Hysteresis of the Pressure-Induced Jahn−Teller Switch in Deuterated Ammonium Copper(II) Tutton Salt, $(ND_4)_2[Cu(D_2O)_6](SO_4)_2$

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Introduction

The copper(II) Tutton salts have been studied extensively as a means to understand Jahn−Teller distortions in a variety of materials.[1] Salts with alkali metals, of general formula $A_2[Cu(H_2O)_6](SO_4)_2$, A = K, Rb, Cs, all contain a distortion in which Cu−O(8) is elongated compared to Cu−O(7) and Cu−O(9), herein designated as structure type **I**, as summarized in Table 1.[1−3] In contrast, in the hydrogenated ammonium salt $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ the elongated bond has switched to Cu−O(7) (structure type **II**).[4] However, the ammonium copper salt exhibits an isotope-induced Jahn−Teller switch such that the deuterated salt, $(ND_4)_2[Cu(D_2O)_6](SO_4)_2$, is isostructural with the alkali metal salts in which Cu−O(8) is elongated (**I**).[5,6] In 1993 we reported a pressure-induced switch, such that at 1.4 kbar and 15 K, the distortion in $(ND_4)_2[Cu(D_2O)_6](SO_4)_2$ is reversed so that it becomes isostructural with the hydrogenated salt $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ (**II**).[6]

In order to examine the pressure-induced Jahn−Teller switch in greater detail and determine precisely where the transition occurs, we have measured the pressure dependence at room temperature of the lattice constants of deuterated $(ND_4)_2[Cu(D_2O)_6](SO_4)_2$ in the region of the phase transition. We also report the pressure dependence of the EPR spectrum at the phase transition.

Experimental Section

Synthesis of $(ND_4)_2[Cu(D_2O)_6](SO_4)_2$. The procedure to prepare the sample has been described previously.[6]

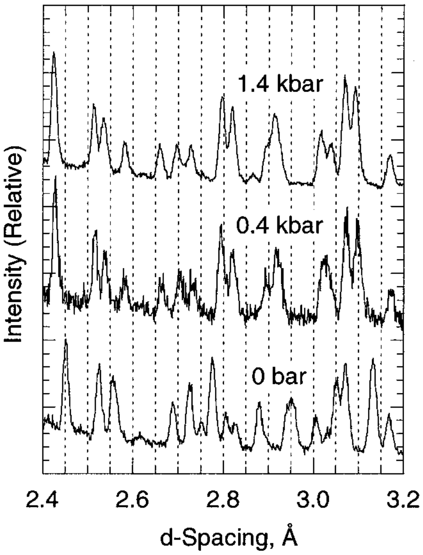

Figure 1. Neutron time-of-flight powder diffraction data for a selected *d*-spacing range at applied pressures of 0, 400, and 1400 bar. Note the similarities of the two high-pressure spectra, indicative of the same structural phase, and their differences from the 0 bar spectrum. The different noise levels in the spectra are related to the counting times of 164 (0 bar), 22 (0.4 kbar), and 316 min (1.4 kbar).

Powder Neutron Diffraction. Data were obtained using the time-of-flight special environment powder diffractometer (SEPD)[7] at the Argonne Intense Pulsed Neutron Source (IPNS) at room temperature using a helium gas pressure cell.[8] The estimated uncertainties in the pressure values are ±10 bar. The duration of each individual measurement, at the 90° scattering angle, was typically 20−30 min, which is not sufficient for full structural analyses. However, the data collection times were more than sufficient to obtain high-precision unit cell parameters which provide a definitive probe of the transition. The powder data were analyzed with the Rietveld technique, using the GSAS program,[9] over a *d*-spacing range of ∼0.9−5.4 Å which includes ∼1380 possible Bragg peaks.

EPR Measurements. EPR spectra were measured at 300 K using a custom-built spectrometer operating at Q-band frequency of 37.56 GHz with a magnetic field modulation frequency of 63 Hz. To vary the uniform pressure, the sample crystal was placed in a special chamber of nonmagnetic beryllium bronze filled with dry oil as the pressure-transmitting medium. The high-pressure chamber was located between the poles of the EPR magnet and was connected to a precise manometer by nonmagnetic tubing. The pressure could be read to an accuracy of ±3 bar, and each measurement was made about 3 min after the pressure was changed. The resonance cavity, made of monocrystalline Al_2O_3, has been described in detail previously.[10]

Results and Discussion

Neutron diffraction powder spectra at three of the 14 applied pressures are shown in Figure 1. As shown from plots of lattice parameters in Figure 2, the structural phase transition from **I** to **II** occurs at around 200 bar and is completed by 250 bar or before with increasing pressure. The transition is characterized by contractions of the *a* and *b* axes and by an increase in the *c*-axis length, all of around 0.07−0.09 Å in magnitude. The increase in the length of the *c* axis is due to the lengthening of

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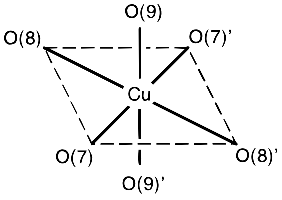
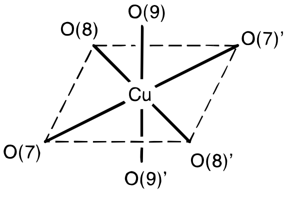
Table 1. Structures of CuO_6 Octahedra in $(Cation)_2[Cu(H_2O)_6](SO_4)_2$ Salts

compd *T*, *P*	Cu−O(7), Å	Cu−O(8), Å	Cu−O(9), Å	type	ref
$(A)_2[Cu(H_2O)_6](SO_4)_2$, A = K, Rb, Cs					1−3
295 K, 1 bar	2.03	2.30	1.96	**I**	
$(NH_4)_2[Cu(H_2O)_6](SO_4)_2$					
295 K, 1 bar	2.230(1)	2.093(1)	1.966(1)	**II**	4
14 K, 1.4 kbar	2.272(2)	2.005(2)	1.979(2)	**II**	6
$(ND_4)_2[Cu(D_2O)_6](SO_4)_2$					
295 K, 1 bar	2.081(6)	2.242(7)	1.927(6)	**I**	5
15 K, 1 kbar	2.022(2)	2.310(2)	1.966(3)	**I**	6
15 K, 1.5 kbar	2.290(2)	2.014(2)	1.988(3)	**II**	6



Type I



Type II

the Cu−O(7) bonds combined with the rigidity of the hydrogen bond network in that direction. Upon decreasing the pressure, the crystal switches back to **I** at about 100 bar. Thus there is a clear hysteresis of about 100 bar as exhibited by the neutron powder data. For the monoclinic unit cell, space group $P2_1/a$, lattice parameters at room temperature and pressure are a = 9.2954(7) Å, b = 12.5074(8) Å, c = 6.1915(5) Å, β = 106.397(3)°, and V = 690.55(12) Å^3. At room temperature and 1.4 kbar, lattice constants are a = 9.1812(6) Å, b = 12.3505(7) Å, c = 6.2723(4) Å, β = 106.143(3)°, and V = 683.19(11) Å^3. These values are in good agreement with single-crystal X-ray diffraction measurements using a diamond anvil cell.[11]

In a previous study[11] of the pressure dependence of the EPR spectrum of a powder sample of $(ND_4)_2[Cu(D_2O)_6](SO_4)_2$ at room temperature, we observed that the structural change is accompanied by a change in the g values. No hysteresis effect was detected, probably because the intervals of 200 bar in pressure at which measurements were made were too large. We have therefore now measured the EPR spectrum of a single crystal of the compound at many pressures between 1 and 600 bar. The crystal was mounted so that the magnetic field could be rotated in the (001) plane and oriented such that the magnetic field vector bisected the a and b crystal axes (see Figure 2a of Rauw *et al.*[11]). In this position, the magnetic field is approximately parallel to the Cu−O(7) bonds of one molecule and the Cu−O(8) bonds of the second molecule in the unit cell.[6]

At ambient pressure, the resonance signals of the two molecules are clearly resolved (Figure 3a), and the observed g-values (2.19, 2.38) agree reasonably well with those derived previously from the powder EPR spectrum of this compound (2.205, 2.350).[11] It is well established that there is a direct correlation between the magnitude of the g-values and the metal-ligand bond lengths of rhombically distorted copper(II) complexes,[12] so that the higher g-value is associated with the complex where the magnetic field is parallel to the longer bonds, the Cu−O(8) bonds, while the lower g-value is due to the second molecule where the magnetic field is parallel to the Cu−O(7) bonds. When the pressure is increased gradually to 234 bar, the two signals move slightly toward one another, and when the pressure is increased further to 246 bar, the signals coalesce, and they remain coalesced as the pressure is further raised to 600 bar, the highest value available for single-crystal EPR measurements. From the powder EPR measurements it was shown that the crossover region extends to 1 kbar, where the g-values diverge again but with reversed relative magnitudes with respect to ambient pressure.[11] Typical single-crystal spectra are shown in Figure 3a, and the pressure dependence of the g-values is indicated in Figure 3b. The pressure at which the EPR signals coalesce corresponds within experimental uncertainty to that at which the unit cell parameters change. When the pressure is lowered, the single EPR signal remains until ∼150 bar, when it diverges into the separate peaks associated with the two molecules in the unit cell (Figure 3). This pressure is slightly higher than that at which the unit cell parameters "switch", but the EPR spectrum exhibits a clear hysteresis effect of ∼100 bar paralleling that shown by the change in unit cell parameters.

The behavior of the EPR spectrum differs from that of the unit cell parameters in an important aspect. At 1 bar, the EPR signals of the two molecules in the unit cell are resolved quite clearly, and these do not alter significantly as the pressure is increased to just below the phase transition. The structural phase transition is accompanied by the coalescence of the two EPR lines to a single signal corresponding to the average g-value of the two molecules, and this remains up to the maximum pressure available in the single-crystal EPR experiment (600 bar) and is shown in the previous powder EPR experiment to diverge above 1 kbar. This contrasts with the powder diffraction data (Figure 1) and the derived unit cell parameters (Figure 2), where no phase midway between the extremes is observed.

Thus, the diffraction data show that there is only one structural phase transition. The difference in behavior reflects the fact that EPR spectroscopy measures a quite different property from neutron diffraction. The diffraction experiment shows that over a rather small pressure range the overall structure changes from one crystal-packing arrangement to another. The EPR spectrum, on the other hand, measures the energy of the magnetic moments of the two molecules in the unit cell in an applied magnetic field.

It might be thought that the observation of an averaged EPR signal implies that in the high-pressure phase the Cu−O(7) and Cu−O(8) bond lengths are equivalent, but this is not necessarily the case. Whether the individual signals of these are resolved or not depends upon the rate at which the unpaired electron exchanges between the molecules. If this is faster than the difference in energy of the two magnetic moments in the magnetic field, expressed in frequency units, then a single

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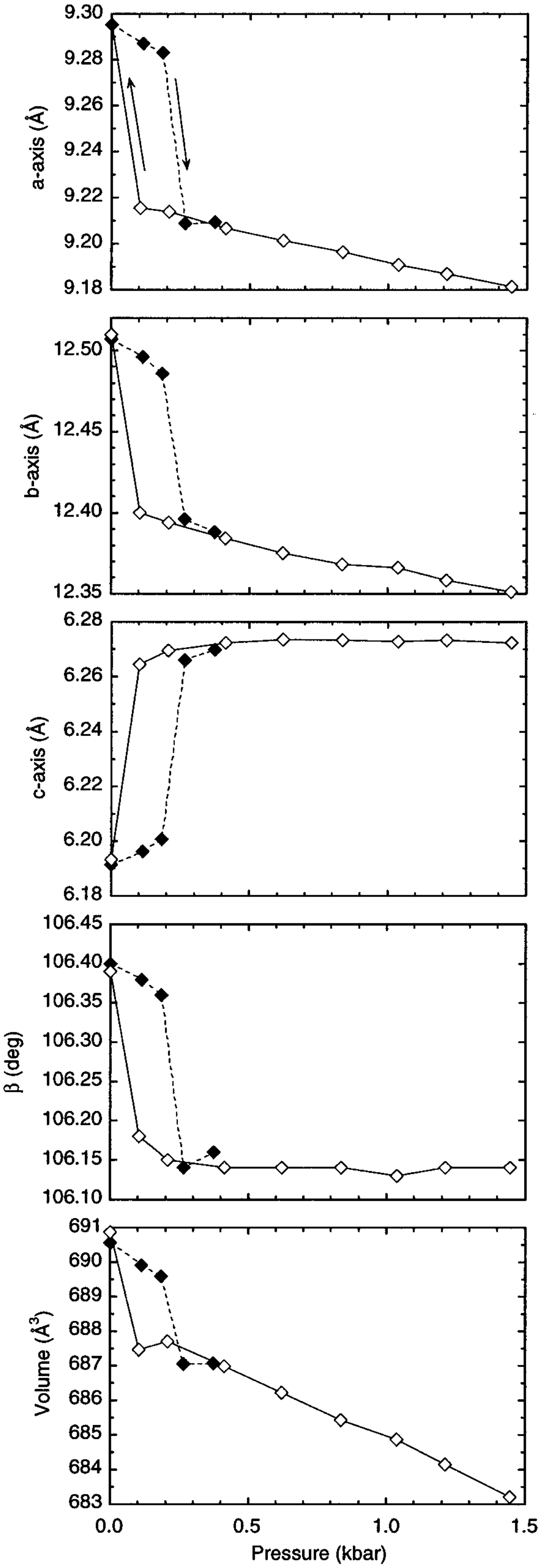

Figure 2. Pressure dependence of the unit cell lattice parameters of $(ND_4)_2[Cu(D_2O)_6](SO_4)_2$ at room temperature. Filled diamonds are data points obtained while the pressure was increased, whereas open diamonds indicate decreasing pressure. Estimated standard deviations range from ±0.0003 to ±0.0011 Å.

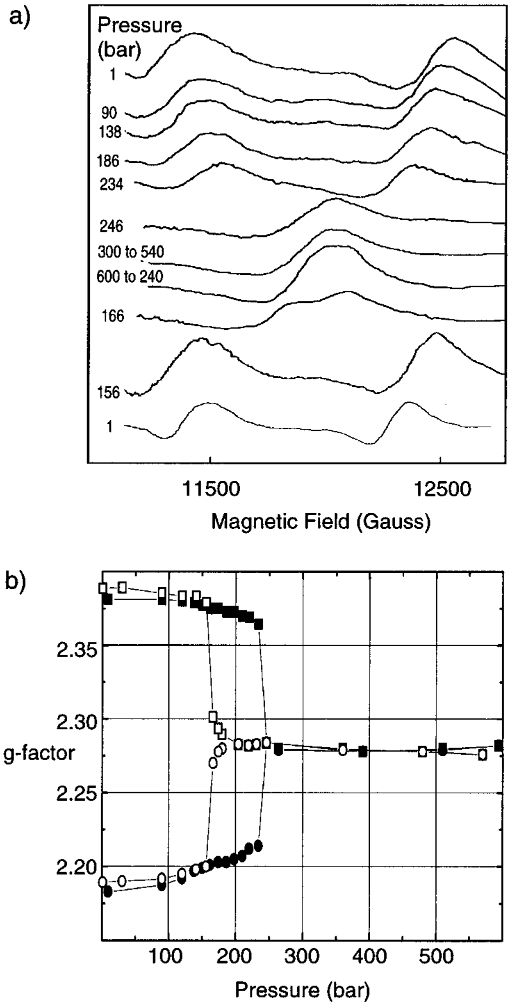

Figure 3. (a) Typical EPR spectra of a crystal of $(ND_4)_2[Cu(D_2O)_6](SO_4)_2$ with the magnetic field midway between the *a* and *b* crystal axes at various pressures. (b) Variation of the two higher molecular *g*-values of $(ND_4)_2[Cu(D_2O)_6](SO_4)_2$ as a function of pressure; the dark symbols show values obtained as the pressure increased, and the light symbols values as the pressure decreased.

“exchange-narrowed” signal will be observed.[13] The present single-crystal results are consistent with the previous, lower resolution powder EPR spectra. The powder spectra showed a **g**-tensor in which the two higher *g*-values were resolved in phase **I** from ambient pressure to the phase transition and then were coalesced from the phase transition up to ~1 kbar, above which pressure the signals due to individual molecules were resolved.[11] When taken in conjunction with the neutron diffraction data, the EPR spectra imply that while the transition from phase **I** to **II** occurs quite sharply at ~240 bar, with the direction of the longest copper−oxygen bonds switching from O(8) to O(7), the rate of electron exchange in phase **II** is more rapid than the frequency difference between the EPR signals of the two molecules below ~1 kbar, but slower than this at higher pressure. This is presumably due to a pressure-related structural change. The previous X-ray study found that the difference between the Cu−O(7) and Cu−O(8) bond lengths decreases from 0.14 Å at ~3.0 kbar to 0.12 Å at ~1.5 kbar, with this anisotropy being considerably smaller than that of 0.175 Å at 1 bar in the low-pressure phase.[11] The frequency difference between the EPR signals depends upon the difference in *g*-values, which will mirror the difference in metal−ligand bond lengths,[12] so that the structural data are indeed consistent with the observed behavior. Presumably the *g*-anisotropy is large enough to allow individual molecular *g*-values to be resolved for phase **I** and for phase **II** above ~1 kbar, but insufficient to

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overcome exchange-narrowing in the high-pressure phase below this pressure. However, it is also possible that the rate of electron exchange is pressure dependent (hence, unit cell volume dependent), and that this plays a role as far as the change in the EPR spectra is concerned.

In summary, for $(ND_4)_2[Cu(D_2O)_6](SO_4)_2$ at room temperature a pressure-induced phase change involving a Jahn−Teller switch is observed at ∼200−250 bar by both neutron diffraction and EPR spectroscopy, with the reverse phase transition occurring some 100 bar lower in pressure. The change in overall crystal structure occurs quite sharply, within ∼50 bar. Signals due to the individual molecules are observed in the EPR spectrum of the low-pressure phase, but these coalesce to a single signal above the phase transition, up to a pressure of ∼1 kbar. It must be stressed that the change to a single EPR signal does not necessarily indicate an averaging of the relevant bond lengths in the $[Cu(D_2O)_6]^{2+}$ complex. It simply indicates that in this region of the high-pressure phase, the rate of electron exchange is faster than the frequency difference between the EPR signals of the two molecules in the unit cell. Thus, the EPR spectra within phase **II** are dependent on the unit cell volume (and possibly the magnitude of the Jahn−Teller distortion) and therefore, consequently on the applied pressure. In both structural phases, the $[Cu(D_2O)_6]^{2+}$ complex is involved in a thermal equilibrium between structural forms similar to those involved in the pressure-induced phase change.[11] The influence of temperature on the phase change is therefore of some interest, and we are currently planning experiments to investigate this aspect.

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