Magnetic Circular Polarization of Luminescence from Self-Trapped Excitons in Alkali Halides

M. J. Marrone and M. N. Kabler

Naval Research Laboratory, Washington, D. C. 20390

(Received 7 September 1971)

Strong magnetic circular polarization has been observed in many of the intrinsic re-combination transitions from a number of alkali halide crystals. The measured g fac-tors, $g \approx 2$, confirm the assignment that these transitions originate in triplet states of the self-trapped exciton. An analysis based on field-induced mixing of the B_{2u} and B_{3u} levels of the zero-field split-triplet state is consistent with the field and temperature de-pendence data for bromides and iodides.

Intrinsic recombination luminescence in alkali halides at low temperatures is known to occur through radiative decay of the self-trapped exci-ton. This metastable electronic excitation may be characterized as a covalent bond between two ad-jacent excited halide ions, that is, as an X_2^{-2} mol-ecular ion. Emission bands have been attributed to transitions from both singlet and triplet states on the basis of data on lifetimes and linear polari-zation.[1] In addition, recent work with pulsed elec-tron excitation has revealed transient optical ab-sorption due to transitions originating in the low-est triplet states of the self-trapped exciton.[2] The present work concerns the observation of large temperature-dependent magneto-optic ef-fects associated with the luminescence, which confirm the triplet and singlet assignments made previously on the basis of less direct evidence. By means of an analysis based on mixing of the triplet sublevels by the applied field, the data are shown to yield information concerning zero-field splittings between the B_{2u} and B_{3u} sublevels.

The measurements were carried out by viewing the luminescence from crystals[3] positioned in the center of a 60-kG superconducting solenoid. The temperature could be varied from about 6 to 40°K by means of a heater coil on the sample holder. The luminescence was excited with 50-kV x rays incident on the back face of the crystal. The light emerged parallel to the field and entered a detec-tion system consisting of a Pockels cell driven at 3050 Hz between quarter-wave voltages, a linear polarizer, a grating monochromator, a magneti-cally shielded photomultiplier tube, and a lock-in amplifier.

The upper curve in Fig. 1 is the emission spec-trum of KBr under x-ray excitation at 6.2°K. The band centered at 4.42 eV (280 nm) has been as-signed to a $^1\Sigma_u^+ \to {}^1\Sigma_g^+$ transition of the self-trapped exciton, and the other band, whose actual peak is at 2.27 eV (545 nm), to a transition from a $^3\Sigma_u^+$ state which assumes $^1\Pi_u$ character due to

spin-orbit coupling.[1] These designations refer to the X_2^{-2} molecular ion, which is isoelectronic with a rare-gas molecule. The lower curve in Fig. 1 shows the circular polarization induced in the luminescence by a magnetic field of 57 kG. The ordinate is proportional to the difference $(I_+ - I_-)$ in the intensities of the left $(E_x + iE_y)$ and the right $(E_x - iE_y)$ circularly polarized compo-nents of the light. The magnitude of the fraction-al circular polarization, $P = (I_+ - I_-)/I$, in the 2.27-eV band is approximately -0.35 at 57 kG and 6.2°K.[4] The negative sign indicates that the luminescence is predominantly right circularly polarized. The luminescence at 4.42 eV is seen to exhibit no net circular polarization,[5] a result which can be interpreted in terms of an initial state into which the applied field induces only neg-ligible orbital angular momentum. This is con-
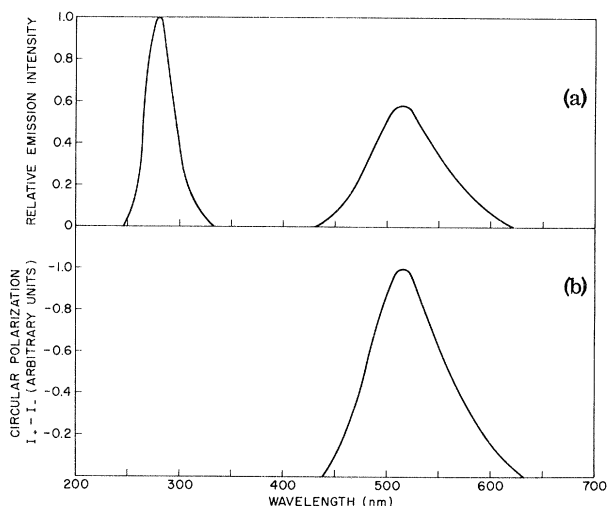

FIG. 1. (a) Emission spectrum of KBr at 6.2°K under x-ray excitation. (b) Circular polarization induced in KBr intrinsic emission by a magnetic field of 57 kG. Spectrum is normalized to the peak value of the differ-ence in the intensities of left and right circularly po-larized light. These spectra have not been corrected for the response of the detection system.
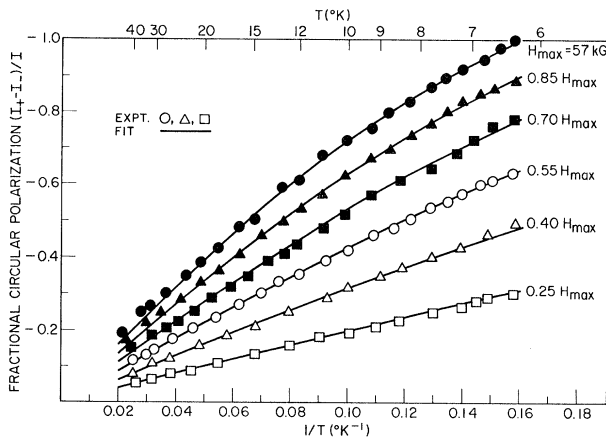
FIG. 2. The changes in the fractional circular polarization of the KBr 2.27-eV emission with variations in magnetic field and temperature. All values are normalized to the peak value of -0.35 at 6.2°K and 57 kG. The solid lines represent a least-squares fit by Eq. (1) for the parameters g and γ.

sistent with the $^1\Sigma_u{}^+$ assignment. Figure 1 illustrates the characteristic qualitative behavior of all alkali halides investigated. Within the accuracy of the measurements, only the zeroth moments of the spectra are found to differ among I_+, I_-, and I.

The data of Fig. 2 for KBr indicate an initial linear dependence of the circular polarization on both reciprocal temperature and field, along with

a tendency toward saturation at high fields and low temperatures. This behavior can be accounted for as field-induced mixing of two nondegenerate levels whose populations achieve equilibrium in times much less than the luminescent lifetimes ($\approx 10^{-4}$ sec for KBr). In the crystal a $^3\Sigma_u{}^+$ state is split into three sublevels, B_{2u}, B_{3u}, and A_u, the appropriate point group being D_{2h}. The symmetries of the spin functions have been included in the designations, e.g., B_{2u} corresponds to B_{1u}(space)$\times B_{3g}$(spin) plus a small spin-orbit-induced admixture of the singlet state B_{2u}(space) $\times A_g$(spin). Dipole transitions from B_{2u} and B_{3u} (but not A_u) to the A_g ground state are thus allowed.[1] The applied field may be taken into account in the Hamiltonian with the terms $g\beta\vec{H}\cdot\vec{S}$ $+\beta\vec{H}\cdot\vec{L}$, where g is assumed to be a constant parameter. The significant matrix elements are those of the factor $g\beta H_z S_z$ between the states B_{2u} and B_{3u} (B_{2u} and B_{3u} transform as y and x, respectively). This interaction is readily diagonalized, and the resulting two wave functions each exhibit a net circular polarization (lower level right, upper level left) for dipole transitions to the A_g ground state. The observed polarization will be proportional to the population difference between the two levels, which we assume to obey a Boltzmann distribution. The splitting is E $=E_0(1+\gamma^2)^{1/2}$, where E_0 is the zero-field splitting and $\gamma = 2g\beta H_z/E_0$. The resulting field and temperature dependences are given by

$$P_z = -2\tanh\left(\frac{E}{2kT}\right)\left[\frac{\gamma}{(1+\gamma^2)^{1/2}-1} + \frac{(1+\gamma^2)^{1/2}-1}{\gamma}\right]^{-1}, \tag{1}$$

when the luminescence is viewed along the z axis.[6] At low H and high T, Eq. (1) becomes simply $P_z \approx g\beta H_z/kT$.

These considerations neglect field-induced mixing of other states, since they are not expected to be close in energy.[1] The B_{1u} ($^1\Sigma_u{}^+$) state sharing the same orbital configuration might, in principle, be near enough to interact. This possibility is minimized, however, by an additional experimental observation that the lifetimes of the 2.30- and 3.10-eV bands in RbI, the 2.27-eV band in RbCl, and the 3.38-eV band in NaCl are not affected measurably by magnetic fields up to 57 kG.

The normalized data for the circular polarization of the KBr 2.27-eV emission as a function of temperature and field were computer fitted by Eq. (1) with a least-squares method with the parameters g and γ. The solid curves of Fig. 2 show the result which yields $g = 1.95 \pm 0.05$ and

$E_0 = 0.24 \pm 0.03$ meV. Taking into account the absolute magnitudes of the measured polarizations[7] and maximum errors in the data and the fitting procedure, the data are incompatible with values $g < 1.5$. This conclusion holds also for the triplet emissions in RbBr (2.10 eV), KI (3.34 eV), and RbI (2.30 and 3.10 eV). The data for these three crystals did not deviate sufficiently from linear dependence on H_z/T to justify a computer fit by Eq. (1); the estimated upper limit for E_0 is 0.2 meV. We note that the data for the 2.30- and 3.10-eV bands of RbI are almost identical. This is consistent with their origins being two distinct triplet states of the self-trapped exciton, a premise which has arisen in reference to other measurements.[9]

Magnitudes of P comparable to those above have been measured also for the intrinsic transi-

tions in NaCl (3.88 eV), KCl (2.32 eV), RbCl (2.27 eV), and CsBr (3.45 eV). The temperature and field dependences do not, however, conform to Eq. (1), the actual behaviors being rather more complicated. These effects are under further investigation; they appear to arise from spin-lattice relaxation times which become too slow to maintain approximate equilibrium.

The above analysis is clearly consistent with the triplet-state assignments, for which one expects $g = 2$. Furthermore, the data actually exclude the alternative case, which is that the luminescent state is predominantly $^{1}\Pi_{u}$-like. It is easily shown that Eq. (1) would still hold in this case, but g becomes an orbital reduction factor g', of magnitude $g' < 1$.[9] The observed g values rule out this possibility.

In order to provide additional information about the nature and ordering of the emitting triplet states, a different type of experiment has also been carried out. It is evident that, in the *absence* of an applied magnetic field, dipole transitions from B_{2u} and B_{3u} states should be *linearly* polarized along the y and x directions, respectively. The linear polarization measurements previously reported have specified only σ or π polarization and have failed to distinguish between the x and y components of the latter.[10,11] Using a similar method involving recombination with aligned self-trapped holes,[12] we have observed a net linear polarization along the y, that is, $\langle 100 \rangle$, direction at a fixed temperature of roughly 10°K. KBr, RbBr, and RbCl were investigated,[12] and the measured polarization values for each fell in the range 0.05–0.10. The true values are somewhat higher as a result of extraneous depolarization effects in the experiment. One can conclude from this that B_{2u} lies lower than B_{3u}, since the magneto-optic measurements show these states to be in equilibrium at this temperature. The expected magnitude of the linear polarization is simply the population difference $\tanh E_{0}/2kT$. With the E_{0} obtained above, this factor is 0.15 for KBr at 10°K, in reasonable agreement with the measured linear polarization. In addition, the comparable values of the linear polarizations for KBr, RbBr, and RbCl indicate that the respective E_{0} probably differ by less than a factor of 2.

The present data thus provide strong confirmation of the triplet nature of these states. The evaluation of E_{0} and the deduction of the ordering

of B_{2u} and B_{3u} furthermore furnish a rationale for theoretical investigation of relationships among these factors and the spin-orbit, crystal-field, and exchange interactions.[13] It is of interest to note that the zero-field splittings in the exciton are orders of magnitude larger than those commonly observed in the triplet states of organic molecules. This is an indication of different effects being dominant, spin-orbit interactions for the exciton and magnetic dipole-dipole interaction of the electron spins for the molecules.

[1]M. N. Kabler and D. A. Patterson, Phys. Rev. Lett. 19, 652 (1967).

[2]R. G. Fuller, R. T. Williams, and M. N. Kabler, Phys. Rev. Lett. 25, 446 (1970).

[3]The crystals were obtained from the Harshaw Chemical Company with the exception of RbBr and RbCl which were grown at the Naval Research Laboratory by the Kyropoulos method.

[4]The experimental technique yields the differences $I_{+} - I_{-}$. I is the total intensity which includes unpolarized light.

[5]The signal-to-noise ratio in the 4.42-eV region is sufficient to detect P values less than 0.001.

[6]M. J. Marrone, thesis, Catholic University, 1971 (unpublished).

[7]Corrections had to be made for the unpolarized contributions to the total light intensity (from excitons at 90° to H) and for the fact that the light viewed at 45° to the molecular axis would be elliptically polarized. Also, the effective magnetic field is $H_{g} = H/\sqrt{2}$ since the exciton axes in crystals of the NaCl structure lie along the $\langle 110 \rangle$ directions and the field was applied along a $\langle 100 \rangle$.

[8]D. Fröhlich, U. U. Fischbach, and M. N. Kabler, to be published.

[9]A related example concerns the luminescence of Tl^{+} in KI; see M. P. Fontana and J. A. Davis, Phys. Rev. Lett. 23, 974 (1969).

[10]M. N. Kabler, Phys. Rev. 136, A1296 (1964).

[11]R. B. Murray and F. J. Keller, Phys. Rev. 137, A942 (1965).

[12]Triplet emissions in other crystals could not be investigated because of the spectral overlap with the principal absorption of the self-trapped hole whose dichroism would lead to ambiguous results.

[13]W. B. Fowler, M. N. Kabler, and M. J. Marrone, to be published.