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2003 J. Phys.: Condens. Matter 15 8899

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J. Phys.: Condens. Matter **15** (2003) 8899–8906 PII: S0953-8984(03)66324-1

Electron paramagnetic resonance of penta-ammino copper fluoroborate: coexistence of isotropic and anisotropic spectra in tetragonal phase

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Received 14 July 2003, in final form 15 October 2003
Published 3 December 2003
Online at stacks.iop.org/JPhysCM/15/8899

Abstract

The results of polycrystalline electron paramagnetic resonance (EPR) on tetra- and penta-ammino copper(II) fluoroborate are reported. The EPR spectra of penta-ammino Cu(II) complexes in perchlorate and fluoroborate $[Cu(NH_3)_5]X_2{\cdot}xNH_3$ depend on the presence of 'lattice ammonia', x, the number of ammonia molecules per Cu(II) ion above $n = 5$ that are not coordinated to Cu(II). In the high temperature cubic phase the spectrum is always an isotropic line. Furthermore, there is a substantial dependence of the averaged g-factor on the amount of 'lattice ammonia'. In the tetragonal phase of $[Cu(NH_3)_5](BF_4)_2{\cdot}0.1NH_3$, below T_c, there are two components to the EPR spectrum: the anisotropic one due to the square pyramid coordination and the isotropic one due to the centres where the averaging mechanism is still efficient. The contribution of the averaged signal to the total EPR spectrum in fluoroborate is significantly different than in isomorphous perchlorate salt. The higher content of isotropic signal in the total EPR spectrum suggests that fluoroborate exhibits a stronger tendency to retain the cubic structure in the low temperature phase than perchlorate.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Penta-ammino copper(II) perchlorate, characterized by total ammonia content $n = 5.2$ per Cu(II) complex, exhibits an isotropic electron paramagnetic resonance (EPR) signal in a wide temperature range [1]. If the isotropic spectrum persists down to helium temperature it means that it cannot be thermally averaged. The alternative explanation is the exchange coupling between at least three mutually perpendicular complexes [2], found

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in e.g. mixed crystals $Sr_2Zn_{1-x}Cu_xWO_6$ [3]. The inherent structural instability of five-coordinated complexes suggests a model of chemically induced orbital dynamics in five-coordinated Cu(II) complexes [4]. If a fifth ammonia is added to the coordination sphere of a square planar Cu(II) complex, an unstable five-coordinated complex is formed [1]. Therefore, it was assumed [4] that the ground state is a superposition of the two close lying states $|x^2 - y^2\rangle$, characteristic for C_{4v} symmetry of the complex (square pyramid—SQP), and $|z^2\rangle$ for D_{3h}—trigonal bipyramid (TBP) coordination:

$$|\,\rangle = \sqrt{1 - b^2}|x^2 - y^2\rangle + b|z^2\rangle \tag{1}$$

where b is the contribution of the $|z^2\rangle$ state. The averaged g-factor $\langle g\rangle$ is assumed to depend on the population of both states (described by trigonal distortion parameter a) [4]:

$$\langle g\rangle = (1 - a)\langle g\rangle_{\mathrm{sq}} + a\langle g\rangle_{\mathrm{bpt}} \tag{2}$$

where $\langle g\rangle_{\mathrm{sq}}$ and $\langle g\rangle_{\mathrm{bpt}}$ are the averaged g-factors for SQP and TBP, respectively. Fast exchange between $|x^2 - y^2\rangle \leftrightarrow |z^2\rangle$ states gives the averaging of local field which is temperature independent. Equation (2) applied to the analysis of the g-factor change at T_c in $[Cu(NH_3)_5](ClO_4)_2{\cdot}0.2NH_3$ (total number of ammonia molecules per Cu(II) ion $n = 5.2$) showed that the decrease in the volume at the phase transition shifts the equilibrium to the SQP configuration of the Cu(II) ion [4].

The analysis of EPR data of penta-ammino copper(II) perchlorate $[Cu(NH_3)_5](ClO_4)_2{\cdot}xNH_3$ [1, 5, 6] revealed that there is a significant influence of additional 'lattice ammonia' molecules (not forming $[Cu(NH_3)_5]^{2+}$ complex), hereafter denoted as x, where $n = 5 + x$, on the g-factor of the EPR line in the high temperature phase [6]. Below the phase transition temperature ($T_c = 142$ K [1] and 153 K [7] for perchlorate and $T_c = 154$ K [5] and 130 K [8] for fluoroborate) the EPR pattern substantially depends on the number of non-coordinated ammonia molecules. For perchlorate and fluoroborate single crystals ($n = 5$), two angular dependent signals are observed [5], whereas for $n = 5.2$ polycrystalline perchlorate the signal is still a single line [1], only the g-factor and linewidth are changed at the phase transition. For $n \approx 5.1$ in the low temperature phase of the perchlorate salt the EPR spectrum is a complex one [6]. An isotropic signal makes ~33% of the total integral intensity of the spectrum. The isotropic component of the spectrum undergoes the same change of the g-factor and the linewidth during the phase transition as the single line in $n = 5.2$ perchlorate [6]. The second component of the spectrum in the low temperature phase is an anisotropic pattern of a SQP five-coordinated copper ion. In some cases it has been observed that iso- and anisotropic spectra coexist in Cu(II) six-coordinated complexes [9–11] even in monocrystals [12]. However, the temperature dependence of relative integral intensities of both components points to thermally activated processes. In case of penta-ammino Cu(II) perchlorate [6] and fluoroborate there is no change in the intensity of the isotropic signal relative to the anisotropic component down to helium temperature.

Penta-ammino copper(II) fluoroborate is an isomorphic crystal with perchlorate salt, having fcc structure with the lattice constant $a = 11.13$ Å at room temperature [8]. X-ray temperature dependent studies showed a continuous phase transition starting at $T_c = 146$ K in fluoroborate from cubic to tetragonal structure [5].

2. Experimental details

The chemical analysis of the sample studied gave total ammonia content per Cu(II) ion equal to $n = 5.0 \pm 0.1$. For the reasons presented in [6] the ammonia content was taken as $n \approx 5.1$, hence the number of lattice ammonias $x \approx 0.1$. To avoid decomposition of penta-ammino

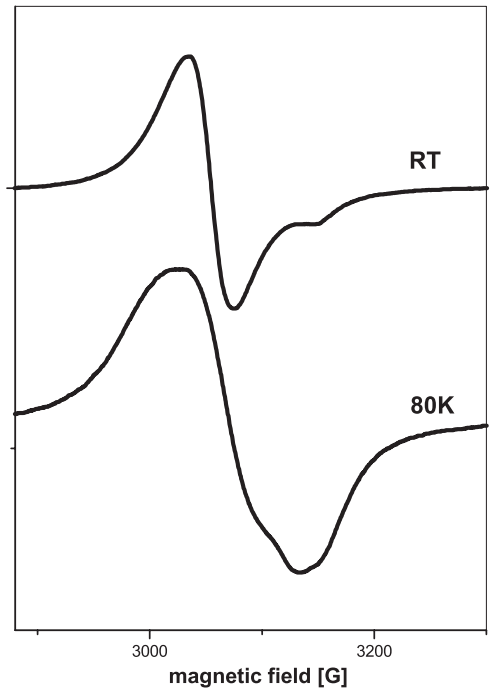

Figure 1. The EPR spectra for $[Cu(NH_3)_4](BF_4)_2$ above and below the phase transition temperature; $T_c \approx 141$ K.

complex, the sample was sealed in a quartz EPR tube. EPR experiments were performed on a CW X-band spectrometer with Oxford liquid helium equipment.

3. Results

3.1. EPR of $[Cu(NH_3)_4](BF_4)_2$

Tetra-ammine copper(II) complexes usually contain the square planar $[Cu(NH_3)_4]^{2+}$ cation and the tetragonal axes of the individual cations are aligned parallel to each other [13]. Polycrystalline $[Cu(NH_3)_4](BF_4)_2$ at room temperature gives an anisotropic EPR spectrum (figure 1, top spectrum) with $g_\parallel = 2.060$ and $g_\perp = 2.114$. However, one should expect $g_\perp < g_\parallel$ for Cu(II) square planar coordination and $d_{x^2-y^2}$ ground state. Thus the spectrum of $[Cu(NH_3)_4](BF_4)_2$ is reversed in form $g_\perp > g_\parallel$ relative to that expected for a square planar (or elongated octahedral) Cu coordination. This EPR pattern enabled us to observe decomposition $[Cu(NH_3)_5]^{2+} \rightarrow [Cu(NH_3)_4]^{2+}$ by EPR, since the spectra of both complexes substantially overlap. Therefore the process of losing ammonia in fluoroborate complex by EPR is not easy to follow as in perchlorate, where $[Cu(NH_3)_4](ClO_4)_2$ gives a typical anisotropic pattern with $g_\parallel = 2.230$ and $g_\perp = 2.051$ [1]. Additionally, the fluoroborate penta-ammino Cu(II) complex is more stable than the perchlorate one [8].

The spectra of tetra-ammino copper(II) fluoroborate are shown in figure 1. $[Cu(NH_3)_4](BF_4)_2$ undergoes a phase transition observed by the DSC method at $T_c = 141$ K [14], which is reflected in the EPR changed pattern at $T < T_c$ (figure 1, bottom spectrum).

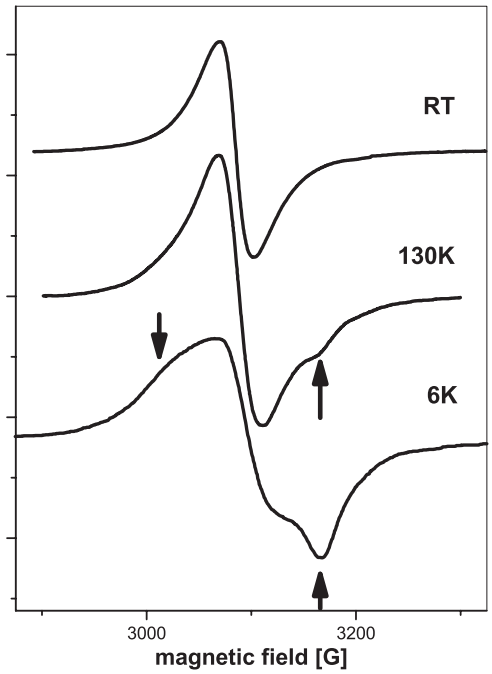

Figure 2. The EPR spectra for $[Cu(NH_3)_5](BF_4)_2{\cdot}0.1NH_3$ above and below the phase transition temperature; $T_c \approx 130$ K.

The reversed room temperature spectrum of $[Cu(NH_3)_4](BF_4)_2$ can result from the exchange coupling between misaligned complexes, thus giving crystal g-tensor values. Exchange coupling between differently oriented molecular axes of complexes with the canting angle 2γ induces a coupled g-tensor. Assuming planar NH_3 coordination of Cu(II) at room temperature and $2\gamma = 90°$ one gets molecular g-tensor components of $g_\parallel = 2.228$ and $g_\perp = 2.060$, characteristic for a square planar configuration in tetra-ammine Cu(II) complexes [13].

3.2. EPR of $[Cu(NH_3)_5](BF_4)_2{\cdot}\ 0.1NH_3$

In the high temperature phase of $[Cu(NH_3)_5](BF_4)_2{\cdot}0.1NH_3$ the EPR spectrum consists of a single Lorentzian line at $g = 2.130$, exactly the same g-factor as in $[Cu(NH_3)_5](ClO_4)_2{\cdot}0.1NH_3$, except that the linewidth at room temperature amounts to 31 G, whereas for perchlorate the peak-to-peak linewidth is 40 G [6].

Below T_c, fluoroborate $[Cu(NH_3)_5](BF_4)_2{\cdot}0.1NH_3$, like perchlorate salt, exhibits a two-component spectrum (figure 2). The g-factor and the linewidth of the isotropic component estimated from the experimental spectrum are presented in figures 3(a) and (b) together with the results for perchlorates: $[Cu(NH_3)_5](ClO_4)_2{\cdot}0.1NH_3$ [6] and $[Cu(NH_3)_5](ClO_4)_2{\cdot}0.2NH_3$ [1].

The coexistence of iso- and anisotropic components has to be characterized by their individual contribution to the spectrum. Therefore, deconvolution of the experimental spectrum of $[Cu(NH_3)_5](BF_4)_2{\cdot}0.1NH_3$ in the low temperature phase was performed. First, the anisotropic spectrum was simulated with $g_\parallel = 2.18$ and $g_\perp = 2.08$ and isotropic linewidth of 30 G (figure 4, spectrum B). The isotropic EPR component (figure 4, spectrum C) after subtraction of the simulated anisotropic component (figure 4, spectrum B) from the total

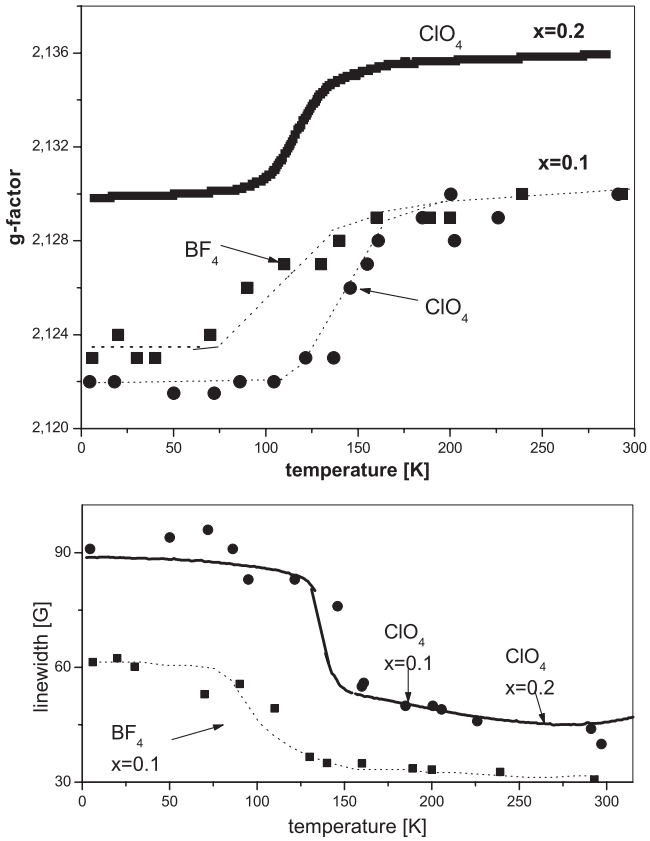

Figure 3. Temperature dependence of isotropic signal for $[Cu(NH_3)_5](BF_4)_2{\cdot}xNH_3$ and $[Cu(NH_3)_5](ClO_4)_2{\cdot}xNH_3$. (a) g-factor: solid curve—$x = 0.2$ perchlorate [1], solid circles—$x \approx 0.1$ perchlorate [6], solid squares—$x \approx 0.1$ fluoroborate. (b) Line width: solid curve—$x = 0.2$ perchlorate [1], solid circles—$x \approx 0.1$ perchlorate [6], solid squares—$x \approx 0.1$ fluoroborate.

experimental spectrum (figure 4, spectrum A) was thus obtained. The isotropic component corresponds to ∼65% of the integral intensity of the two-component experimental spectrum.

4. Discussion

4.1. The role of 'lattice ammonia' molecules in the averaging of the crystal field of the penta-ammino Cu(II) complex

Cubic phase. In the cubic phase of the $[Cu(NH_3)_5](BF_4)_2$ single crystal ($x = 0$) there is one isotropic line and no angular dependence. The g-factor is equal to 2.123. The linewidth was not reported [5]. EPR results on $[Cu(NH_3)_5](BF_4)_2{\cdot}0.1NH_3$, presented in this paper, give $g = 2.130$ and a linewidth of 31 G. For perchlorates $[Cu(NH_3)_5](ClO_4)_2{\cdot}xNH_3$ the EPR data are available for $x = 0$ [5], $x \approx 0.1$ [6] and $x = 0.2$ [1]. The same x-value ($x = 0$ [5] and $x \approx 0.1$ [6]) gives the same value of $\langle g \rangle$-factor for both salts.

The cubic phase of penta-ammino perchlorates and fluoroborates is always characterized by a single EPR line regardless of the contents of 'lattice ammonia' in the structure. The

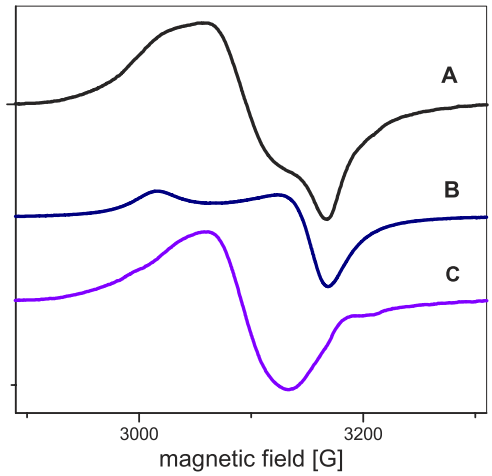

Figure 4. Deconvolution of the EPR spectra of $[Cu(NH_3)_5](BF_4)_2{\cdot}0.1NH_3$ at $T < T_c$; A designates the experimental spectrum, B the simulated anisotropic component and C the isotropic component of the experimental spectrum obtained from the subtraction (A − B).

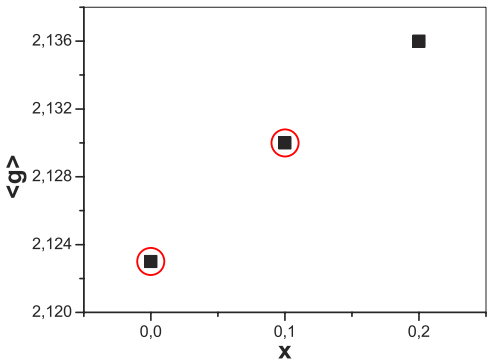

Figure 5. The averaged g-factor, $\langle g\rangle$, versus x, the number of non-coordinated ('lattice') ammonia molecules per Cu(II) ion in the cubic phase of $[Cu(NH_3)_5]X_2{\cdot}xNH_3$ [6]; squares—X = ClO_4, open circles—X = BF_4^-.

presence of 'lattice ammonia' is displayed in shifting the single line $\langle g\rangle$ towards higher values. The g-factor dependence on the number of 'lattice ammonia' molecules for fluoroborate and perchlorate salts is shown in figure 5 [6]. The $\langle g\rangle$-factor increases with x, the number of 'lattice ammonia' molecules per Cu(II) penta-ammino complex. According to equation (2) the $\langle g\rangle$-factor increases with x due to the shifting of the $|x^2 - y^2\rangle \leftrightarrow |z^2\rangle$ equilibrium towards the $|z^2\rangle$ state. This shows that in the cubic phase the role of 'lattice ammonia' in the crystal field averaging of the penta-ammino Cu(II) complex is to increase the averaged $\langle g\rangle$-factor of the complex from $\langle g\rangle = 2.123$ in the absence of 'lattice ammonia' (single crystals [5]) to $\langle g\rangle = 2.130$ and 2.136 for $x \approx 0.1$ and $x = 0.2$ [1], respectively. Such an increase in $\langle g\rangle$ according to equation (2) corresponds to higher trigonal distortion parameter changed from $a = 0.33$ ($x = 0$) to $a = 0.5$ ($x \approx 0.1$) and $a = 0.65$ ($x = 0.2$).

Tetragonal phase. In the tetragonal phase of the $[Cu(NH_3)_5](BF_4)_2$ single crystal ($x = 0$) the averaging mechanism becomes ineffective. Two angular dependent signals due to two

magnetically inequivalent $[Cu(NH_3)_5]^{2+}$ polyhedra were observed in both perchlorate and fluoroborate [5]. The $x \approx 0.1$ 'lattice ammonia' contents gives coexistence of the iso- and anisotropic spectra in the tetragonal phase. The integral intensity of the isotropic component constitutes ~65% of the integral intensity of the complex spectrum in fluoroborate, whereas in perchlorate only ~33% [6]. This means that ~65% of Cu(II) complexes are subjected to the averaging mechanism in fluoroborate and ~33% in perchlorate. The rest of the centres give an anisotropic powder spectrum related to the anisotropy of the g-tensor. For $x \approx 0.1$ in the tetragonal phase of the perchlorate salt, unlike fluoroborate, an increase in intensity of the isotropic component with time after synthesis to the equilibrium value of ~33% was observed [6], which points to the process of 'lattice ammonia' ordering in the structure and, again, to the essential role of ammonia molecules in the averaging mechanism of the crystal field at Cu(II) in penta-ammino complexes. Higher ammonia content, $x = 0.2$, results in an isotropic EPR spectrum only, thus the averaging mechanism is effective for all $[Cu(NH_3)_5]^{2+}$ complexes in the $[Cu(NH_3)_5](ClO_4)_2{\cdot}0.2NH_3$ tetragonal phase.

4.2. The averaging of the crystal field in penta-ammino complexes of Cu(II) and the phase transition

The most interesting feature of penta-ammino complexes of Cu(II) is the averaging of the crystal field resulting in the isotropic temperature independent EPR signal. For $x = 0$ single crystals the isotropic signal is present only in the high temperature phase; two angular dependent lines were observed below the phase transition temperature [5]. For $x > 0$ in $[Cu(NH_3)_5](BF_4)_2{\cdot}xNH_3$ and $[Cu(NH_3)_5](ClO_4)_2{\cdot}xNH_3$ polycrystalline samples ($x = 0.2$ and $x \approx 0.1$) the continuous phase transition gives a g-factor decrease and approximately doubles the linewidth, ΔH_{pp}, of the isotropic component still present in the tetragonal phase. Figures 3(a) and (b) show all available data of the g-factor and the linewidth of an isotropic signal for polycrystalline samples with different lattice ammonia contents $x \approx 0.1$ and $x = 0.2$, in the whole temperature range studied. From figure 3(b) it is evident that the linewidth of the isotropic component for the lower ammonia content ($x \approx 0.1$) compared to $x = 0.2$ is not substantially different, whereas g-factors are just shifted towards lower values (figure 3(a)). Both Δg and the change in the linewidth of the isotropic signal at the phase transition do not seem to depend on x in perchlorate as it is rather related to the change in the crystal structure at T_c [4]. The phase transition from cubic to tetragonal phase, accompanied by both Δg and ΔH_{pp} changes, looks more diffuse in fluoroborate than in perchlorate. The Δg decrease at the phase transition seems smaller in fluoroborate, which may be related to a smaller change of the volume than in perchlorate. A decrease in the volume has been determined only for perchlorate as $\Delta V/V \sim 1\%$ [1].

The loss of integral intensity of the isotropic EPR component at the phase transition in $[Cu(NH_3)_5](BF_4)_2{\cdot}0.1NH_3$ (~35%) found in this work is markedly different (smaller) than in perchlorate $[Cu(NH_3)_5](ClO_4)_2{\cdot}0.1NH_3$ (~67%) [6], i.e. for the same 'lattice ammonia' contents. Therefore, for $x \approx 0.1$ a much bigger number of $[Cu(NH_3)]^{2+}$ complexes are subjected to the averaging mechanism in the low temperature phase of fluoroborate than in perchlorate. Since in the cubic phase the EPR signal is always isotropic, the difference in the effectiveness of the averaging mechanism in the low temperature phase for $x \approx 0.1$ has to be related to the change in the crystal structure from cubic to tetragonal at the phase transition. The stronger isotropic component relative to the anisotropic one in the low temperature phase in fluoroborate implies that fluoroborate exhibits a stronger tendency to retain the cubic structure than the perchlorate salt.

5. Conclusions

The averaging mechanism is evidenced to be present at all times in the cubic phase in penta-ammino copper(II) perchlorate and fluoroborate. However, there is a substantial averaged g-factor dependence on the number of 'lattice ammonias' x. Therefore, unlike the case in the tetragonal phase, in the cubic phase the averaging process is effective even in the absence of 'lattice ammonia' molecules ($x = 0$) [5], whereas their presence only shifts the averaged line towards higher $\langle g \rangle$-values.

In the low temperature tetragonal phase the EPR pattern, hence the effectiveness of the averaging mechanism, depends strongly on x. For $x = 0$ there is no isotropic line in the EPR spectrum [5]. For $x \approx 0.1$ the isotropic line coexists with an anisotropic pattern. The low temperature phase EPR spectrum of fluoroborate is dominated by an isotropic component ($\sim$65%), unlike the case in perchlorate ($\sim$33%). Hence, the averaging mechanism is effective for $\sim$65% and $\sim$33% of complexes in fluoroborate and perchlorate, respectively. For $x = 0.2$ the averaging mechanism is effective for all Cu(II) centres: there is a single EPR line [1].

Since there is always an isotropic spectrum in the cubic phase, and in the low temperature tetragonal phase for $x \approx 0.1$ the fluoroborate exhibits a higher contribution of isotropic component to the EPR pattern than perchlorate, the fluoroborate tetragonal structure might be much less distorted from the cubic one than perchlorate. This conclusion is supported by an x-ray result, that the c/a ratio in tetragonal unit cell is very near unity [5].

The coexistence of iso- and anisotropic spectra in tetragonal phases of both salts implies that there is no x-value at which the pure $|x^2 - y^2\rangle$ (SQP) state and the mixed state of $|x^2 - y^2\rangle$ and $|z^2\rangle$ would be separated.

Acknowledgments

We are pleased to acknowledge helpful discussions with Professor J Stankowski and Professor S Waplak. Thanks are due to Dr hab A Migdał-Mikuli and Dr hab E Mikuli for providing samples, and Dr W Bednarski for assisting in the EPR measurements. This paper was supported by KBN grant P03B06120.

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