Negative magnetic circular polarization in the emission of Jahn-Teller systems

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The magnetic circular polarization of the high-energy emission of Tl^+ phosphors under excitation in the A band has been measured at low temperature as a function of field intensity. The effect, which exhibits an opposite sign with respect to the results previously obtained in the low-energy emission band or with similar monovalent impurities, is accounted for by a double-minimum Jahn-Teller model.

Zeeman-effect measurements on the emission of Tl^+-like impurities in alkali halides were performed at low temperature by Fukuda *et al.*[1] and revealed strong magnetic circular polarization (MCP) in both high-energy (A_T) and low-energy (A_X) emission bands (in the case of KI:Ga the MCP degree is about 80% with a field intensity of 4.2 T). These results were well interpreted on the basis of a model[2] which predicts the coexistence of nonequivalent Jahn-Teller minima with suitable degeneracy and symmetry on the relaxed excited states of the impurity.[3]

Till now, as far as we are aware, the only existing results on the emission of Tl^+ were those of Fontana and Davis[4] who measured, with excitation in the D band, a relatively high degree of circular polarization in the A_X band of KI:Tl ($\sim$ 14% with a field intensity of 2.3 T), while a negligible effect was observed in the A_T band. This suggests that in the case of Tl^+ a different level scheme should be adopted.

In this paper we report the results of a systematic investigation on the A_T emission of Tl^+ phosphors and their interpretation on the basis of a double-minimum potential that, although fitting in the framework of the coexistence model, is directly connected with a previous simplified analysis.[5]

Samples of KI:Tl, KBr:Tl, and KCl:Tl (with thallium concentration in the range 10^{-4}–10^{-2} mol %) were placed in the bore of a superconducting coil ($\vec{H} \parallel [001]$) immersed in liquid helium. The temperature was lowered below the λ point ($\sim$2 K) by pumping over the helium reservoir in order to avoid the boiling which introduces strong noise in the signal. The samples were single crystals supplied by K. Korth (Germany) or grown by our Kyropoulos apparatus. The phosphors were excited in the A band with a 150-W xenon lamp through a monochromator and an interference filter. The emitted light was viewed along the magnetic field axis and analyzed for its left (I_-) and right (I_+) circular polarization by an electro-optic light modulator. The light was then collected through a monochromator by a photomultiplier whose output was sent to a lock-in amplifier.

A typical MCP signal ($I_+ - I_-$) obtained with the KI:Tl in a field $H \simeq 5$ T is shown in Fig. 1 together with the emission spectrum ($I = I_+ + I_-$). This signal corresponds in the A_T band (340 nm) to a negative zero-moment change, while in the A_X band (420 nm) to a positive zero-moment change; a variation in the first moment of the A_T band is also seen.

The field dependence of the degree of MCP [$P_c = (I_+ - I_-)/I$] of A_T emission in KI:Tl (340 nm), KCl:Tl (300 nm), and KBr:Tl (310 nm) is reported in Fig. 2 after the spurious effects, likely due to the apparatus, have been compensated. This has been accomplished by fitting each experimental set of data

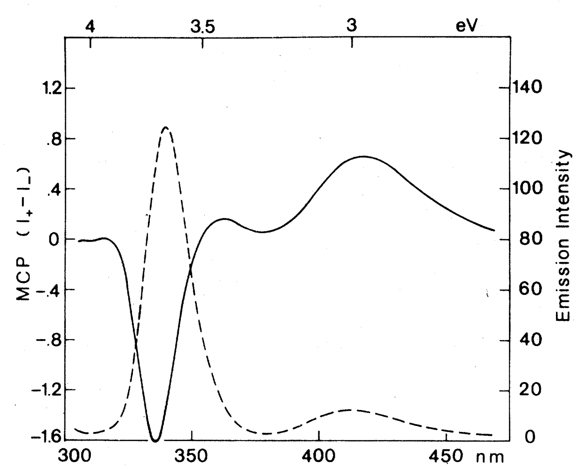

FIG. 1 MCP signal (solid line) and emission intensity (dashed line) vs wavelength of KI:Tl at 2 K with a magnetic field intensity of 5 T and excitation at 2820 Å.

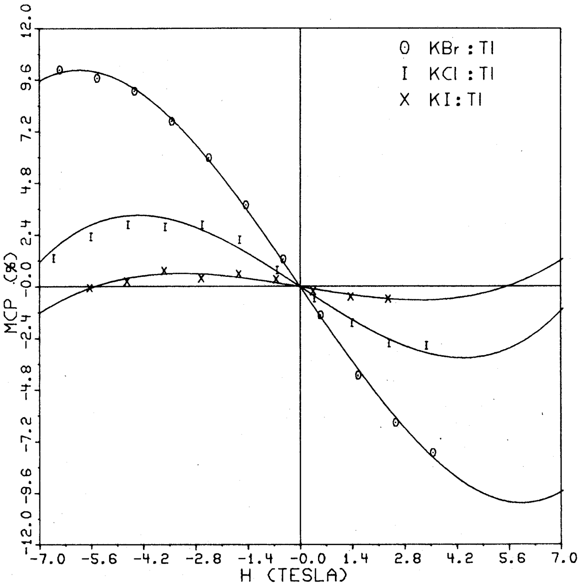

FIG. 2 Degree of circular polarization as a function of the field intensity of A_T emission in KBr:Tl, KCl:Tl, and KI:Tl. Solid lines represent the fitting of the experimental data.

with a function of the type

$$P_c - P_0 = \alpha(H - H_0) + \beta(H - H_0)^3 \quad (1)$$

and then subtracting H_0 and P_0 from the coordinate values of the experimental points. In all the considered systems, the MCP of the A_T emission turns out to be negative ($\alpha < 0$) while in the case of In^+ we obtained (as a test) an opposite sign. There is also a sensitive deviation from linearity (with $\beta > 0$) which causes, with increasing H, first a saturation and then an inversion of the slope. The maximum of the effect corresponds to a field intensity of 3.5–5.5 T where we have a MCP degree of a few percent, although increasing from KI:Tl (<1%) to KCl:Tl (~3%) and KBr:Tl (~10%).

Now we shall attempt to interpret the negative sign of the effect, its field dependence as well as the shape of the MCP spectrum on the basis of a semiclassical calculation. The relatively small size of the polarization indicates that the magnetic field has mainly a mixing effect between nondegenerate levels rather than between degenerate ones. According to Ref. 4, the degree of circular polarization can be expressed

$$P_c = 2\frac{g\mu_B H}{\delta}\tanh\frac{\delta}{2kT} , \quad (2)$$

where μ_B is the Bohr magneton and δ the energy separation between the mixed levels. Assuming for the g factor the value of 2,[3(b)] Eq. (2) with $H \simeq 5$ T and T $\simeq 2$ K reproduces the absolute values of the experimental data in KI, KCl, and KBr:Tl with a separation δ of ~1000, 300, and 100 cm^{-1}, respectively.

The excited state of Tl^+ involved in the A-band absorption and emission is the ${}^3T_{1u}$ (slightly admixed with ${}^1T_{1u}$ by spin-orbit interaction) with the underlying ${}^3A_{1u}$ trap level. After absorption, the original symmetry (O_h) is lowered by the Jahn-Teller effect and configurations of different symmetries can arise; the A_T emission originates from potential minima of tetragonal symmetry (D_{4h}).[2] In such a symmetry, the level scheme consists of a double-degenerate level E_u and two nondegenerate levels A_{1u} and A_{2u}, see Fig. 3. In presence of a magnetic field parallel to z axis, the degenerate $E_{u,x}$ and $E_{u,y}$ states are mixed at the 001 sites and strong positive circular polarization arises. The $A_{2u,x}$ ($A_{2u,y}$) and $E_{u,y}$ ($E_{u,x}$) levels are mixed at the 100 (010) sites and weaker circular polarizations arise depending on the energy separation.[6] If the A_{2u} level is in the upper position (that is E_u and A_{1u} are lower lying) and preferentially populated after absorption and relaxation, the left-circular component (I_-) can prevail and a negative effect arises. This hypothesis is based on a possible solution of the static Jahn-Teller problem and represents a plausible luminescence mechanism in Tl^+ centers.[2,5] As for the A_X emission, where a positive MCP is observed, we have to suppose that the level scheme is simply reversed (that is, in order of decreasing ener-

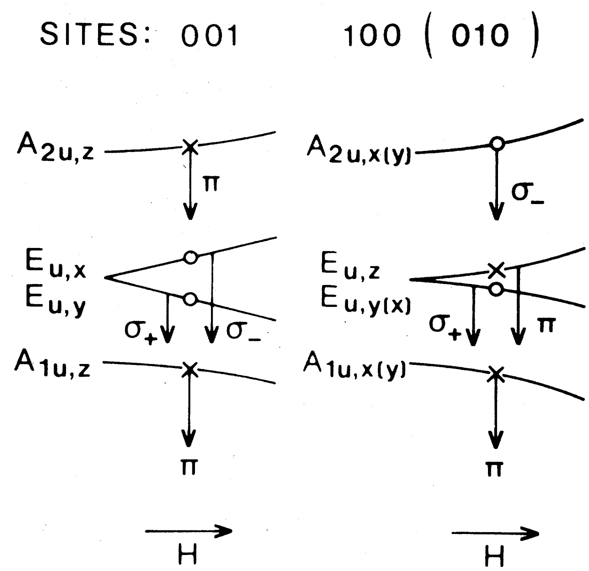

FIG. 3 Schematic energy-level positions of the relaxed excited state of Tl^+-impurity in D_{4h} symmetry vs magnetic field intensity, $\vec{H} \parallel [001]$ direction. In each site the levels coupled by the field are labeled by the same symbol (○ or ×). Vertical arrows indicate emission related to linear polarization π, completely circular polarization $\sigma_\pm$ (whose intensities are $I_\pm$) at the 001 sites, or partially circular polarization $\sigma_\pm$ (with $I_+ \gtrless I_-$) at the 100 and 010 sites.

gy, we have E_u, A_{2u}, and A_{1u}, as in Ref. 6). However, when the MCP, besides being positive, becomes strong, the most plausible origin of the emission is the E_u level (with underlying A_{1u} trap level) like in the lighter impurities In^+ and Ga^+.[1,3(b)]

A complete analysis of the problem should be performed in the five-dimensional space of tetragonal and trigonal distortions. If however we limit ourselves to analyze the x and y minima, a simplified model can be constructed in the two-dimensional Q_2-Q_6 space. Here, given the comparable strength of the coupling to tetragonal (b) and trigonal (c) modes, the potential assumes the shape of a circular trough with two tetragonal minima and two intermediate saddle points.[7] Assuming for simplicity a complete circular symmetry ($b=c$), the potential for the A_{2u} (upper branch) and E_u (lower branch) states, both with minimum, has been obtained by diagonalizing the interaction matrix as given by Honma[8] in the basis $|A_{x(y)}\rangle$, $|^3T_{2ux(y)}\rangle$, $|C_{x(y)}\rangle$ and can be approximated as (see Fig. 4)

$$V_e^{(\pm)}(\rho)=-[b^2(\rho\mp\rho_0)^2+\lambda^2]^{1/2}+\rho^2 \ , \qquad (3)$$

where $\rho=(Q_2^2+Q_6^2)^{1/2}$, $b=c=(3E_{\mathrm{JT}})^{1/2}$, λ is a coupling constant related to the spin-orbit coefficient, $\rho_0 \simeq \delta/2b$ is the crossing-point coordinate of the uncoupled levels. The degree of MCP with a magnetic field parallel to z axis turns out to be[9]

$$P_c=\mp\frac{2\epsilon}{1+\epsilon^2}\simeq\mp 2(\epsilon-\epsilon^3) \ ,$$

where the minus sign holds for the upper branch and plus for the lower branch, $\epsilon=g\mu_B H/\delta \ll 1$, $\delta=V^{(+)}-V^{(-)}$. This relation reproduces well, for the presence of the cubic term, the field dependence of the experimental data [Eq. (1)].

We have evaluated the Franck-Condon integral for the emission and for the MCP in the transitions from

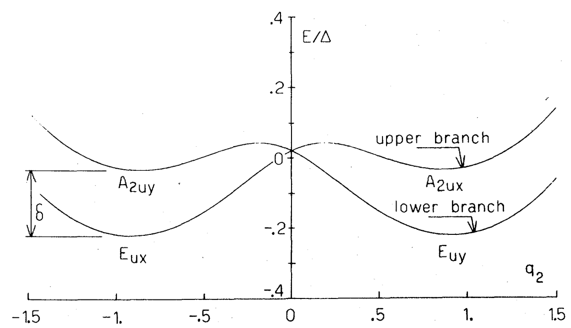

FIG. 4 Cross section of the potential containing the q_2 axis obtained for $q_3=q_3^0$ of x and y minima; for $b=c$, the cross section containing q_6 is identical and there is a complete circular symmetry in the q_2-q_6 plane. Here, $q_2=bQ_2/\Delta$, $\Delta=E_C-E_A$ is the difference between C and A absorption-band energies. The two branches of the potential are fitted by Eq. (3).

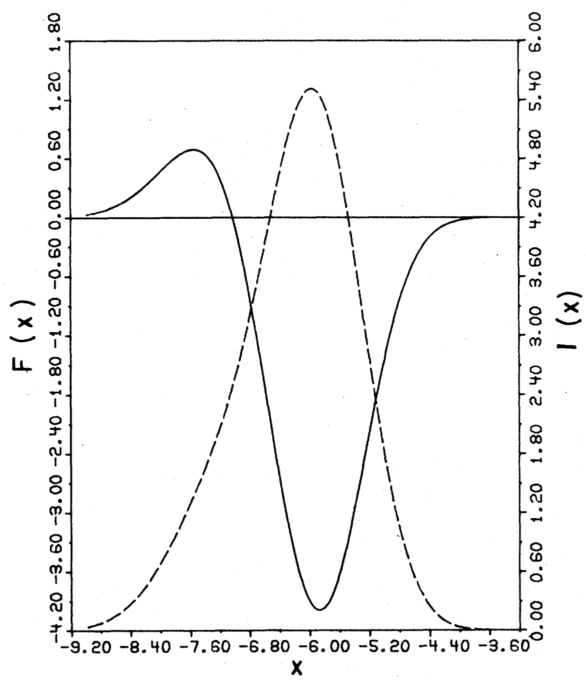

FIG. 5 Computed MCP [$F(x)$, solid line] and A_T emission intensity [$I(x)$, dashed line] for KI:Tl vs normalized photon energy $x=(\hbar\omega_e-\epsilon_0)/b(kT)^{1/2}$ where ϵ_0 is the energy difference between the ground and the excited states at the crossing point. The ordinate scales are in arbitrary units.

the excited states [Eq. (3)] to the A_{1g} ground state [$V_g(\rho)=\rho^2$]. Figure 5 shows the computed spectra with a choice of parameter values compatible with KI:Tl ($E_{\mathrm{JT}}\simeq 3000$ cm^{-1}, $\rho_0\simeq 5$ cm$^{-1/2}$, $\lambda\simeq 2000$ cm^{-1}) and assuming the contribution from the upper branch (A_{2u} level) to be four times greater than the contribution from the lower branch (E_u level). This fitting factor coincides with the population ratio of the levels only if 100 and 010 sites are considered; inclusion of 001 sites raises this factor in order to compensate their contribution. The resemblance of the diagrams of Fig. 5 to the A_T experimental spectra of Fig. 1 is self-evident, and therefore we may conclude that the model accounts rather well for the experimental data. The extension of this semiclassical calculation to KCl:Tl and especially to KBr:Tl requires some caution for the breakdown of the adiabatic approximation (δ comparable with the vibrational quantum). Moreover, especially when the MCP is not very low (as in KBr:Tl), other possible level arrangements cannot be completely excluded.

ACKNOWLEDGMENTS

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