

## Vibronic Averaging Effect in ESEEM Spectra of $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ Single Crystal Doped with Jahn–Teller Active $\text{Cu}(\text{H}_2\text{O})_6$ Complexes

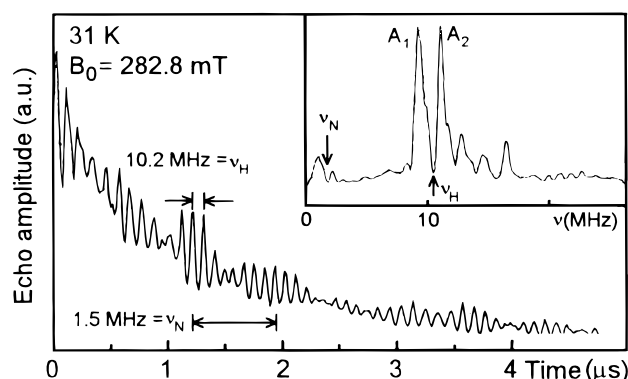
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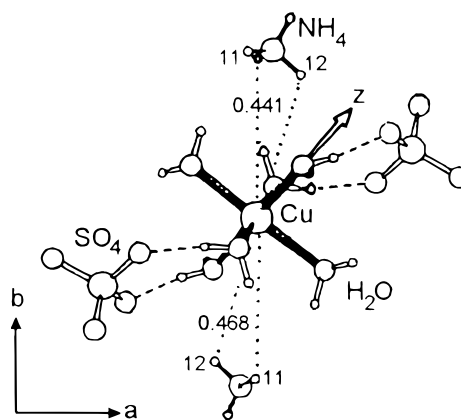
Received May 19, 1998

Copper(II) ions introduced into the diamagnetic Tutton salt crystals  $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  substitute metal  $\text{Me}^{2+}$  ions and deform the host  $\text{Me}(\text{H}_2\text{O})_6^{2+}$  octahedron due to the strong Jahn–Teller effect. The three Jahn–Teller distorted configurations of the octahedron are inequivalent and are stabilized by strong local strains produced by hydrogen bonds between coordinated  $\text{H}_2\text{O}$  molecules and  $\text{SO}_4$  groups.<sup>1</sup> The vibronic dynamics, i.e., reorientations, between the distorted configurations determine the local dynamics of the  $\text{Cu}^{2+}$  complexes and influence the EPR spectra and electron spin relaxation. A description of this dynamics may be simplified to the two-potential-well model, since the highest potential well, appearing for the configuration along the shortest  $\text{Cu}–\text{H}_2\text{O}$  bond, is essentially unpopulated up to about room temperature.<sup>2</sup> An understanding of the dynamics is not satisfied, as we discussed previously.<sup>3</sup> The question is at what temperature the vibronic dynamics producing the dynamic Jahn–Teller effect appears? It seems that this temperature differs in different Tutton salts despite the very similar crystal and molecular structures. Another open question is what is the relationship between the vibronic dynamics of the  $\text{Cu}(\text{H}_2\text{O})_6$  complex and the molecular motions of the surrounding  $\text{SO}_4$  and  $\text{NH}_4$  groups coupled by the hydrogen-bonding network.<sup>4</sup>

In this note, we show that the electron spin-echo (ESE) technique allows a closer look at this problem in  $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}/\text{Cu}^{2+}$  single crystals. Three-pulse stimulated ESE was generated by three identical 16 ns pulses with the interval between the first and the second pulse equal to 96 ns and an initial delay of 600 ns between the second and third pulses. The pulsed Bruker ESP380E FT/CW spectrometer was used. The stimulated echo amplitude decay was recorded in a single-crystal orientation with  $B \parallel z$ , where  $z$  is the  $g$ -tensor axis with  $g_z = 2.432$ , for the  $m_1 = -1/2$  hyperfine line, in the temperature range 7–55 K. The decay was strongly modulated, and the ESE envelope modulation pattern recorded at 31 K is shown in Figure 1, where the two characteristic frequencies of  $^1\text{H}$  and  $^{14}\text{N}$  can be recognized. Their existence is confirmed by the corresponding Fourier transform ESEEM spectrum (inset of Figure 1), where nitrogen and hydrogen peaks are identified. ESEEM patterns and ESEEM spectra are generally used to obtain information about a distribution of magnetic nuclei



**Figure 1.** Electron spin-echo envelope modulations ESEEM pattern at 31 K showing proton  $\nu_{\text{H}}$  and nitrogen  $\nu_{\text{N}}$  modulations recorded for the  $m_1 = -1/2$  line of the EPR spectrum along the  $z$ -axis of the  $\text{Cu}(\text{H}_2\text{O})_6$  complex. The inset shows the ESEEM spectrum.



**Figure 2.** Molecular arrangement around  $\text{Cu}(\text{H}_2\text{O})_6$  complex in the  $ab$ -plane, with two  $\text{NH}_4$  groups producing the modulation pattern shown in Figure 1. The modulations are due to the weak hyperfine coupling between Cu and two pairs of protons nos. 11 and 12. The  $\text{Cu}–\text{H}$  distances (in nanometers) are shown.

around a paramagnetic center, especially in disordered and biological materials.<sup>5</sup> In a single crystal of a known structure, as in our case, one can identify the magnetic nuclei producing peaks in ESEEM spectra and then observe their behavior under various conditions.

The two intense proton peaks  $A_1$  and  $A_2$ , split by 1.75 MHz, result from overlapping signals from the nearest protons of  $\text{NH}_4$  groups. From the crystal structure data,<sup>6</sup> the protons can be identified as belonging to the  $\text{NH}_4$  groups located at a distance of 0.494 nm from  $\text{Cu}^{2+}$ , with the  $\text{Cu}–\text{N}$  direction about  $33^\circ$  from the  $z$ -axis (Figure 2). The four protons marked as 11 and 12 located at distances of 0.441 and 0.468 nm, respectively, produce the  $A_1$  and  $A_2$  peaks. The peak positions are temperature independent below 45 K; then, the lines broaden and collapse to a single line at about 55 K (Figure 3). One can assume that this typical dynamical averaging effect can be explained as a result of an acceleration of  $\text{NH}_4$  group reorientation. However, such an effect is not observed in the ESEEM

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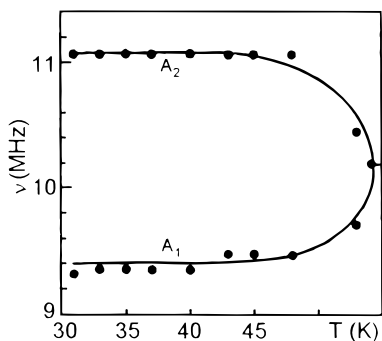
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**Figure 3.** Vibronic averaging of the  $A_1$  and  $A_2$  peak positions of ESEEM spectra.

spectra of  $Mn^{2+}$  ions,<sup>7</sup> indicating that this is a characteristic feature of the  $Cu^{2+}$  doped crystal. So, we assume that the averaging is connected with the vibronic  $Cu(H_2O)_6$  complex behavior. Thus, the reorientations between Jahn–Teller distorted configurations start above 45 K and are transmitted via the hydrogen-bond network to the neighboring molecular groups, producing local magnetic field fluctuations larger than the  $(A_1 -$

$A_2) = 1.75$  MHz splitting. The similar effect is observed for  $g$ -tensor components but at higher temperatures, since the splitting between EPR spectra from two lower energy potential wells is much larger than the  $(A_1 - A_2)$  splitting and reaches about 80 mT (2.2 GHz) at the rigid lattice limit. The  $g$ -factor averaging starts at about 60 K, and the maximal averaging efficiency is reached at about 110 K, where the thermal population of the upper well increases rapidly.<sup>3</sup>

Thus, the ESEEM spectra are much more sensitive to the vibronic dynamics due to their high spectral resolution as compared to that of the EPR spectrum. Our data show that the vibronic dynamics is not restricted to the  $Cu(H_2O)_6$  complex only. The neighboring molecular groups are also involved, forming large vibronic clusters. An existence of such clusters can explain an appearance of the elastic coupling between vibronic centers for high  $Cu^{2+}$  concentrations in diamagnetic crystals.<sup>4,8</sup>

**Acknowledgment.** This work was supported by Scientific Research Committee under Project KBN-2-P03B-122-14.

IC9805675

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