Intersystem Crossing, Polarization, and Defect Formation Induced by Optical Excitation of Self-Trapped Excitons in Alkali Halides

R. T. Williams
U. S. Naval Research Laboratory, Washington, D. C. 20375

(Received 29 December 1975)

Metastable relaxed excitons created by pulsed electron irradiation in alkali-halide crystals are excited to higher states by a laser pulse. Consequent changes in excitonic absorption and emission yield data on triplet-singlet conversion and on polarization of the optical transitions. It is found that *F* centers are formed upon promotion of self-trapped excitons from the lowest metastable level to the second excited level in KCl.

Excitons in many simple halide crystals are self-trapped by the localized lattice relaxation they induce. Strongly Stokes-shifted phosphorescence resulting from electron-hole recombination in alkali halides originates in the lowest triplet level of the self-trapped exciton (STE).[1] Excitonic fluorescence observed at 1 or 2 eV higher energy than the phosphorescence is attributed to radiative decay of a higher STE singlet; the lowest excited singlet appears not to fluoresce.[2,3] Optical-absorption spectra corresponding to transitions from the lowest triplet to higher states of the STE have been reported previously.[4] In the present study certain of these transitions are excited by an intense laser pulse and major effects on emission and absorption are observed.

The key results are summarized as follows: The observed simultaneous extinction of the phosphorescence and excited-state absorption provides a new confirmation of the earlier assignment of these transitions to a common level of origin.[4] The probability of crossing from the higher triplet states into the singlet manifold approaches the statistical limit of 0.25, consistent with the very small exchange energies for STE states deduced from optically detected EPR.[5] For the first time, the linear polarization of STE emission has been measured without the necessity of preparing oriented self-trapped holes (V_k centers). That is, in the present experiment a collection of oriented self-trapped excitons is prepared by the laser pulse *after* the excitons have relaxed to the lowest metastable level. Thus the measured polarization is independent of reorientation (of the bond axis of the halide-ion pair on which the exciton is localized) which may occur during recombination of a free electron with a self-trapped hole, or during relaxation from highly excited STE states. Comparison of these data with earlier studies using aligned V_k centers[6,7] indicates that STE reorientation during relaxation occurs to a significant degree, thus implicating "dissociative" STE states in the very fast relaxation processes recently observed.[8] The polarization of optical-absorption transitions out of the lowest metastable exciton level has also been deduced from these measurements, providing new data for testing level assignments. Finally, an important channel for nonradiative decay of STE's is the creation of lattice defects. The experiment being reported shows that promotion of metastable triplet STE's to higher states in KCl results in enhanced *F*-center formation. This supports the conclusion that defects are not readily formed out of the lowest relaxed exciton state at low temperature[8-12] and provides the first direct evidence that defect formation is initiated from (at least) the second excited triplet STE level in KCl.

In the experiments, a 5-nsec pulse of x rays or 500-keV electrons is used to generate electron-hole pairs in an alkali-halide crystal at low temperature. Vibrational relaxation of the excitons leads rapidly to population of the low-lying radiative levels. After a time greater than the decay time of the radiative singlet state a pulse from a *Q*-switched ruby or Nd:glass laser irradiates the crystal, elevating excitons from the phosphorescent triplet level to higher triplet levels. The nature of these transitions was discussed in Ref. 4. Optical absorption and emission following the electron pulse and laser pulse are recorded using techniques described in Ref. 4.

In Fig. 1 I show the response of the 610-nm absorption, 360-nm phosphorescence, and 220-nm fluorescence of a NaCl crystal ($T \approx 10$ K) which is irradiated sequentially by an electron pulse and a 694-nm laser pulse. The absorption (a) and phosphorescence (b) both originate from the lowest triplet STE level, which is depleted about 80% in population by the laser pulse (100 mJ/cm^2 incident normal to the electron-irradiated surface). Also, we observe ultraviolet fluorescence (c) in response to the 694-nm laser light. The areas

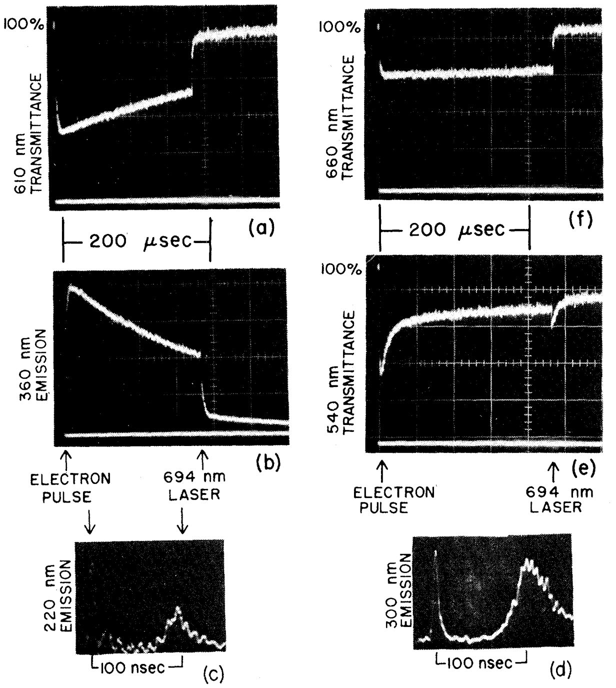

FIG. 1. (a)–(c) Optical response of NaCl at low temperature to a pulse of energetic electrons followed by a pulse of 694 nm light. Fluorescence in KI resulting from an electron pulse and subsequent 1.06-μm laser pulse is shown in (d). Optical transmittance of KCl at low temperature is shown for 540 nm (e) and for 660 nm (f) in response to a pulse of energetic electrons followed by a pulse of 694 nm light.

under the recorded pulses in (c) indicate that the time-integrated fluorescence in response to the laser pulse in NaCl is about 2 times as great as the fluorescence excited initially by the electron irradiation. In Fig. 1(d) I show for comparison the response of 300-nm fluorescence in KI to an electron pulse followed by a 1.06-μm laser pulse. In this case the integrated fluorescence in response to the laser pulse is 5 times that in response to the electron pulse. This is in basic agreement with the ratio of triplet-state emission to singlet-state emission under continuous x-ray excitation,[7] indicating that few excitons are lost from the radiative channels in the repeated excitation and relaxation that occurs during a laser pulse strong enough to extinguish most of the triplet-state phosphorescence.

If the response of the uv fluorescence is measured as a function of delay between the electron pulse and the laser pulse, its magnitude is found to decrease in close correspondence to the triplet STE lifetime. If the laser irradiation occurs after essentially all of the triplet STE's have decayed, only a small fluorescence response ($\approx 10\%$ of maximum in NaCl, $<3\%$ in RbI) is observed, presumably due to photoexcitation of electrons from traps and subsequent recombination with self-trapped holes.

Under the conditions employed in taking the data of Fig. 1 for NaCl, STE's generated by the electron pulse absorb about 0.7% of the laser pulse energy, raising the temperature of the electron penetration layer no more than 4 deg above 10 K. Data for RbI were taken while varying the laser intensity over 5 decades. The fluorescence response was found to be linear in laser pulse energy densities in the range 0.01 to 1 mJ/cm^2, but saturation set in as triplet-state depopulation became significant above this range.

I interpret the data in terms of crossing from higher triplet states of the STE to states in the singlet manifold. In RbI the probability per absorbed 1.06-μm photon of crossing out of the triplet manifold is about 0.25. Values of roughly the same order are found in other crystals. This apparent lack of discrimination between higher triplet and singlet states may be understood partly in terms of the small exchange energies found generally in STE states,[5] and of the sizable halogen spin-orbit parameter.[1] The energy gap between the excited triplet and the fluorescent singlet can be estimated, on the basis of optical spectroscopy,[2,4] to be much smaller than the gap between the excited triplet and the lowest triplet. Thus the vibrational overlap factors should favor crossing to the higher singlet over relaxation directly to the lowest triplet.

At low temperature, each STE has a distinct symmetry axis along one of the [110] crystallographic directions in the NaCl structure, although the distribution among the six possible [110] axes is random if the STE's are created in a pure crystal by ionizing radiation. Absorption of polarized light which preferentially excites STE's aligned along a particular crystallographic direction can be expected, on the basis of the preceding discussion, to lead to polarized luminescence.

Experiments to measure polarization utilized the basic techniques discussed in connection with intersystem crossing above. The plane of polarization of the laser was aligned along a [110] crystal axis of the sample, and the luminescence was detected at near-normal incidence through two separate optical systems having polarization analyzers in and normal to the plane of polarization of the laser.

When self-trapped excitons in NaCl at $T \approx 10$ K are excited by a linearly polarized 347-nm laser pulse, the resulting singlet-state fluorescence measured at 240 nm is polarized parallel to the plane of polarization of the laser:

$$P=(I_\parallel - I_\perp)/(I_\parallel + I_\perp)=0.21\pm0.08.$$

The triplet-state phosphorescence measured at 395 nm has polarization $P=0.18\pm0.06$ after being 40% extinguished by the 347-nm laser pulse. Note that this latter polarization characterizes those STE's which do not absorb 347-nm light; thus the positive sign of P indicates that the phosphorescence and 347-nm absorption have opposite polarizations.

The polarization of uv fluorescence in NaCl determined by recombination of electrons with previously oriented self-trapped holes[6] is $P=0.27$. Comparison with the present data indicates that 347 nm light is absorbed by a STE transition polarized along the halide-halide bond axis. This is in agreement with the assignment of the broad uv transient absorption band in Refs. 3 and 4 to the transition

$$A1s\sigma_g,{}^3\Sigma_u^+ \rightarrow D1s\sigma_g,{}^3\Sigma_g^+.$$

Here A and D denote, respectively, occupation by the hole of σ_u and σ_g molecular orbitals constructed from valence p orbitals on two neighboring halide ions, in the approximation of $D_{\infty h}$ point symmetry.[4] Reorientation of self-trapped holes is known to proceed efficiently upon excitation to the antibonding state ${}^2\Sigma_g^+$ analogous to $D1s\sigma_g,{}^3\Sigma_g^+$, so the relatively small polarization of fluorescence in the present experiment is reasonable.

It is significant that I have found a larger polarization of the phosphorescence in NaCl than the value $|P|\lesssim 0.03$ reported in Ref. 6; that is, the present experiment detects the phosphorescence from STE's which are selectively bleached or oriented *after* reaching the lowest metastable state, and hence have no chance for randomization at low temperature. Comparison of these data with Ref. 6 suggests that exciton relaxation following electron-hole pair generation even at low temperature involves untrapping of the exciton via antibonding STE excited states before the lowest state is reached, thus giving the STE temporary mobility during electronic relaxation.

Upon excitation of NaCl with linearly polarized light at 694 nm, it was found that $P=-0.13\pm0.07$ for the singlet-state fluorescence and $P=-0.07\pm0.02$ for the triplet-state phosphorescence, indicating that the absorption at 694 nm is weakly π polarized with respect to the principal STE symmetry axis. This polarization, though weak, appears to favor the assignment of 694-nm absorption to the transition $A1s\sigma_g,{}^3\Sigma_u^+ \rightarrow A2p\pi_u,{}^3\Pi_g$ (Ref. 3) rather than $A1s\sigma_g,{}^3\Sigma_u^+ \rightarrow A2p\sigma_u,{}^3\Sigma_g^+$ (Ref. 4). Further investigation should therefore include a search for possible σ-polarized STE absorption at energies below the 0.5-eV limit of the measurements in Ref. 4.

I have undertaken experiments to determine if promotion of metastable triplet STE's to higher states causes an enhancement of F-center formation. Figures 1(e)-1(f) show results of such measurements in KCl at $T\approx10$ K, using the techniques described in the first part of this Letter. In Fig. 1(f) I show the STE absorption at 660 nm, which arises upon electron irradiation and is abruptly extinguished by 694-nm laser light. The absorption at the F-band peak (540 nm) under the same circumstances is shown in Fig. 1(e). In response to the electron irradiation, the absorption increases abruptly and then decays rather rapidly to a level which includes contributions to absorption from self-trapped excitons and from more stable F centers. Coincident with the laser pulse one can see an abrupt increase of absorption followed by a small replica of the initial F-band decay.

The crystal had not been irradiated prior to the recording of Fig. 1(e). As the delay between electron pulse and laser pulse was varied, the magnitude of the laser-induced F absorption decreased in approximate accord with the triplet-STE decay time (5 msec), leaving no residual response distinguishable above noise after 11 msec. Thus the growth of F centers associated with excitation of electrons from traps is negligible in this experiment if the crystal has not been previously irradiated.

The immediate state reached by 694-nm excitation of triplet STE's in KCl, according to the assignment $A2p\sigma_u,{}^3\Sigma_g^+$ in Ref. 4, would be the "$2p_z$" state suggested as the defect-forming level by Toyozawa.[11] However other recent models of F-center formation[10,12] invoking higher STE states in proximity to $A2p\sigma_u,{}^3\Sigma_g^+$ are also consistent with the present observations. Experiments using tunable excitation for population of selected higher STE states should help answer the question posed by the results of Ref. 8, on whether defects are formed in KCl before a recombining electron-hole pair reaches the level of the STE state $A2p\sigma_u,{}^3\Sigma_g^+$.

The processes I have described ought to occur quite generally following two-quantum band-gap excitation of halide crystals if the exciting laser wavelength overlaps transitions of the metastable relaxed excitons.

I wish to thank M. N. Kabler for many helpful discussions.

---

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

[2] J. U. Fischbach, D. Fröhlich, and M. N. Kabler, J. Lumin. 6, 29 (1973).

[3] K. S. Song, A. M. Stoneham, and A. H. Harker, J. Phys. C 8, 1125 (1975); A. M. Stoneham, J. Phys. C 7, 2476 (1974).

[4] R. G. Fuller, R. T. Williams, and M. N. Kabler, Phys. Rev. Lett. 25, 446 (1970); R. T. Williams and M. N. Kabler, Phys. Rev. B 9, 1897 (1974).

[5] M. J. Marrone, F. W. Patten, and M. N. Kabler, Phys. Rev. Lett. 31, 467 (1973); A. Wasiela, G. Ascarelli, and Y. Merle d'Aubigne, Phys. Rev. Lett. 31, 993 (1973).

[6] R. B. Murray, H. B. Dietrich, and F. J. Keller, J. Phys. Chem. Solids 31, 1185 (1970).

[7] M. N. Kabler, Phys. Rev. 136, A1296 (1964); R. B. Murray and F. J. Keller, Phys. Rev. 137, A942 (1965).

[8] J. N. Bradford, R. T. Williams, and W. L. Faust, Phys. Rev. Lett. 35, 300 (1975).

[9] Y. Kondo, M. Hirai, and M. Ueta, J. Phys. Soc. Jpn. 33, 151 (1972).

[10] M. N. Kabler, in *Radiation Damage Processes in Materials*, edited by C. H. S. Dupuy (Noordhoff, Leyden, The Netherlands, 1975), p. 171.

[11] Y. Toyozawa, in *Vacuum Ultraviolet Radiation Physics*, edited by E. E. Koch, R. Haensel, and C. Kunz (Pergamon, New York, 1974), p. 317.

[12] N. Itoh and M. Saidoh, J. Phys. (Paris), Colloq. 34, C9-101 (1973).

Spin Waves in the Cubic Ferrimagnet $Ho_{0.88}Tb_{0.12}Fe_2$ †

R. M. Nicklow
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

and

N. C. Koon, C. M. Williams, and J. B. Milstein
Naval Research Laboratory, Washington, D. C. 20390

(Received 12 January 1976)

Using neutron spectrometry we have investigated the magnon dispersion relation for the ferrimagnetic cubic Laves compound $Ho_{0.88}Tb_{0.12}Fe_2$ at room temperature and 12 K. The results are described surprisingly well by a very simple near-neighbor exchange model which includes only iron-iron and iron–rare-earth interactions, crystal field anisotropy, and temperature renormalization that is derived from the sublattice magnetization.

The magnetic properties of the rare-earth–iron compounds $R\mathrm{Fe}_2$, both in the crystalline Laves phase ($MgCu_2$ structure) and in the amorphous form, are currently of considerable interest. Extensive investigations of the amorphous form of $TbFe_2$ have recently been carried out by magnetic-susceptibility,[1,2] neutron-scattering,[2-4] and magnetic-resonance[5] measurements. These studies may be particularly valuable for the understanding of amorphous magnetism because of the possibility of comparing properties of the crystalline and amorphous forms of the same compounds. While such comparisons have led to new theoretical models,[6] they have depended on somewhat uncertain assumptions and speculations about the nature and magnitude of the exchange and anisotropy interactions in these compounds. Similarly, interpretations of the unusual spin-orientation phase diagrams for crystalline ternary alloys of the type $(R^1)_x(R^2)_{1-x}\mathrm{Fe}_2$, recently measured as a function of x and temperature by Mössbauer-effect[7] and torque-magnetometry[8] techniques, have been based on incomplete information about these magnetic interactions.

In this Letter we present the first measurements of the magnon dispersion relation in a rare-earth–iron compound—$Ho_{0.88}Tb_{0.12}Fe_2$. To date, there have been no other experimental results which could give direct information on the exchange interactions in these materials. The only previous data on the magnetic excitations were obtained from neutron scattering on polycrystalline and amorphous samples of $TbFe_2$.[2,4]

The experiment was carried out on a three-axis neutron spectrometer at the high-flux isotope reactor of the Oak Ridge National Laboratory, by using the standard techniques of coherent neutron inelastic scattering. The energy of

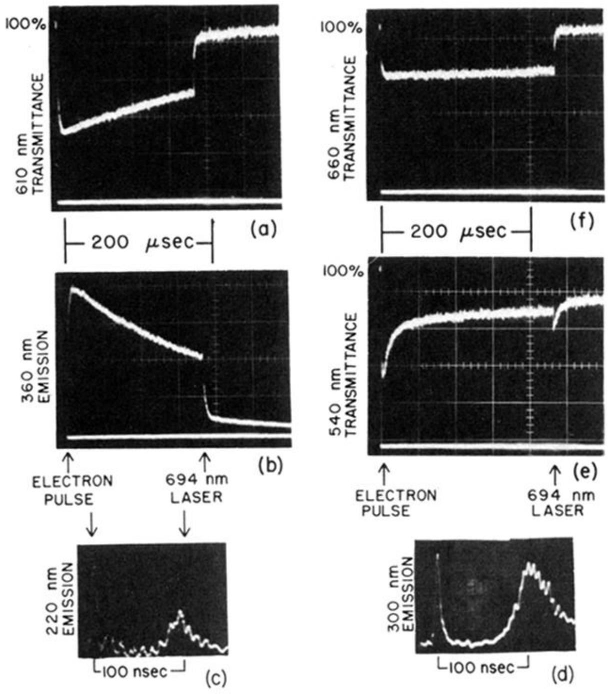

FIG. 1. (a)–(c) Optical response of NaCl at low temperature to a pulse of energetic electrons followed by a pulse of 694 nm light. Fluorescence in KI resulting from an electron pulse and subsequent 1.06-μm laser pulse is shown in (d). Optical transmittance of KCl at low temperature is shown for 540 nm (e) and for 660 nm (f) in response to a pulse of energetic electrons followed by a pulse of 694 nm light.