MAGNETIC FIELD EFFECTS IN THE LUMINESCENCE OF THE $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ DOPED WITH $\text{Os}(\text{bpy})_3^{2+}$

Elmars KRAUSZ and Grainne MORAN

Research School of Chemistry, Australian National University, G.P.O. Box 4, Canberra 2601, Australia

ABSTRACT

Magnetic field and temperature dependent (<10 K) luminescence from both $\text{Ru}(\text{bpy})_3^{2+}$ (RBY) of the host material, and the $\text{Os}(\text{bpy})_3^{2+}$ (OBY) dopant, are reported as a function of the orientation of B. Differences are seen for $E||B$ and $E \perp B$, little effect is seen for $B||c$. Strong energy transfer previously reported between RBY and OBY is seen to be dependent on the applied magnetic field. OBY luminescence has more detailed fine structure, first seen here, with some similarities but striking differences to the weak structure seen for RBY in the PF_6 host. A marked triplet structure, with $\sim 35 \text{ cm}^{-1}$ spacing, is seen throughout the spectrum. The triplet has two origin patterns spaced by $7 \pm 1 \text{ cm}^{-1}$. The two higher energy components of the triplet pattern move $(+1 \text{ cm}^{-1})$ at 5T ($B \perp c$). Of the two triplet patterns, only the lower energy set has a strongly enhanced intensity ($\times 400$) for $B(4T)||E$ at 1.4 K. The phonon structure built upon these origins is analysed.

1. INTRODUCTION

The strong magnetic field dependence in luminescence spectra of the $\text{Ru}(\text{bpy})_3^{2+}$ (RBY) below $\sim 10 \text{ K}$ was observed some time ago.[1] Recent measurements[2] of induced polarizations and time resolved spectra in applied magnetic fields force an entirely new perspective of the low temperature dynamics in the excited state of this much studied system. It is clear that the strong absorption process observed in the visible region is metal to ligand charge transfer in nature and that the luminescence is fundamentally spin forbidden in nature, but controversy has centered on the question of localization of the excitation to a single 2-2' bipyridine (bpy) ligand. Evidence for localization comes mostly from observations of excited state resonance raman (ERR) spectra which correlate well with the frequencies of bpy^+ . [3] Polarized spectroscopic measurements, particularly the MCPL[4] demand the involvement of the three ligands in a luminescence process. This paradox seems to have been resolved by the observation of solid phase ERR[5] and time resolved luminescence and MCPL.[4],[6] In fluid solutions, an environmentally driven localization of the excited electron takes place[7] as the solvent relaxes around the luminophore.

The interpretation of magneto-optical phenomena of RBY has been dominated by ideas based on the existence of two closely spaced ($\sim 10 \text{ cm}^{-1}$) E states (within the D_3^* double group) that split and mix in a magnetic field.[1] Recently, fine structure in both absorption and luminescence, has been reported[8],[9] for single crystal pure compounds of RBY such as the title compound $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ (RPF). These results seem to support the existence of levels spaced by $\sim 7 \text{ cm}^{-1}$, though the initial basis for proposing such a scheme has been thoroughly discounted.[2],[4] Zeeman effects on fine structure in both luminescence and absorption of RPF reveal an anomalous transverse effect but a null axial result.[10],[11] This effect cannot be simply understood in terms of current models of the electronic structure of RBY, nor can the MCD of the singlet states.[12] The appearance of fine structure seems correlated with the temperature (10 K) at which thermal equilibrium is lost in the low temperature luminescence in dilute RBY systems.[4] The purpose of this work is to investigate the unique magneto-optical behaviour of these systems further.

The RPF crystal structure has hexagonal symmetry ($P3c1$) and only two RBY,s per unit cell, separated by 0.8nm along the c axis and related by a mirror plane.[13] It is an attractive system to study, but the question arises as to whether fine structure observed is due to intrinsic RBY or extended interactions (exciton structure). Clear evidence has been given for energy transfer (and thus substantial inter-unit interaction) in RPF, based on temperature dependent and sample dependent luminescence spectra and the behaviour of samples doped with OBY.[14] In this work we measure RPF and RPF doped with OBY luminescence spectra as a function of applied magnetic field, with $B||$ and $\perp$ to c and significantly $E(\text{light electric vector})||$ or $\perp B$.

2. EXPERIMENTAL

Crystals of RPF were grown from 1:1 ethanol/acetonitrile. OBY doped materials were grown from the same solvent by adding a small amount of $\text{Os}(\text{bpy})_3(\text{PF}_6)_2$ and concentrations were determined from the known absorbance of OBY.[15] The crystal used had a concentration of 0.25 mole percent OBY.

Spectra were measured in an Oxford instruments SM4 cryostat, with the sample either in exchange gas or liquid helium (<4K). A Spex 1401 monochromator was used fitted with a 1μ blaze grating and a cooled RCA C31034 photomultiplier. Excitation was with $\sim 1\text{mW}$ of the 458 nm line of a Ar^+ laser or He-Ne 633 nm laser in 180° geometry. The former laser excited predominantly the host and the second only the dopant. System response was calibrated with a standard lamp, and phototube sensitivity to stray magnetic fields calibrated. Spectra were accumulated on a MINC-11 laboratory computer, corrected, and further processed on a VAX-11/750.

3. RESULTS AND DISCUSSION

The spectra in FIG. 1 show sharp structure developing for OBY luminescence around 10 K. The RBY luminescence is somewhat distorted by reabsorption by OBY (see inset). OBY luminescence is however largely due to temperature dependent energy transfer, from studies with more dilute crystals.[14] Luminescence and absorption is dominantly σ polarized and at higher temperatures energy transfer clearly becomes more effective with enhanced OBY intensity, although lifetimes above 10 K become an order of magnitude shorter.[2]

FIG.1 Luminescence (arb. linear units) of OBY/RPF at indicated temperatures excited at 458nm. Absorption ... (r.h.scale) of crystal at 1.4 K.

Magnetic field dependent luminescence spectra at 1.4 K, exciting the RBY system, are presented in FIG. 2. Spectra taken at 4.2 K show a smaller increase in luminescence for $E||B$ and a decrease in intensity for $E \perp B$ relative to 1.4 K spectra. The total field induced intensity in OBY luminescence is less than for RBY but relatively more of the enhancement is retained at 4.2 K.

FIG. 2 Luminescence of OBY/RPF at 1.4 K in applied fields as indicated. Orientation was $B||E$ and B perp. to crystal c axis. Excitation is at 458 nm as in fig 1, and the intensity in this and other figures is in arbitrary linear units.

Excitation at 633 nm is purely into OBY and no RBY luminescence is seen. The field induced intensity changes are presented in FIG 3, and there are some significant differences in the spectra, compared to FIG'S. 1. and 2., where excitation is into the RBY, and OBY activation is principally by energy transfer. Although band positions and shapes are similar, the relative intensity of the field independent and the enhanced transitions, are significantly different, with the broader envelope being $\sim x2$ stronger (relatively) for 458 nm excitation.

FIG. 3 Field induced luminescence for OBY/RPF at fields indicated. Excitation was at 633 nm and geometry and temperature as fig. 2. Upper triplet patterns increase strongly upon applied field, lower set are largely field independent.

Detail of the origin region is given in Fig. 4, along with some temperature dependence data and the σ absorption spectrum of the crystal in the same region. The triplet pattern seen is repeated throughout the spectrum, apparently combined with (other) phonon modes. The lowest energy triplets are built around the two apparent origins (labelled E_1 and E_2), that are themselves separated by ~ 7 cm^{-1} . Only the E_1 feature is present in absorption, and no evidence for absorption features at lower energies (corresponding to the other components of the E_1 triplet pattern) were found even with a B of 5T $||$ or $\perp$ to c . It thus seems unlikely that the pattern is due to sites of OBY in the crystal. The three components of the triplet shift differently in an applied magnetic field.

Little effect is seen with $B||c$, but the two higher energy components shift $\sim(+)1\pm0.3\text{ cm}^{-1}$ with $5T \perp c$, but the strongest (lowest energy) component does not show a noticeable shift. Most of the shift occurs for fields less than $2.5T$, with no noticeable increase to $5T$. Finally E_1 in absorption shifts for $E||B$ but not noticeably for $E \perp B$. Shifts in phonon sidebands seem similar though increased linewidths limit precision. The phonon sideband structure is separable into field dependent and field independent systems, which aids identification. This can be compared with the temperature dependence, where the E_1 based triplet is weak at $0T$, even at 1.4 K , and fades with increasing temperature, becoming lost above 10 K . The E_2 origin gains intensity upon warming, but does not change significantly upon application of a field.

FIG. 4 Absorption (l. h. scale) ... at 1.4 K and $0T$, and luminescence spectra of OBY/RPF at the indicated fields and temperatures. Field orientation, excitation wavelength and light polarization are as for fig. 3

Only E_1 is visible in absorption (FIG. 4) and shows a $\sim 20\text{ cm}^{-1}$ (phonon) sideband progression. There is a second sharp feature, shifted by 73 cm^{-1} that also has a positive field induced shift and sideband structure and may be yet another electronic origin. E_2 is not visible in absorption, even in an applied field, as is the seemingly analogous transition in RPF. The lattice phonon sideband structure is similar to that seen in RPF.[9],[11] In luminescence, E_1 and E_2 , and the other two components of their triplets have a sideband structure based on the same 23 cm^{-1} mode. In RPF the exciton-phonon coupling of the two origins are similar, but in OBY intensity at $0T$ seems strongly associated with E_1 . The field induced E_1 intensity however does not carry comparable sideband intensity.

TABLE 1 summarizes peak positions and assignments for some of the main sharp features in luminescence. Most features appear as triplets, either associated with E_1 (strongly field dependent) or as field independent bands. The field independent bands cannot be easily associated with the E_2 origin, which is experimentally observed as strongly temperature dependent. None of the main sharp, field independent features are noticeably temperature dependent, apart from some broadening. Some weaker features however, are temperature dependent. The E_1 system has a progression of a 680 cm^{-1} mode and an identifiable mode of 1491 cm^{-1} . These can be associated with localized ring deformation modes of the bpy ligand. Significantly, such modes are enhanced in the ERR spectrum of OBY.[16] The field independent system however, dominates the sharp line intensity at $0T$. Except for broadening, this system seems largely independent of temperature, until it is lost in the increasing broad luminescence above 10 K .

Again, the intensity of the field independent sharp system cannot be correlated with E_1 , which is strongly field dependent while quite temperature independent in the range $1.4\text{--}6\text{ K}$, nor with the E_2 based system which though not obviously field dependent, is strongly temperature dependent. The increase in the main broad band around 14350 cm^{-1} with temperature may be related to the E_2 variation, but the magnetic field dependence of E_2 seems small and appears to be not connected with the increase in intensity of the broad band. The broad luminescence is better correlated with the increase in intensity of E_1 luminescence although the ratio depends on the OBY excitation mode (direct at 633 nm or energy transfer from RBY).

The sharp field independent structure is more complex than the field induced part. The strongest feature seems to be an induced origin, 220 cm^{-1} from the origin region, with a progression in a totally symmetric mode of 270 cm^{-1} built upon this (false) origin. Some triplets clearly have satellites $\sim 7\text{ cm}^{-1}$ away that are not strongly temperature dependent. Furthermore,

Origin Region	
14 509	E_2
14 471	$E_2 - P$
14 437	$E_2 - 2P$
14 502	E_1
14 467	$E_1 - P$
14 427	$E_1 - 2P$
14 482	$E_1 - 20$
14 447	$E_1 - 20 - P$
14 404	$E_1 - 23 - 2P$
Field Induced	
14 391	$E_1 - 111$
14 349	$E_1 - 112 - P$
14 312	$E_1 - 113 - 2P$
13 824	$E_1 - 678$
13 787	$E_1 - 680 - P$
13 748	$E_1 - 679 - 2P$
13 179	$E_1 - 1323 \text{ or } (-678-645)$
13 153	$E_1 - 1318 - P$
13 102	$E_1 - 1335 - 2P$
13 011	$E_1 - 1491$
12 931	$E_1 - 1491 - 2P$
12 871	$E_1 - 1491 - 4P$
Field Independent	
14 292	C
14 250	C - P
14 213	C - 2P
14 022	C - 270
13 980	C - 270 - P
13 943	C - 270 - 2P
13 764	C - 528 or (-270-258)
13 734	C - 516 - P
13 692	C - 521 - 2P
13 655	C - 528 - 3P
13 620	C - 528 - 4P
13 580	C - 528 - 5P
13 543	C - 528 - 6P

(P = 35 cm^{-1} progression, C = False Origin)

these satellites appear higher in energy to the stronger component in some, and lower in others, but the resolution of our current apparatus is insufficient to report these details.

The present data need to be carefully compared to that obtained for pure RPF. We have observed the same weak, (RBY) sharp line origin structure in our doped RPF crystal as in the pure material. Two temperature and field dependent origins are seen, separated by 7 cm^{-1} both having a 23 cm^{-1} sideband structure. In both cases the lower energy origin (E_1) luminescence becomes more intense in an applied magnetic field if $B \parallel c$, and a stronger effect is seen for $B \parallel E$ than for $B \perp E$. There are however striking differences. Firstly it is E_2 that is seen in absorption for RPF and the corresponding E_1 for OBY in RPF. Secondly, the E_1 emission and absorption move to higher energy (towards E_2) in a magnetic field, whereas in RPF E_1 and E_2 move apart, each origin shifting by $\sim 2\text{ cm}^{-1}$ at 5T. The shift in RBY is also at least linear in magnetic field if not quadratic.

The analysis for RPF given by Yersin et al.[10] proposed the two E states to be in thermal equilibrium and mixed in the field, transferring intensity from the (more allowed) E_2 system to the E_1 system. This analysis seems inconsistent with the observed null axial Zeeman effect and the B to E orientation dependence [11], and certainly the current data do not seem compatible with this overall model. What is striking is that the same origin separation of 7 cm^{-1} is maintained in both OBY and RBY in this host. It is difficult to imagine an electronic property of the two chromophores (RBY and OBY) that remained quite that constant. The source of the pronounced triplet structure for OBY in RPF and not present for RPF itself is also difficult to ascertain at the current level of understanding of the electronic nature of these systems. The possibility of the triplet structure being due to sites is contra-indicated by the lack of absorption from any but the E_1 feature, and the distinctly different magnetic field shifts (though not intensity enhancements) of the three peaks. The structure may arise by interaction of the OBY with the band structure of RPF, though it is difficult to see why three lines of comparable intensity should occur.

The triplet pattern seems to combine quite remarkably with the 7 cm^{-1} spacing, the 23 cm^{-1} lattice mode and a number of other modes, including modes clearly identifiable as ligand deformation modes. Such combinations only seem possible in a strongly vibronically coupled system, where the usual selection rules are relaxed.

Although it has been reported[8] that there is no time dependence of the luminescence of RPF in σ polarization, such measurements may of course be strongly influenced by energy transfer. We feel that the anomalous sharp structure and field dependences are intimately associated with non-thermalization between electronic levels in these systems,[4] or a dynamical change in the luminophore during the lifetime of the luminescence.[2] The observation that the ratio of the sharp to broad field induced luminescence intensity varies with excitation technique, is taken as evidence that the E_1 and E_2 (or perhaps other) systems of OBY in RPF can be preferentially populated, and thus are not in equilibrium.

5. CONCLUSIONS

Results presented provides further evidence for a complex, dynamical process occurring in RBY type systems at low temperature. As pointed out in the discussion, recent time resolved luminescence evidence on RBY in dilute crystal systems[2] has established that the application of a magnetic field does not initially lead to thermalization of levels, but must be related to a change in the basic intensity processes in the luminophore. When a magnetic field (or other perturbation) mixes a weakly allowed electronic level with an allowed level, this does not, in general, lead to the phonon couplings and the bandwidths of the mixing level, in consideration of the spectrum of the (enhanced) weakly allowed level. Thus the present data cannot be easily understood as due to levels of differing dipole strengths, in thermal equilibrium, and mixing in an applied magnetic field. Our data further would limit the possibility of the dominant triplet structure in the luminescence spectra as being due to distinct (extrinsic) crystal site splittings, but high resolution excitation spectra may help resolve this question. Despite a large number of spectroscopic studies on RBY type systems, a concrete model for the nature of the low temperature states is still lacking and time resolved luminescence measurements of OBY in RPF (and in optically dilute crystals), particularly in the presence of a magnetic field, are called for.

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