Photoinduced phase transition of coordinationally unsaturated d^9 metal centers within the thermal hysteresis of the spin exchange interaction

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Diffraction evidence is presented that the structure of one-dimensional arrays of strained, coordinationally unsaturated d^9 pseudo-Jahn–Teller centers is affected by excitation of the LMCT bands within the hysteresis region of the low-temperature ferromagnetic-to-antiferromagnetic phase transition.

Novel materials with physical properties that can be efficiently controlled by light is one of the main goals of modern materials science.[1] Non-linear molecules with a partially filled set of degenerate orbitals are inherently Jahn–Teller (JT) unstable,[2] an effect which is considered to underpin important phenomena such as high-temperature superconductivity[3] and colossal magnetoresistance.[4] In this study, a pseudo-JT crystal composed of d_{z^2} arrays of coordinationally unsaturated copper(II) ions was utilized as a potentially light-susceptible medium for which significant structural perturbations are expected upon excitation.

Fig. 1 shows the structure of the low-temperature ordered (**A**) and high-temperature disordered (**B**) phases of CuCO from single crystal diffraction data. Each of the two disordered ring atoms in **B** was modelled with two components with approximate occupancies of 0.64/0.36 (carbon) and 0.80/0.20 (nitrogen).

As a coordinationally unsaturated unit, the *trans*-square-planar bis(*N*,*N*-diethylethylenediamine) copper(II) (CuDED) cation in its perchlorate salt was selected (Fig. 1).[5] The bulky gem-dialkylamine ligands play multiple structural roles: first, they determine the square-planar geometry by shielding the apical metal valences from approach of the anions beyond non-bonded distances; second, they effectively space out the metal ions preventing dimerization; and third, they provide sufficient flexibility for distortions of the primary coordination sphere. The resulting instability can be compensated for by pressure[6] or by heating above 317.6 K,[7] where the internal strain overweighs the energy gain from the electronic states' ordering and the respective lattice distortions, resulting in spontaneous transition of the triclinic lattice ($P\bar{1}$, phase **A**) to a monoclinic one ($I2$, phase **B**) with doubled volume and tetrahedral distortion of the square-planar ligand plane (Fig. 1).[8] In this paper we show that besides the two known phases, phase **A** which exists below 317.6 K, and phase **B** which exists between 317.6 K and the thermal decomposition point, below 60 K this material undergoes another thermal phase transition to a third phase, denoted phase **C**.

The magnetic susceptibility† of $(\mathrm{CuDED})(\mathrm{ClO_4})_2$ single crystals cycled thermally in the dark below the phase transition $\mathbf{A}\leftrightarrow\mathbf{B}$ (2–300 K)[9] exhibits reproducible anomalies at low temperature (Fig. 2). On cooling (↓) from ambient temperature a single-step transition occurs at 48 K ($T_\downarrow$), with onset at 60 K. During subsequent heating (↑), the susceptibility is recovered in two steps between 25 and 57 K, at 30 K ($T_{\uparrow,1}$) and 52 K ($T_{\uparrow,2}$). The hysteresis is reproducible by repeated thermal cycling with the magnetic field vector oriented perpendicular to each of the three crystal faces. The modified Curie–Weiss model[10] reveals change of the exchange interaction at $T_\downarrow$ from the high-temperature ferromagnetic regime I, phase **A** (80–290 K, Θ = 2.6(3) K, μ_{eff}, g = 1.743(3), 2.0126, $\chi_0 = -3.36(3) \times 10^{-4}$ cm^3/Cu-mol), to a low-temperature antiferromagnetic regime II, phase **C** (2–28 K, $\Theta = -0.467(15)$ K, μ_{eff}, g = 1.916(2), 2.2124, $\chi_0 = -1.0(4) \times 10^{-5}$ cm^3/Cu-mol), with hysteresis in the range 25–55 K. The two steps at $T_{\uparrow,1}$ and $T_{\uparrow,2}$ resolved on heating indicate that the one-step transition at $T_\downarrow$ on cooling from region I to region II involves two simultaneous processes. From the two steps on heating, the one at $T_{\uparrow,1}$ probably corresponds to switching of the exchange interaction of the antiferromagnetic phase **C** in region

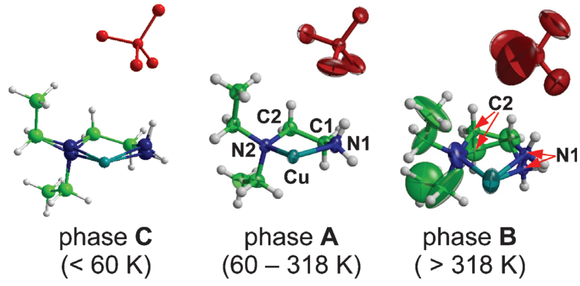

Fig. 1 Thermal ellipsoid plots of the half formula unit of (CuDED)$(\mathrm{ClO_4})_2$ in the ambient-temperature ordered (**A**) and high-temperature disordered (**B**) phases from single crystal diffraction data, and the suggested structure of the low-temperature/photoinduced phase (**C**). Each of the two disordered ring atoms in **B** is modelled with occupancies of 0.64/0.36 (C2) and 0.80/0.20 (N1).

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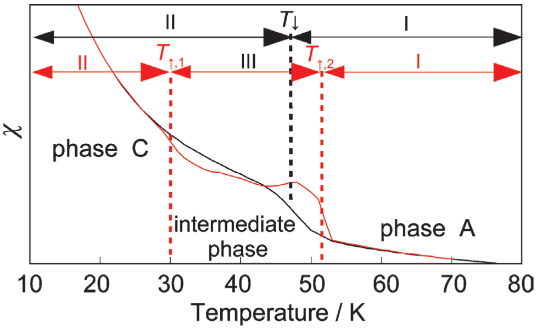

Fig. 2 Magnetic susceptibility (arbitrary units) recorded from a (CuDED)(ClO$_4$)$_2$ single crystal with the magnetic field vector approximately perpendicular to the {100} face (black line—cooling, red line—heating).

II to an intermediate phase in region III, which by structural change of the lattice at $T_{\uparrow,2}$ is transformed back to the lattice of **A** in region I.

Due to the combination of internal strain and weak electronic coupling along the one-dimensional cationic chains, it is expected that local perturbations of this structure in the region of bistability are feasible and that they might influence the long-range structural order. In order to test such an hypothesis, the effect of photoexcitation was examined with a specially designed system for temperature-controlled powder photodiffraction at laboratory scale (Fig. 3). Upon 365 nm flash-excitation of the ligand-to-metal charge transfer bands of (CuDED)(ClO$_4$)$_2$ (200–400 nm), the strong reflections shift 0.04° on average, most of them to higher 2Θ values, with various trends of the intensity change[2,3] and remarkable color change from bright orange to violet. The long time for data collection relative to the irradiation assured that the respective cell shrinkage is not due to heating effects but to the creation of a long-lived photoinduced groundstate. From the direction of the peak shift, the overall effect of the excitation on the lattice is analogous to cooling of the crystal. The temperature dependence of the photoinduced structural change, monitored by the position of the $(1\bar{1}0)$ reflection (Fig. 3) showed that the photoexcitation strongly affects the lattice on cooling within the hysteresis region III, where phase **C** and the intermediate phase exist on cooling and heating, respectively. From the magnitude of the shift, it is concluded that the largest structural change occurs at 45 K, right after the transition of **A** to **C** has been completed (Fig. 2). This is indication that the excitation induces transition from the low-temperature phase **C**, obtained *in situ* from cooled **A**, to the intermediate phase between **C** and **A**, close to the transition point. Excitation below 30 K is less effective and results in qualitatively different structural change, which was confirmed by comparison of the difference powder diffraction patterns in the 2Θ region of 5–60°. The photoinduced phase persists at 50 K, but it decays by thermal annealing to 300 K or by irradiation with visible light. Therefore, the diffraction experiments are conclusive that within and around the bistable region III, the photoexcitation significantly affects the crystal and electronic structure, particularly of the cationic centers. Detailed structural studies are now underway.

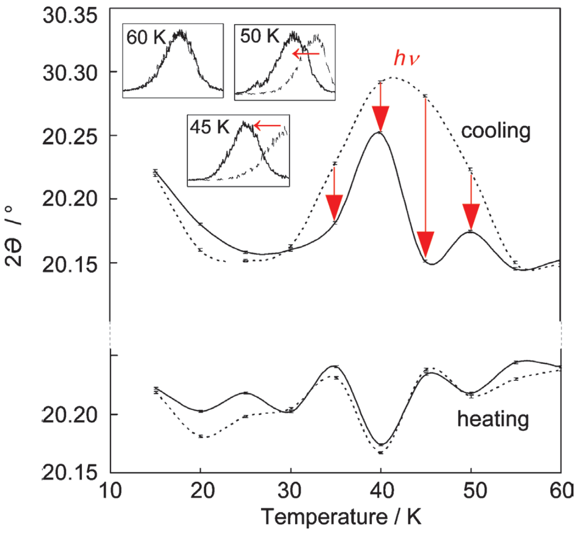

Fig. 3 Temperature profile of the position of the $(1\bar{1}0)$ reflection before (dotted line) and after (solid line) flash excitation with polychromatic UV light. The sample was excited at λ_{max} = 365 nm through bi-convex fused-silica lenses and quartz windows, with polychromatic output from high-pressure Hg lamp (SP-7, Ushio) and annealed at 300 K between the consecutive flashes. Inset: Shift of the $(1\bar{1}0)$ reflection. The arrows denote the direction of the peak shift.

In conclusion, the weakly electronically coupled planar pseudo-JT cations in the one-dimensional cationic chains of (CuDED)(ClO$_4$)$_2$ are subject to internal strain, balanced by a relatively strong, but moderately flexible ligand field. The lattice can withstand such strain only between 60 and 318 K; it collapses by applying external pressure, or by alteration of the internal pressure by heating/cooling out of this temperature range. Above 318 K, the strain is released by tetrahedral distortion of the valence orbital orientation, enhanced ring puckering, disorder of the side ligand chains and positional and rotational disorder of the counteranion. Below 60 K, switching of the exchange interaction in virgin single crystals occurs from ferromagnetic to antiferromagnetic regime, with hysteresis between 25 and 55 K. In the region of low-temperature bistability, the phase transition can also be induced by partial charge transfer in the excited state, which results in overall shrinkage of the lattice. The possibility of employing the interplay between the JT instability and the ligand field strain, determined by moderate flexibility of the primary coordination sphere, for triggering structural transitions by light, pressure and temperature, paves the way for design of new switching devices capable of multi-stimulus control.

Notes and references

† Magnetic susceptibilities, $\chi = M/H$, were measured with a SQUID magnetometer (Quantum Design, MPMS) between 2 and 300 K in an applied field of 10 kOe (1 Oe = $(10^3/4\pi)$ A m^{-1}). The temperature steps were 1 K between 2 and 100 K, and 5 K between 105 and 300 K. The heating/cooling rate was 10 K min^{-1} between the steps.

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9 No other anomaly was detected up to 300 K in the magnetization measurements.

10 The modified Curie–Weiss law of the form $\chi(T) = \chi_0 + \mu^2_{\mathrm{eff}} N_A (3k_B(T-\theta))^{-1}$ was used, where χ_0 is the temperature independent term, μ_{eff} is the effective magnetic moment, N_A is Avogadro's number, k_B is Boltzmann's constant, θ is the Weiss constant and g is the g-value. Heating/cooling rate: 10 K min^{-1}.