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TITLE: Optical Absorption Spectroscopy in the Metastable State SI of Na2[Fe[CN]5NO]-2H2O

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TITLE: Applications of Ferromagnetic and Optical Materials, Storage and Magnetoelectronics: Symposia Held in San Francisco, California, U.S.A. on April 16-20, 2001

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Mat. Res. Soc. Symp. Proc. Vol. 674 © 2001 Materials Research Society

Optical absorption spectroscopy in the metastable state SI of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$

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ABSTRACT

The metastable state SI in single crystals of orthorhombic $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ (sodiumnitroprusside, SNP) was investigated by absorption spectroscopy. The development of the spectra with increasing population of SI was monitored and a new band in the red spectral range was assigned to SI. By comparing with density functional theory (DFT) calculations we were able to assign the band to the electronic transition $2b_2 \rightarrow 7e$. In addition we found that very strong holographic light scattering influences the absorption spectra measured with light polarization along the a- or b-axis of the crystals.

INTRODUCTION

The metastable electronic states in single crystals of nitrosyl-compounds like $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ (sodiumnitroprusssside, SNP) are of fundamental interest because of their extremely long lifetime of $\tau > 10^8$s below characteristic decay temperatures and the reversibility of the excitation process [1]. They can be used for optical information storage with extremely high capacity by volume holography. The modulation of the refractive index is $\Delta n \geq 4 \cdot 10^{-2}$, which exceeds those of the well known photorefractive materials like doped $LiNbO_3$, $BaTiO_3$, $LiTaO_3$, $Sr_xBa_{1-x}Nb_2O_6$, etc. by at least two orders of magnitude.

In SNP two metastable states SI and SII can be excited by irradiation with light below characteristic decay temperatures of 198K and 147K, respectively. About 50% of the $[Fe(CN)_5NO]^{2-}$ anions can be transferred into SI with a light polarization perpendicular to the quasi four-fold axis N-C-Fe-N-O using a wavelength of 440-470nm. De-excitation into the ground state (GS) takes place by irradiation with light in the spectral range of 600-1200nm or by thermal heating over the decay temperatures, whereby illumination with light in the region of 900-1200nm transfers about 32% of the anions in SII and the rest into the ground state. In this article we will concentrate on the metastable state SI which we investigated systematically by absorption spectroscopy.

EXPERIMENT

Single crystals of orthorhombic sodiumnitroprusside, space group Pnnm [2] with four molecules per unit cell were grown from aqueous solution and cut perpendicular to the crystallographic axes. Specimens of dimension $20 \times 10 mm^2$ were ground to thickness between 0.3 and 0.05mm using a mixture of Al_2O_3 and propanol and finally etched with a mixture of water and propanol. They were mounted on a sample holder diving into a nitrogen-filled quartz-dewar.

The temperature was kept constant at 95K. The expanded beam of an Ar+ Laser (λ=476.5nm) strikes the sample perpendicular to the entrance face with an intensity of I_L=80mW/cm^2. In order to obtain the maximum population of 50% of SI a total exposure of $Q=I_Lt$=2500Ws/cm^2 has to be reached, the laser beam being polarized parallel to the crystallographic c-axis. The absorption spectra were measured with a two-beam spectrophotometer (Perkin-Elmer) equipped with a Glan-Thompson polarizer and a quartz-dewar. The wavelength resolution was about 4nm over the whole spectral range of 300-1200nm. Deconvolution of the spectra was done by fitting a sum of Gaussian curves to the corresponding electronic transitions together with a horizontal baseline because we have not made any corrections of the transmission by the reflection given through the refractive indices. Irradiation with a wavelength of λ=476.5nm produces simultaneously about 2% of SII and 45% of SI. By heating the crystal to T=150K the metastable state SII can be completely depopulated so that only absorption caused by the ground state and SI is measured.

RESULTS

Figure 1 shows the absorption spectra of the ground state in a b-cut of SNP at room temperature and at 95K for two different polarization directions of the probing light: $E\parallel c$-axis, $E\parallel a$-axis. Also indicated in Figure 1 is the deconvolution of the spectra with four Gaussian curves and a horizontal baseline. The fit parameters: position ν_{max}, area A and FWHM Γ of the Gaussian bands are summarized in Table I. Parallel to the crystallographic c-axis we can clearly see three transitions whereas along the a-axis the third band is visible only as a shoulder in the steep slope of the very strong fourth absorption band, over which we could not measure. We know from absorption spectra of solutions of SNP in H_2O at room temperature that there is a fourth band lying around 37000cm^{-1}. This transition was therefore constrained to values ν_{max} around 37000cm^{-1} in the fit varying only the width Γ and the area of the Gaussian. The width Γ stays within reasonable values around 4000cm^{-1} and therefore we can estimate its influence on the third transition with good accuracy. The third transition is considerably narrower than the others and shows strong temperature dependence in position and size. There exist several theoretical approaches to calculate the orbitals of the $[Fe(CN)_5NO]^{2-}$ anion: calculations based on an idealized ligand-field model [3], the MSXα-method [4] and density functional theory (DFT) [5], all of them using 4m (C_{4v}) symmetry. According to these calculations we made an assignment (notation after [3,5]) for the observed transitions as indicated in Figure 1 and Table I. The two transitions around 20000cm^{-1} and 25800cm^{-1} are allowed whereas the third transition

Table I. Electronic transitions of the ground state in SNP. Values ν_{max} [cm^{-1}] from theory for comparison.* $2b_2 \rightarrow 5a_1$ from [5] as in DFT calculations the $5a_1$ and $3b_1$ appear in inversed order compared to [3] and [4].

$E\parallel c$	ν_{max} [cm^{-1}]	A [cm^{-2}]	Γ [cm^{-1}]	ν_{max} [3]	ν_{max} [4]	ν_{max} [5]
$2b_2 \rightarrow 7e$	20190	0.32×10^6	3750	20540	21170	18490
$6e \rightarrow 7e$	25770	1.12×10^6	5420	25110	23360	22840
$2b_2 \rightarrow 3b_1$	31630	1.56×10^6	3330	33570	33230	36250*
$E\parallel a$	ν_{max} [cm^{-1}]	A [cm^{-2}]	Γ [cm^{-1}]			
$2b_2 \rightarrow 7e$	19790	0.16×10^6	3750			
$6e \rightarrow 7e$	25960	1.30×10^6	5060			
$2b_2 \rightarrow 3b_1$	31720	1.13×10^6	3360			

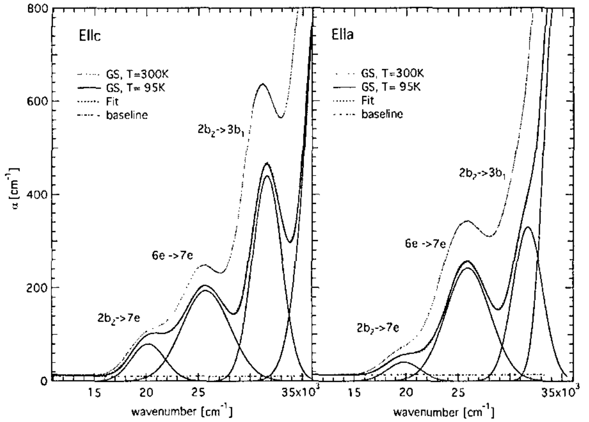

Figure 1. Polarized absorption spectra of SNP in the ground state at room temperature (dotted line) and at T=95K (full line) for polarization of the measuring light along c-axis (left) and a-axis (right) of the crystal. The fit to the 95K data (dashed line) consists of four Gaussians and a baseline (dash-dotted line). Results are given in Table I.

around 31700cm^{-1} is forbidden in 4m-symmetry. The selection rules for electronic transitions in the solid state can be overcome by coupling to phonons. The observed temperature dependence of the third transition can therefore be explained by the freezing of the phonons with decreasing temperature.

By irradiating the single crystals with laser light anions are transferred from the ground state into the metastable states, i.e. the absorption caused by the ground state decreases whereas new absorption bands from the new states appear. Figure 2 shows this process during the population of SI. We measured the absorption spectrum for several different total exposures Q. For the measurement with E||c we find two isosbestic points at 17800 cm^{-1} and 26700 cm^{-1}, i.e. at these wavenumbers the absorption coefficient α is independent of Q. Inside this interval only the ground state decreases whereas at lower and higher wavenumbers the new bands of SI appear. If only two states (the ground state and SI) are present this gives us the possibility to determine the population P_{SI} of the metastable state SI as a function of exposure Q because the decrease of the ground state must be transferred into the new state SI:

$$P_{SI}(Q)=\frac{n_{SI}}{n_{tot}}=\frac{n_{tot}-n_{GS}}{n_{tot}}=\frac{n_{GS}(Q=0)-n_{GS}(Q)}{n_{GS}(Q=0)}=\frac{\alpha_{GS}(Q=0)-\alpha_{GS}(Q)}{\alpha_{GS}(Q=0)} \qquad (1)$$

where n_{SI} and n_{GS} denote the number density of anions in the state SI and the ground state, respectively, and the relation $\alpha_{GS}=n_{GS}\cdot\sigma(\lambda)$ was used with $\sigma(\lambda)$ being the wavelength-dependent cross-section in the ground state. For the polarization of the probing light along the a-axis of the crystal we cannot detect any isosbestic points. Instead we observe an increase of the baseline over the whole spectral range and a very narrow band around 20000 cm $^{-1}$, which increases in size and changes its position with increasing exposure. Therefore from the absorption spectrum measured along the a-axis we cannot determine the population of SI, which we have to know to perform the deconvolution of the spectrum with Gaussian curves. This problem can be solved by first measuring along the c-axis and then after turning the polarizer by 90° measuring along the a-axis at the same population. Figure 3 shows the two spectra and their deconvolution for a population P_{SI} of SI of about 41%. We observed one new band in the red spectral range around 13200 cm^{-1}. The fitted parameters of this transition of SI are given in Table II.

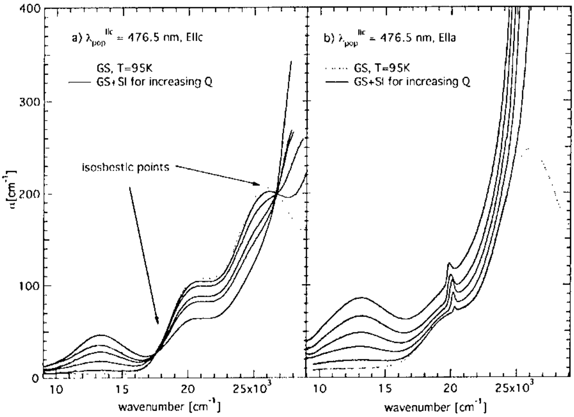

Figure 2. Absorption spectra for different populations of SI showing the two characteristic isosbestic points at 17800 cm^{-1} and 26700 cm^{-1} for E||c (a) and the increase of the baseline and the very narrow band at 20000cm^{-1} for E||a (b).

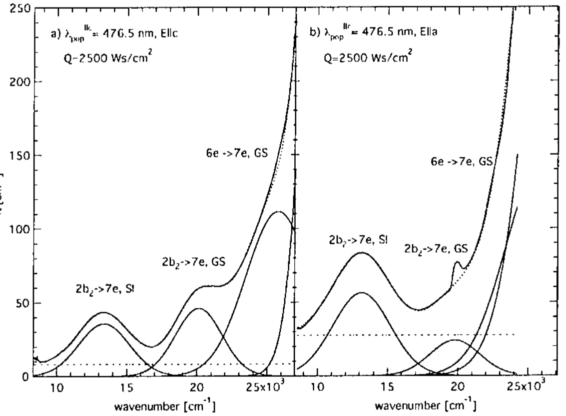

Figure 3. Spectra of a crystal populated to saturation showing the new band of SI in the red spectral range with E||c-axis (a) and E|| a-axis (b). The population of SI was determined from equation (1) to about 41%.

Table II. Electronic transitions of the metastable state SI in SNP for 41% population.

E‖c	ν_{max} [cm^{-1}]	A [cm^{-2}]	Γ [cm^{-1}]	ν_{max} [8]
$2b_2 \rightarrow 7e$	13430	0.11×10^6	4200	10160
E‖a	ν_{max} [cm^{-1}]	A [cm^{-2}]	Γ [cm^{-1}]	
$2b_2 \rightarrow 7e$	13180	0.28×10^6	4790	

In the literature the metastable state SI is explained by an elongation of the N-O-bond distances [6] or an inversion of the N-O-bond [7]. In the inversion model the ground state configuration Fe-N-O is inverted by 180° to Fe-O-N in SI. This model is also supported by DFT calculations [5], whereby the 4m-symmetry of the $[Fe(CN)_5NO]^{2-}$ anion is conserved. Since the symmetry of SI is the same as in the ground state we can use the same assignments for the transitions. We tentatively assign the absorption band to the $2b_2 \rightarrow 7e$ transition, assuming that the transition is shifted to the red compared to the ground state, i.e. the 7e orbital is lowered in energy as proposed by DFT [8].

We consider now the origin of the increasing baseline and the narrow extinction band in the spectra measured along the a-axis of the crystals. By illuminating single crystals of SNP with laser light, one writes parasitic holographic gratings into the crystals [10]. The probing light is diffracted at these gratings. Due to the distance between sample and detector the cone of the diffracted light is wider than the area of the detector. Therefore parts of the diffracted light miss the detector, which appears in the spectra as a further extinction. This leads to the increase of the baseline over the whole spectral range with increasing population of SI. The narrow band even shows dynamic behavior. It changes its position as a function of exposure until a saturation value is reached (see Figure 4). We can fit this behavior with the following function, which is typical for the population dynamics of the metastable states:

$$\nu(Q) = \nu_0 + B(1 - e^{-\frac{Q}{Q_0}}) \qquad (2)$$

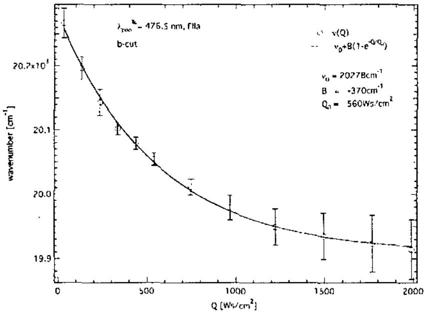

Figure 4. Position of the narrow band in the absorption spectra measured parallel to a-axis of crystal as a function of the exposure. The full line is the fit using equation (2) and yielding the indicated parameters.

The fit yields ν_0=20278cm^{-1}, B=-370cm^{-1}, Q_0=560Ws/cm^2 and with I_L=80mW/cm^2 we get τ=7000s. These values are in reasonable agreement with measurements of Q_0 by differential scanning calorimetry [10].

CONCLUSION

We found four electronic transitions in the ground state and one transition of the metastable state SI using polarized absorption spectroscopy on single crystals of SNP. We assigned them to the corresponding orbitals by using group theoretical arguments and by comparing them with DFT calculations. During population of the metastable state SI we observed two isosbestic points. They appear only for the measurement along the c-axis of the crystals and allow us to determine the population of SI directly from the absorption measurement. These isosbestic points indicate also the spectral range where the population of the metastable states is possible as no absorption bands of SI appear between them. Therefore the absorption measurements allow finding the optimal wavelength for populating the metastable states. The measurements with the electric field vector of the probing light along the a-axis revealed an increase of the baseline over the whole spectral range and a narrow extinction band connected with the population of SI. The same band has first been observed by Morioka [11] in a crystallographic c-cut, and is explained by optical activity of SNP in the metastable state SI. Contrary to this explanation we attribute this extinction to the diffraction of the probing light on written parasitic holographic gratings (optical damage). As the refractive index changes with increasing population of SI, the wavelength fulfilling the Bragg-condition for readout of these gratings changes correspondingly, leading to the observed shift of the narrow extinction band. A detailed description of this phenomenon will be given in a forthcoming paper [12].

ACKNOWLEDGEMENTS

Financial support by the Swiss National Science Foundation, grant NF21-57084.99, is gratefully acknowledged.

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