J|/\partial T$ coefficient is positive in the former case and negative in the latter case. One can expect that in some crystals the antiferromagnetic contribution to the effective exchange coupling can be negligible. As a result the effective ferromagnetic J value should be only very weakly temperature dependent because of a low sensitivity of ferromagnetic coupling to structural changes. Indeed, we have found such situation in $(\text{NH}_4)_2\text{Cu}(\text{BeF}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(4\text{-pic } N\text{-oxide})_6(\text{ClO}_4)_2$ crystals (unpublished results) with very weak exchange coupling between $\text{Cu}(\text{II})$ ions.

Acknowledgment. This work was supported by the Polish Academy of Sciences under Project CPBP 01.12. We wish to thank Mrs. L. Szczepańska for growing the crystals.