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ENERGY TRANSFER BY EXCITON-POLARONS IN $RbMnF_3$

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Energy transfer in $RbMnF_3$ was studied by time-resolved spectroscopy of the $^4T_{1g}$-exciton luminescence. The threefold orbital degeneracy of the $^4T_{1g}$-state is lifted by a Jahn–Teller coupling to e_g-modes. The JT-effect leaves an orientational degeneracy of distorted MnF_6-octahedra, which is lifted by application of uniaxial stress. The dynamics of exciton and trap luminescence after pulse excitation was investigated with and without stress. It was found that stress reduces the excitonic transfer rate considerably. The most striking effect was obtained with [110]-stress which produced a very slow nonexponential decay of the exciton luminescence. This behavior was interpreted as evidence for [110]-stress induced 2-dimensional energy transfer.

1. Introduction

The present paper reports on a study of energy transfer by $^4T_{1g}$-excitons in $RbMnF_3$. This substance, which crystallizes in the cubic perovskite structure (fig. 1), undergoes an antiferromagnetic transition at $T_N = 83$ K, but the structure remains cubic down to LHeT. The weak absorptions in the visible correspond to intra-ionic transitions of Mn^{2+}, such as $^6A_{1g} \rightarrow {}^4T_{1g}$, $^4T_{2g}$ etc., which are parity- and spin-forbidden and give the crystals a pink color [1]. We studied the exciton line in the zero-phonon spectrum of the $^4T_{1g} \rightarrow {}^6A_{1g}$-luminescence band. The zero-phonon and zero-magnon transition energy at LHeT is 18232 cm^{-1}, the radiative lifetime $\tau = 60$ ms. Whereas [001]- and [110]-stress shifts and splits the exciton band, [111]-stress causes only a shift (fig. 2). These observations suggest that the threefold degeneracy of the $^4T_{1g}$-states is lifted by a Jahn–Teller coupling with the twofold degenerate local ϵ_g-vibrations Q_θ and Q_ϵ [1–3]. However, without an applied stress the Jahn–Teller effect (JTE) leaves an orientational degeneracy of distorted MnF_6-octahedra. The x-, y- and z-orientation of the distortion axis are equally probable. Application of stress lifts this degeneracy. [001]-stress leaves the $^4T_{1g}^{x,y}$-orbitals as lowest lying states which are coupled with an x- and y-distortion of the MnF_6-octahedra correspondingly. [110]-strain, on the other hand, leaves the $^4T_{1g}^{z}$-orbital as lowest state connected with a dilatation of the z-axis [1].

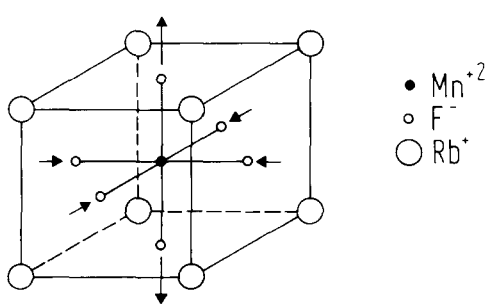

Fig. 1. The lattice cell of $RbMnF_3$. The arrows indicate the distortion by the Jahn–Teller effect. Without stress the distortion axes are equally distributed along all 3 4-fold axes of the cubic crystal.

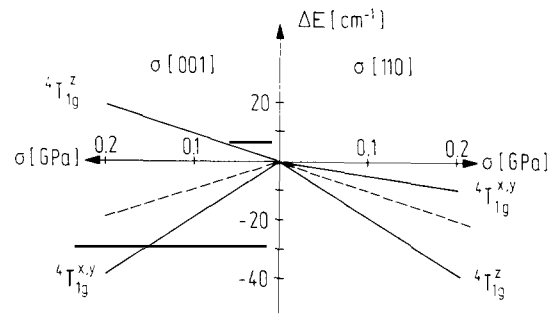

Fig. 2. The splitting of $^4T_{1g}$-states by uniaxial compressive stress. Spin–orbit coupling is neglected.

We suggest in such systems energy transfer via small exciton-polarons. However in contrast to the ordinary coupling to fully symmetrical lattice modes we have to consider coupling to the symmetry breaking ϵ_g-modes [4]. The excitonic lifetime is limited by energy transfer to traps. We investigated the transfer by time resolved measurements of exciton luminescence. Uniaxial stress is applied to lift the orbital degeneracy. Thus we are able to investigate distinct transfer channels. Moreover we recorded the luminescence of shallow traps 27 cm^{-1} (G-line) and 123 cm^{-1} (R-line) below the intrinsic exciton emission [5] and measured the corresponding rise time. This gave us a second independent way of probing the exciton-polaron transfer.

2. Experimental

We used two samples of size $1.3 \times 1.3 \times 6.0$ mm^3. One was cleaved along (100)-planes to be used for [001]-stress experiments, the other was cut along (110)-planes and polished to be used for [110]-stress. In order to guarantee approximately equal impurity concentration the two samples were prepared from the same single crystal. They

were vertically mounted in a combined bath-gasflow cryostat. The sample temperature was measured with a carbon resistor with an accuracy of ± 0.05 K at 4.2 K. A torsion free compressional stress was applied to the sample.

The excitation source was a dye laser pumped by an excimer laser. The dye laser was operated with Coumarin 153 at 553 nm. The laser pulses have a duration of 10 ns, an energy of 10 mJ and a repetition rate of 3 Hz. In order to avoid nonlinear effects the laser beam was expanded to 3 mm diameter. The luminescence was focussed on the slit of a 1 m-monochromator and detected by a cooled photomultiplier which was inactivated during the laser pulse. The photomultiplier signal was fed into a conventional photon counting system and the amplified pulses were stored time-selectively in a multichannel analyser.

We used the phonon sideband of the $^4T_{1g}$-absorption to excite the intrinsic exciton since resonant excitation has proved to be too inefficient.

3. Results

The data presented in this paper were all obtained at a temperature of 1.4 K. Figure 3 shows the integrated intensity of the intrinsic exciton luminescence. The decay at zero stress and with [001]-compressional-stress is purely exponential with a decay time of 50 and 170 μs, respectively. However, when [110]-stress is applied the decay is very slow and has a nonexponential characteristic. The rise of the impurity luminescence from R-traps (fig. 4) which are obviously fed by excitonic energy transfer shows a close correspondence to the excitonic decay: a fast rise at zero stress, a slower rise with [001]-stress and a very slow rise with [110]-stress. We have selected here only those results obtained with a comparatively high stress of 0.165 GPa. Under these conditions the spin and orbital momenta are completely decoupled and the excited state wavefunctions, $^4T_{1g}^x$, $^4T_{1g}^y$ and $^4T_{1g}^z$ are the correct eigenfunctions.

4. Discussion

It is evident from the experiments that the dynamics of exciton and trap emission are determined by radiative decay and by transfer to traps. Actually the total transfer rate to traps, K, was always found to be much larger than the radiative decay rate $1/\tau$. Under the conditions of exponential decay the emission intensity of the exciton is given by

$$I(t) = I_0 \exp(-t/\tau - Kt) , \tag{1}$$

where

$$K = \sum_i K_i . \tag{2}$$

The sum runs over various types of traps. Eq. (1) has been applied to evaluate K from experiments with stress free crystals and with applied [001]-stress (table 1). 110]-stress, however, induces a nonexponential decay and the simple description cannot be applied. The value of K given in table 1 for this case was obtained from the measured $I(t)$-curve which was empirically extrapolated to large times. Then K was determined from an average decay time by

$$\langle \tau \rangle = K^{-1} = \int_0^\infty I(t)t\,\mathrm{d}t / \int_0^\infty I(t)\mathrm{d}t . \tag{3}$$

A more general treatment of energy transfer is achieved by a random walk model with nearest neighbor transfer. The decay is given in the general case by

$$I(t) = I_0 \exp(-t/\tau)\Phi(t) \tag{4}$$

$\Phi(t)$ is the probability of survival after a time t and only for special cases it is an exponential. We used computer simulations to obtain $\Phi(t)$. For that purpose we constructed a lattice with 40^3 lattice sites and let the excita-

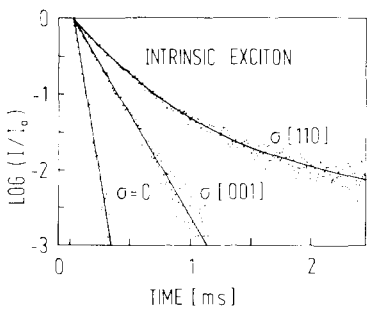

Fig. 3. The decay of intrinsic exciton luminescence $I(t)$ after pulse excitation at 553 nm.

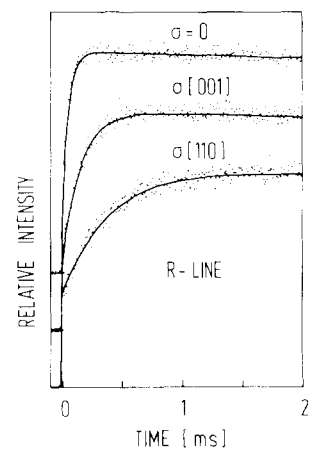

Fig. 4. The rise of shallow trap luminescence after pulse excitation at 553 nm.

Table 1
Transfer rates obtained with eqs. (1) and (3) from measurements of fig. 3

	$\sigma = 0$	$\sigma[001] = 0.165$ GPa	$\sigma[110] = 0.165$ GPa
K	20 840 s^{-1}	5 921 s^{-1}	2 267 s^{-1}

tion move on the lattice in a random walk process connecting nearest neighbors only. A trap concentration of 1% was assumed. The trapping time was obtained by averaging the walk of 10^4 excitations. In order to simulate the effect of uniaxial stress we introduced an anisotropy of nearest neighbor transfer rates. Let us denote the transfer rate to one of the 4 nearest neighbors in the (001)-plane by W_{xy} and that to one of the 8 neighbors outside this plane by W_x. In cubic symmetry $W_z = W_{xy}$. The computer simulations give for this case an exponential decay. The introduction of a weak anisotropy does not change this result. However, if the random walk is essentially 2-dimensional, i.e. if $W_z/W_{xy} \leqslant 10^{-2}$ the decay becomes slow and follows a nonexponential time dependence. From these results we may conclude that the transfer under [110]-stress is indeed 2-dimensional. In the other limiting case $W_z/W_{xy} \gg 1$ the simulation reproduces the [001]-stress experiments quite well. Analytic methods lead to a similar conclusion [6,7].

It is interesting to discuss the condition of maximum transfer in terms of excited state wavefunctions. As shown in fig. 2 [110]-stress splits the $^4T_{1g}$-levels and leaves a $^4T_{1g}^{\bar{z}}$-state as lowest level. A 2-dimensional transfer under [110]-stress means that $W_z = 0$, therefore transfer is only possible between ions in a (001)-plane. In this case the $^4T_{1g}^{\bar{z}}$-wavefunctions have the maximum overlap. (Note that the maximum charge density of the $^4T_{1g}^{\bar{z}}$-state is in the (001)-plane.) The situation is different for [001]-stress. In this case the lowest states are $^4T_{1g}^{x}$ and $^4T_{1g}^{y}$, and transfer is always possible between ions which share the (100)- or the (010)-plane. The transfer, therefore, is clearly 3-dimensional.

Unfortunately the computer simulation does not explain the relatively large transfer rate at zero stress. The correct wave functions for this case are spin orbitals which are eigenfunctions of the spin orbit coupling. Application of stress demixes these linear combinations leaving the orbitals $^4T_{1g}^{i}$ mentioned above.

5. Summary and conclusion

We analysed the dynamics of exciton- and trap-luminescence in $RbMnF_3$. The lifetime was found to be dominated by transfer to traps. The free exciton luminescence exhibits an exponential decay. This decay is slower under [001]-stress but still exponential. However, [110]-stress induces a very slow nonexponential decay which is interpreted as the consequence of a 2-dimensional energy transfer to traps. A microscopic model has to consider the Jahn–Teller effect and the $^4T_{1g}$-sublevel splitting under stress. Transfer under [110]-stress is mediated by the orbital singlet state $^4T_{1g}^{\bar{z}}$. We require that nearest neighbor transfer is only possible between those Mn^{2+}-ions with maximum overlap of $^4T_{1g}^{\bar{z}}$-states. The restriction is plausible concerning the symmetry of the charge distribution. It confines the energy transfer to (001)-planes.

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