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1989 J. Phys.: Condens. Matter 1 4251

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LETTER TO THE EDITOR

Evidence of a new first-order phase transition at 92 K in $((\text{CH}_3)_4\text{N})_2\text{MnCl}_4$ single crystals

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Received 25 April 1989

Abstract. A new first-order phase transition at $T = 92$ K has been detected in single crystals of $((\text{CH}_3)_4\text{N})_2\text{MnCl}_4$ by means of several optical techniques. The phase transition displays a large thermal hysteresis, $\Delta T = 12$ K. Coexistence of phases below 92 K is also detected. The sensitivity of the optical absorption of the crystal, as well as that of emission, excitation and lifetime of MnCl_4^{2-} units for detecting this phase transition is analysed in detail. The results are also compared with those corresponding to the $\text{P}112_1/n$ – $\text{P}12_1/c1$ phase transition at $T = 171$ K.

$(\text{TMA})_2\text{MnCl}_4$ crystals with $\text{TMA} \equiv \text{N}(\text{CH}_3)_4$ (tetramethylamide ion) belong to the family of compounds whose general formula is $(\text{TMA})_2\text{XCl}_4$ ($\text{X} \equiv \text{Fe}, \text{Co}, \text{Zn}, \text{Mn}$). All of them display the same orthorhombic $\text{Pm}cn$ crystallographic structure at high temperatures. At atmospheric pressure, each crystal undergoes a different sequence of structural phase transitions when the temperature is varied. In the case of $(\text{TMA})_2\text{MnCl}_4$ single crystals, this sequence is known to be [1, 2]:

Phase I (Orthorhombic $\text{Pm}cn$)–292.6 K–II (Incommensurate)–292.3 K–III (Monoclinic $\text{P}2_1/c1$) 268.65 K–IV (Monoclinic $\text{P}112_1/n$)–175.63 K–V (Monoclinic $\text{P}12_1/c1$).

These phase transition temperatures were recently obtained by Zubillaga and co-workers through calorimetric measurements [3].

The increasing interest excited by this family of crystals lies in the existence of some common mechanism which accounts for the different phase transition sequences. In fact, their transition temperatures as well as their dependence upon hydrostatic pressure can be represented in a common PT phase diagram in which the pressure associated with a given crystal appears to increase as the divalent ionic radius of the substitutional cation decreases [4, 5]. A large number of experiments have been done at different temperatures and applied hydrostatic pressures in order to construct this phase diagram as well as to elucidate the nature of such transition sequences. The experimental techniques which have been used most widely in these studies are x-ray diffraction, NMR, calorimetric, birefringence and dielectric measurements ([3–8] and references therein).

The present work investigates the sensitivity of several optical techniques for detecting phase transitions in $(\text{TMA})_2\text{MnCl}_4$ crystals in the temperature range 10–200 K. Two types of measurements have been carried out. A first set includes optical absorption (OA), excitation, emission and lifetime spectra which are very sensitive for detecting local changes in the neighbourhood of Mn^{2+} ions [9]. A second, more macroscopic type,

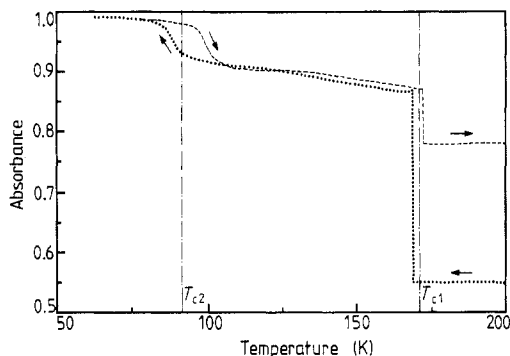


Figure 1. Temperature dependence of the absorbance at $\lambda = 500$ nm of $(\text{TMA})_2\text{MnCl}_4$ in the range 50–200 K. The cooling (\cdots) and heating ($---$) runs were obtained at a constant rate of 1 K min^{-1} . The two transition temperatures marked are $T_{c1} = 171$ K and $T_{c2} = 92$ K. Crystal pathlength: 0.75 mm.

consists of monitoring the variations undergone by the absorbance at a given wavelength as a function of the temperature. This type of measurement is useful for exploring the changes induced by light scattering processes at critical temperatures due to the multidomain structure. In particular, it has been successfully employed in the same way to determine the phase transition temperatures in mixed ammonium halide crystals $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$ [10] as well as in double mixed-alkali halide cyanide crystals $\text{KBr}_{1-x}\text{KCN}_x$ [11].

An important result of the present research is the clear evidence of a *new* first-order phase transition at 92 K in $(\text{TMA})_2\text{MnCl}_4$ single crystals. The existence and character of such a transition were not well established by earlier calorimetric measurements [3]. Throughout this Letter, we compare the experimental results concerning this new phase transition with those obtained for the IV–V phase transition at $T_{c1} = 171$ K. A tentative explanation is proposed for the lack of clear evidence of this new transition at 92 K from calorimetric measurements.

Single crystals of $(\text{TMA})_2\text{MnCl}_4$ were grown by slow evaporation of an acidic aqueous solution ($\text{pH} \sim 3$) containing the appropriate stoichiometric amounts of $\text{N}(\text{CH}_3)_4\text{Cl}$ and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ at about 30°C . The high-temperature *Pm $\bar{c}n$* space group of these crystals was checked by x-ray powder diffractometry. Single crystals of good optical quality polished perpendicular to the *c* axis were employed in the experiments. Optical absorption spectra were carried out on a Lambda 9 spectrophotometer using both natural and polarised light. Excitation, emission and lifetime spectra were obtained from a JY3D Jobin Yvon spectrofluorimeter adapted for lifetime measurements and data acquisition through a HP 89640 A analogue input card attached to a HP Series 300 microcomputer. The lifetime parameter was obtained from the emission decay curves by means of least-squares fitting to a single exponential function. Every emission decay curve was averaged 300 times in order to improve sensitivity in the determination of the lifetime parameter. Temperature variations were accomplished by means of a Scientific Instruments DE-202 closed cycle cryostat. The temperature was stabilised to within 0.05 K with a APD-K temperature controller, the absolute temperature accuracy being ± 0.5 K.

Figure 1 shows the variation of the absorbance at $\lambda = 500$ nm as a function of the temperature in the range 50–200 K for $(\text{TMA})_2\text{MnCl}_4$ single crystals. Both the heating and cooling rates were 1 K min^{-1} . Inspection of this figure reveals the existence of two phase transitions at $T_{c1} = 171$ K and $T_{c2} = 92$ K. The abrupt changes in the absorbance $\Delta A = 0.315$ at $T_{c1C} = 169$ K upon cooling (C) and $\Delta A = 0.088$ at $T_{c1H} = 173$ K upon heating (H) correspond to the well known IV–V phase transition. Such a large increase in the absorbance at 169 K is not explained in terms of crystal reflectance by changes in

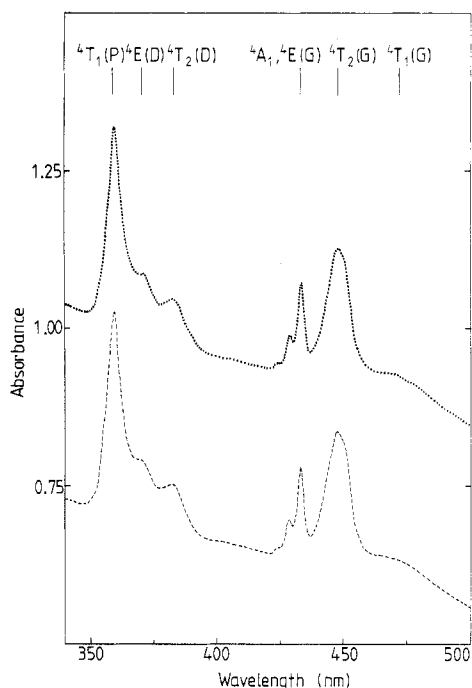


Figure 2. Optical absorption spectra of $(\text{TMA})_2\text{MnCl}_4$ obtained just before (----, $T = 170$ K) and after (\cdots , $T = 168$ K) the IV \rightarrow V phase transition temperature $T_{\text{c1C}} = 169$ K (cooling run). Crystal field peaks of MnCl_4^{2-} complexes are labelled according to the irreducible representations of tetrahedral point group symmetry. Crystal pathlength: 0.75 mm.

the birefringence but has been attributed, as we discuss below, to multidomain formation in phase V. The thermal hysteresis $\Delta T_{\text{c1}} = 4$ K is near the 5 K reported in [5] through dielectric measurements. The fact that the absorbance values do not coincide above 173 K is an indication of the different domain structure in phase IV after cycling. Around $T_{\text{c2}} = 92$ K, the absorbance depicts a hysteresis loop characteristic of a first-order transition. The corresponding thermal hysteresis $\Delta T_{\text{c2}} = 12 \pm 2$ K is the largest of all the different phase transitions which take place in $(\text{TMA})_2\text{MnCl}_4$ [3, 5].

The existence of this new phase transition at $T_{\text{c2}} = 92$ K is also confirmed by the variations in the lifetime and emission spectra of Mn^{2+} . At this point, it is worth noting that the emission band associated with the ${}^4\text{T}_1(\text{G}) \rightarrow {}^6\text{A}_1(\text{S})$ crystal field transition of the MnCl_4^{2-} tetrahedral complexes, which is responsible for the green luminescence characteristic of the MnCl_4 compounds, is much more sensitive for detecting the phase transitions than the Mn^{2+} crystal field bands observed through the OA spectra. This fact is clearly seen by comparing the experimental results of figures 2 and 3. The OA spectra of $(\text{TMA})_2\text{MnCl}_4$ obtained just before and after the IV \rightarrow V phase transition temperature $T_{\text{c1C}} = 169$ K (figure 2) are the same within our experimental resolution. Neither the peak positions nor the intensities of the crystal field spectrum seem to 'feel' this phase transition. The same thing is observed for the new transition at $T_{\text{c2}} = 92$ K. The sole modification is the abrupt increase in the absorbance background throughout the whole wavelength range, as was pointed out in figure 1. At variance with this result is the corresponding emission band, which undergoes an important shift $\Delta E = 145$ cm^{-1} on passing the IV–V phase transition (figure 3). This demonstrates that the emission peak which involves the *relaxed* excited ${}^4\text{T}_1(\text{G})$ electronic state is more sensitive to local changes around Mn^{2+} , even those outside the first Cl^- coordination sphere, than the absorption peak involving a transition from the ${}^6\text{A}_1(\text{S})$ ground state to the *unrelaxed*

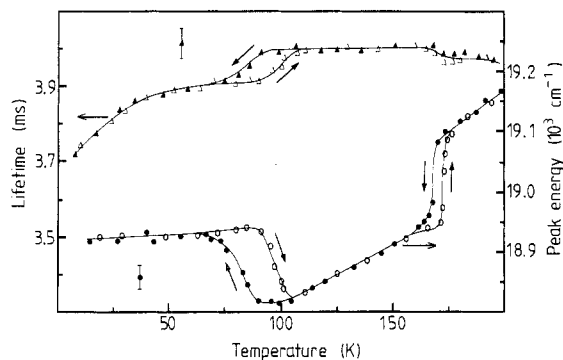


Figure 3. Evolution of the ${}^4T_1(G) \rightarrow {}^6A_1(S)$ Mn^{2+} emission peak energy (\bullet , cooling; \circ , heating) and the lifetime parameter, τ , (\blacktriangle , cooling; \triangle , heating) of $(TMA)_2MnCl_4$ in the temperature range 10–200 K. Full curves are drawn as a guide to the eye. Excitation wavelength $\lambda = 355$ nm. Errors in lifetime and peak energy are ± 0.05 ms and ± 20 cm^{-1} , respectively.

${}^4T_1(G)$ state. This type of influence on the emission band has been previously suggested by Presser and co-workers through Mn^{2+} emission lifetime measurements in $(Bu_4N)_2MnCl_4$ single crystals [12]. Thus, the emission band of Mn^{2+} appears to be a sensitive probe for detecting phase transitions in these crystals. The results in figures 2 and 3 are clear examples of this. Two hysteresis loops appear in the emission peak curves of figure 3 in the 10–200 K range. The first one at $T_{c1C} = 169$ K (cooling run) and $T_{c1H} = 173$ K (heating run) with $\Delta E = 145$ cm^{-1} corresponds to the IV–V phase transition, while the second one at $T_{c2} = 92$ K displaying a thermal hysteresis of $\Delta E = 130$ cm^{-1} and $\Delta T_{c2} = 12 \pm 3$ K, confirms the existence of a new phase transition in $(TMA)_2MnCl_4$ crystals. In the same figure, this new phase transition is also seen through lifetime measurements. Although this parameter is less sensitive than the emission peak position, the lifetime also undergoes a small hysteresis loop $\Delta\tau \approx 0.1$ ms at $T_{c2} = 92$ K which is not well detected in the IV–V phase transition at $T_{c1} = 171$ K.

An interesting result is also provided by the evolution of the emission intensity. The intensity versus temperature curve (not shown here) shows essentially the same behaviour of the absorbance of figure 1. The changes in the emission intensity at the phase transition temperatures T_{c1} and T_{c2} do not correspond to analogous changes either in the ${}^6A_1(S) \rightarrow {}^4T_1(G)$ transition oscillator strength or in the emission lifetime as discussed above. This resemblance between the absorbance and the emission intensity behaviours clearly indicates that the changes induced in both parameters at phase transitions should be attributed to the light scattering due to the multidomain structure. This allows one to explain why the emission intensity increases when the crystal transmittance decreases. Light scattering from domains would provide a longer effective pathlength for the excitation light leading to a greater number of photo-excited Mn^{2+} ions and, thus, to an increase in the luminescence intensity. The latter point has been confirmed by analysing the crystal field excitation spectra obtained under the same experimental conditions as the OA spectra of figure 2. Crystal field bands in the excitation spectrum duplicate their intensities on passing the IV \rightarrow V phase transition temperature in the same way as the emission intensity does. This result clearly indicates that all the luminescence intensity arises from the photo-excited Mn^{2+} , excluding other possibilities

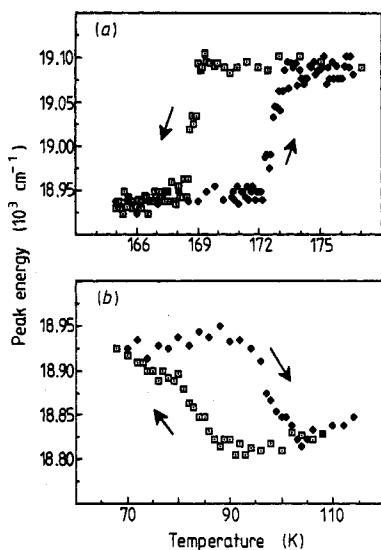


Figure 4. Variation of the Mn²⁺ emission peak energy around the phase transition temperatures: (a) $T_{c1} = 171$ K, and (b) $T_{c2} = 92$ K. The hysteresis cycles are expanded for clarity. The hysteresis temperatures are $\Delta T_{c1} = 4$ K and $\Delta T_{c2} = 12$ K. In both the cooling (\square) and heating (\bullet) runs, the temperature was changed in steps of 0.1 K at a rate of 0.3 K h⁻¹ for the transition at $T_{c1} = 171$ K, and steps of 1 K at a rate of 3 K h⁻¹ for that at $T_{c2} = 92$ K. Excitation wavelength $\lambda = 355$ nm.

such as energy transfer from impurities to Mn²⁺ or even emission from the impurities themselves.

It is worth noting here that at variance with the phase transition at $T_{c1} = 171$ K, no abrupt changes are observed either in the absorbance or in the emission peak positions for the new phase transition at $T_{c2} = 92$ K. A better insight into this behaviour is provided by figure 4 where both hysteresis loops are expanded in detail. Furthermore, while the temperature hysteresis for the new phase transition is always $\Delta T_{c2} = 12 \pm 3$ K, the corresponding hystereses in both the emission peak energy, ΔE , and the absorbance, ΔA , change upon successive heating-cooling cycles (the departure temperature always being $T = 300$ K). This behaviour has been attributed to the sluggish character of this new transition. Depending on the domain structure and the thermal history of the sample, each domain could 'feel' this new phase transition at a different temperature and some might even 'miss' it. In such conditions, we could explain not only the continuous variation of the optical parameters along the new phase transition at $T_{c2} = 92$ K but also the different hysteresis ΔE and ΔA observed after successive cycles.

The latter point, in particular the position of the emission peak which is sensitive to the crystallographic structure of the crystal but not to the domain pattern, probably reflects the coexistence of phases below $T_{c2} = 92$ K. A similar result has recently been found in single crystals of Cu²⁺-doped NH₄Br following the evolution of the charge transfer bands of the (NH₃)₂Br₄Cu²⁻ complex along the tetragonal-to-cubic phase transition at $T_c = 78$ K [13].

With the present results, we are able to explain qualitatively why this new phase transition at 92 K has not been clearly seen through previous calorimetric measurements [3]. Besides the particular values of the thermodynamic functions, the specific heat peak associated with this new phase transition should be reduced and spread out respectively by the coexistence of phases and the large temperature interval $\Delta T = 12$ K over which this transition takes place and therefore it may be observed as a broad hump or shoulder in the specific heat curve. In any case, recent calorimetric measurements support the existence of this new phase transition [14].

Though we have no evidence about the crystallographic structure of the new phase below 92 K, we tentatively suggest that this phase could belong to the orthorhombic $P2_12_12_1$ in clear analogy to the phase transitions observed in both $(TMA)_2CoCl_4$ and $(TMA)_2ZnCl_4$ crystals of the same family at $T = 122$ K [6] and $T = 161$ K [7] respectively, both corresponding to the monoclinic $P12_1/c1$ –orthorhombic $P2_12_12_1$ phase transition.

As a final remark, we would like to emphasise the usefulness of these optical techniques not only for detecting the phase transition temperatures but also for providing evidence about multidomain formation and the changes induced in the vicinity of the optically active cations. Further work is in progress in order to investigate the phase transitions over the whole temperature range 10–300 K using optical techniques.

The authors thank A G Breñosa for kindly growing the crystals and Professor M Moreno for the critical reading of the manuscript. We are also grateful to Professor A López Echarri for useful information and discussions. This work has been supported by the CICYT project No PB86-0304.

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