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Energy Transfer and Optical Properties of Tl^+ Centers in NaI(Tl) Crystals*

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Excitation and luminescence emission spectra of NaI(Tl) single crystals with high Tl content (>0.1 mole%) have been analyzed as a function of temperature and concentration. At high Tl concentrations, both single and dual Tl centers influence the optical properties of the crystal. We have found evidence that energy absorbed in the dimer bands is transferred to nearby monomer centers, which then emit it as perturbed or unperturbed monomer emission; the perturbation diminishes and finally vanishes with decreasing temperature.

INTRODUCTION

ALTHOUGH the Tl impurity in alkali halide crystals has been investigated for more than 30 years, some of its basic characteristics, such as the nature of the state responsible for the Tl-related luminescence of Tl phosphors, are still not quite understood and are the subject of some controversy.[1,2] Moreover, the behavior of the absorption and luminescence of the Tl center with temperature and Tl concentration is rather complex and requires a considerably more sophisticated approach for its explanation than the original Seitz model.[3]

At high Tl concentrations the situation is complicated by the appearance of the dimer center, made of two Tl ions interacting with each other. The dimer center was discovered by Yuster and Delbecq[4] in KI(Tl) and by Van Sciver[5] in NaI(Tl). Up to now it was thought to have a $\langle 110 \rangle$ orientation,[6] but very recent evidence[7] shows that, at least for NaI(Tl), it has a $\langle 100 \rangle$ orientation; this has been found to be true also for Ga dimers.[8] The dimer center introduces a new set of absorption and emission bands in the optical spectra of the phosphor and is thought to play an important role in the scintillation process in NaI(Tl).[9]

Most investigations on the subject of the Tl luminescent center have been performed on potassium halides; NaI(Tl) has not been investigated as extensively because of the added experimental difficulty of its high hygroscopicity.

In this paper we present an investigation of absorption and emission spectra in NaI(Tl) for temperatures ranging from room temperature (RT) to liquid-helium temperature (LHeT), and for Tl concentrations ranging from 0.1 to 4 mole%.

EXPERIMENTAL

The light source was a Gates deuterium lamp. Its output was focused by a LiF lens condensing system onto the slit of a grating monochromator which could be driven with a synchronous motor. The output was focused onto the sample by a LiF lens. The sample was maintained at any desired temperature between RT and LHeT by a helium-exchange research cryostat made by Andonian Associates. The sample temperature was measured with a carbon resistor. The crystal luminescence was viewed at 90° and focused by a quartz lens onto the slit of an Engis grating monochromator the output of which was focused on an EMI 9502–S phototube. The phototube output was fed into a lock-in amplifier (made by Princeton Research Associates) which drove a Varian servo-recorder and also provided the lamp modulation necessary to use the lock-in amplifier. The excitation monochromator band pass was set at 1.6 nm, and the emission monochromator band pass was set at 17 nm.

The spectra were taken in the form of excitation and emission spectra. An excitation spectrum was taken by setting the emission monochromator at the desired wavelength and scanning with the excitation monochromator. An emission spectrum was taken by setting the excitation monochromator at the wavelength of interest and scanning with the emission monochromator. All the spectra reported in this paper depict the phototube signal versus light energy.

The Tl concentration was determined by a spectrophotometric method adapted by us for use with NaI(Tl) from a standard method for detecting traces of Tl in organic materials.[10] The precision is of a few percent. All our crystals were furnished by the Harshaw Chemical Co.

As mentioned above, a major difficulty in working with NaI(Tl) is its high hygroscopicity. Therefore, care must be taken that the sample never comes in contact

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with room air. In order to transfer the sample from the dry box, where it is stored, into the cryostat, the following procedure was followed: The sample, freshly cleaved on all surfaces, is loaded onto the sample holder inside the dry box. The sample holder is attached to a $\frac{1}{4}$-in.-diam stainless-steel tube, the length of which is such that when the crystal is in position in the optical cavity of the cryostat, the tube extends out of the top of the cryostat. The tube is suspended from an O-ring compression seal connected by a second O-ring seal to a 1-in.-i.d. Pyrex tube, which in turn is connected by another O-ring seal to a 1-in. ball valve. This latter is finally connected to the top of the dry box by an O-ring junction. In this arrangement the assembly in effect extends the dry box to accommodate the long stainless-steel tube. After the sample is loaded, the sample holder is raised until the sample is inside the Pyrex tube, and the valve is closed. The assembly is then disconnected from the dry box and placed on top of the cryostat. The O-ring seal was designed so that it could seal either the junction at the top of the dry box or the junction with the top of the cryostat. After having expelled the room air between the top of the cryostat and the valve with the aid of the evaporating refrigerant gas, the valve is opened and the crystal is lowered into the sample chamber. The procedure is speedy and has been found to be reliable by making repeated transfers using the same sample.

RESULTS

In Fig. 1 we report excitation spectra for 420- and 325-nm luminescence emission[11] taken at 160°K. In the figure we have marked the positions of the A, B, C, A′, B′, C′ bands (primes refer to dimer bands). We see that the single Tl (monomer) bands emit only at 420 nm, whereas the dimer bands, although emitting predominantly at 325 nm, show some emission in the 420-nm region; this is especially evident with regard to the B′ band.

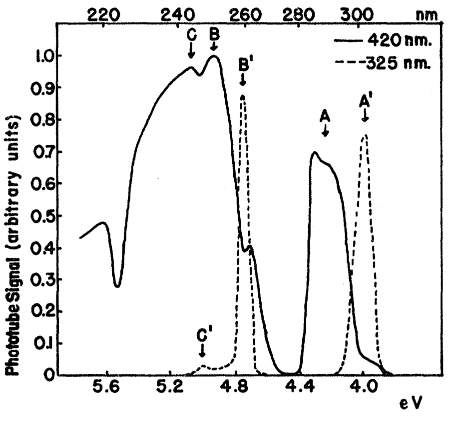

FIG. 1. Excitation spectra for 420-nm luminescence (solid line) and 325-nm luminescence (dashed line) at $T=160$°K. Tl concentration: 0.7% wt.

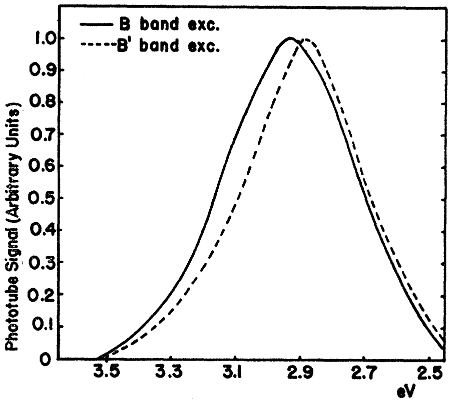

FIG. 2. Emission spectra, in the monomer luminescence region, for excitation in the B band (solid line), and in the B′ band (dashed line); $T=160$°K. Tl concentration % wt: 0.7 % wt.

In Fig. 2 are the luminescence emission spectra for excitation in the B and B′ band, respectively, for $T=160$°K. The B light emission peaks at 420 nm, whereas the B′ light emission peaks at 428 nm. This result was previously reported for the A and A′ bands by Uchida and Matsui[6]; they then postulated that the dimer center had two separate emitting states.

We have measured the luminescence yield of the 428-nm "dimer" luminescence emission for samples containing various Tl concentrations and have compared it to the corresponding yield for the 325-nm dimer luminescence emission. If the assumption of Uchida and Matsui is correct, the luminescence yield ratio should be independent of Tl concentration. According to our data, it is not so. In Fig. 3 we report the

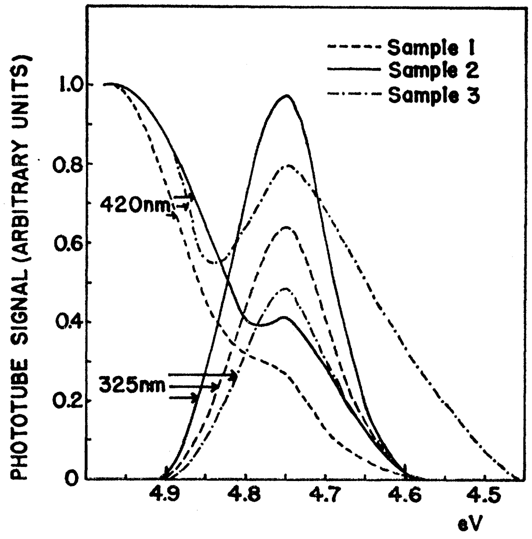

FIG. 3. Excitation spectra for emission at 420 and 325 nm for crystals of different concentrations: dashed line, 0.15 % wt; solid line, 0.7 % wt; dash-dot line, 3 % wt. $T=160$°K.

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[11] Hereafter, we shall qualify luminescence emission bands by their peak position.

excitation spectra for 428- and 325-nm emissions for three samples of differing Tl content. The spectra were taken at 160°K and were both normalized to the peak intensity of the B band.

The peak intensity of the B band is a good normalization point because in the concentration range of our samples the absorption coefficient in the B band region is so large that the monomer luminescence yield is practically independent of Tl concentration. Figure 3 shows that the luminescence yield for 325-nm emission increases in going from crystal 1 (0.15% weight) to crystal 2 (0.70% weight). On the other hand, the yield decreases for crystal 3 (3% weight). Since the absorption coefficient in the B′ band varies as the square of the Tl concentration, one should expect the luminescence to vary likewise. The fact that this is not observed can be attributed to two factors: One is that, as can be seen from the absorption spectra reported in Fig. 4, the absorption at the B′ band peak is almost total even for crystal 1. Because of this, one begins to have the situation already present with regard to the monomer luminescence yield which in our concentration range is effectively independent of Tl concentration. The second factor is, anticipating some of the conclusions we shall reach in the discussion of our data, represented by the transfer of energy from excited dimer centers to nearby monomer centers. The transfer efficiency increases with the Tl concentration, and therefore it is to be expected that luminescence yield at 325 nm will be decreased by this effect.

Another peculiarity in the behavior of the dimer excitation bands is that the A′ band does not behave like the B′ band as the Tl concentration is increased. We have found that the A′ bands for crystals 2 and 3 have the same intensity in contrast to the behavior of the B′ bands. This behavior is peculiar because one would expect the peak ratio of the B′ to the A′ band to be independent of Tl concentration. We can explain this peculiarity by the same arguments used to explain the behavior of the B′ band. In fact, the over-all absorption in the A′ band region is not as high as in the B′ band region, so that the saturation of the 325-nm luminescence will take place at higher Tl concentrations; also, as we shall see later on, the energy transfer efficiency is lower in the A′ band than in the B′ band, so that the loss of 325-nm luminescence because of energy transfer will be appreciable at higher Tl concentrations.

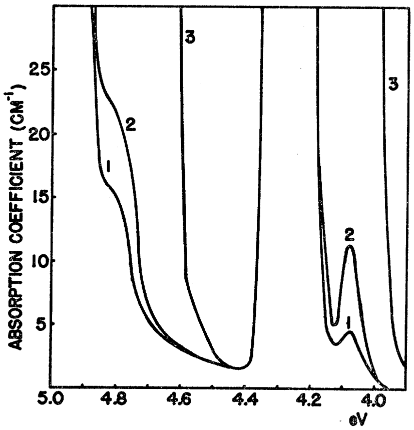

FIG. 4. Absorption spectra of the samples, taken at LNT. (1) 0.15% wt; (2) 0.7% wt; (3) 3.0% wt.

For all the above-mentioned reasons, a direct comparison between luminescence yields at 428 and 325 nm for excitation in the B′ band as a function of Tl concentration would not be very meaningful. On the other hand, the basic result is that the yields at 428 and 325 nm do not increase at the same rate as the Tl concentration is raised, and that the 428-nm luminescence yield increases strikingly as the Tl concentration is increased, as can be seen from Fig. 3.

These facts indicate that the 428-nm luminescence excited by B′ and A′ band absorption is not a dimer emission, at least in the same sense that the 325-nm luminescence is a dimer emission.

We have also followed the behavior of the 420- and 428-nm luminescence emissions, with regard to peak position and half-width, as the crystal temperature was lowered all the way down to LHeT. The excitation of the 420-nm luminescence emission was done on the high-energy side of the B band, and also on the A and C band regions for control purposes. Excitation of the 428-nm luminescence emission was done at various wavelengths, starting from the peak of the B′ band [4.84 eV at liquid-nitrogen temperature (LNT)] through 4.59 eV (270 nm). No appreciable difference was noted in the shape of the emission spectra for the various excitation wavelengths in crystals Nos. 1 and 2. Also, the peak intensity of the 428-nm emission seemed to follow the shape of the B′ band. In this respect we must note that the 420- and 428-nm emissions cannot be discriminated by the emission monochromator, as an inspection of Fig. 2 will readily show; therefore, the corresponding excitation spectra will actually be composed of the excitation spectrum for the 420-nm emission and the excitation spectrum of the 428-nm emission. When the same measurements were performed on crystal 3, the 428-nm emission spectra varied with the excitation wavelength. In particular, although excitation in the peak region of the B′ band still yielded the same 428-nm emission spectrum as for crystals 1 and 2, excitation in the 4.6- to 4.5-eV region yielded an emission peaking at 445 nm. An excitation spectrum for this emission (taken with the emission monochromator band pass reduced to 8 nm) revealed a main excitation band peaked at 4.62 eV (268 nm). Absorption spectra taken for our samples (Fig. 4) revealed that the absorption shape in the 4.5- to 4.7-eV region varies in going from low to high Tl concentrations. It seems that at very high Tl concentrations a new center appears, which absorbs at 4.62 eV (and possibly at higher energies too) and emits at 2.79 eV (445 nm) at LNT. Since when taking the excitation spectra it is not possible to discriminate completely between the 428- and the 445-nm emissions (the half-width of the 445-nm emission at LNT is 0.44 eV), the presence of the new center (possibly made of aggregates of Tl ions) will alter the shape of the low-energy part of the excitation band for the 428-nm emission in the most heavily concentrated crystals.

In Table I the half-width and peak position of the 420- and 428-nm emissions are reported for various temperatures. We note the striking result that the two emissions coalesce for temperatures below about 40°K.

A good handle in the understanding of a luminescent state is offered by the measurement of its decay mode. We have therefore endeavored to measure the decay time of the 428-nm luminescence. The experimental setup was described by Herb *et al.*[7] The decay time was found to be roughly the same as that for the 420-nm emission, and showed the same behavior with temperature. In both these characteristics it is very different from the decay time of the 325-nm emission, which is less than 7 nsec and does not depend on temperature.[7]

DISCUSSION OF THE RESULTS

The data reported in Fig. 3 show that the 428-nm emission excited by absorption in the B′ band cannot be attributed to dimer centers in any simple way. Indeed, its decay time and general peak position and band shape indicate that it is rather similar to a monomer emission. We therefore believe it to be an emission from a monomer located close to a dimer center; because of its proximity to a dimer center, the monomer emission will be perturbed. The perturbation seems to be temperature-dependent because, for temperatures below about 40°K, this emission and the emission excited by A, B, and C band light have the same peak position and half-width. At low enough temperatures the two emissions are indeed one and the same, at least as far as their main characteristics are concerned, and can be attributed to the monomer center. This means that there is an energy transfer from the dimer center to a nearby monomer center. In this case, there will be an average interaction distance for this transfer to take place, and the probability that a monomer be at or within this distance will naturally depend on Tl concentration. We should therefore expect a dependence of the quantum efficiency of the transfer[12] luminescence on the Tl concentration. This is indeed what is observed experimentally.

TABLE I. Peak positions and half-width of luminescence excited by B and B′ band light as a function of temperature.

	B band excitation		B′ band excitation	
T (°K)	Half-width (eV)	Peak pos. (nm)	Half-width (eV)	Peak pos. (nm)
180	0.44	420	0.41	428
125	0.40	423	0.39	428
64	0.26	427	0.26	430
25	0.20	430	0.20	430

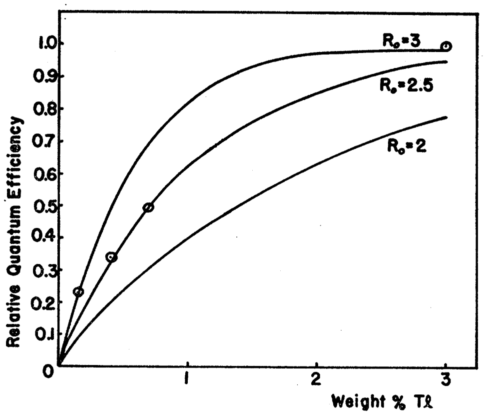

FIG. 5. Theoretical quantum efficiency for transfer luminescence versus Tl concentration for various values of R_0. Our experimental points are also depicted. (R_0 is in units of a, the lattice parameter, and is therefore dimensionless.)

Furthermore, because of the nearness of the monomer to the dimer, the vibrational lattice modes with which it interacts will be perturbed, leading to a perturbed relaxed excited state; the extent of the perturbation, however, would be expected to decrease with decreasing temperatures, since the perturbation is essentially due to a coupling between monomer and dimer via lattice vibrations. This would explain the coalescing of the transfer and monomer emissions as the temperature is lowered. We can try to predict the behavior of the quantum efficiency versus concentration on the basis of our transfer model by using the same formalism used by Miehlich in his work on the concentration dependence of F-center luminescence.[13] According to its results with our model, we would expect the quantum efficiency for transfer luminescence to go as $1-\exp(-0.062R_0^3c)$, where R_0 is a characteristic length measured relative to the lattice parameter, c is the Tl concentration, and $(16\pi/3)(1/a^3)=0.062$, where a is the lattice constant. R_0 essentially describes how close a monomer has to be to interact with the dimer. In Fig. 5 we plot $f(c)=1-\exp(-0.062R_0^3c)$ versus c for various values of R_0. On the same figure are also our experimental points. We can see that the data roughly follow the theoretical curve; we can also conclude that the value for R_0 will lie between 2 and 3 lattice parameters as the mean interaction distance.

Finally, we note that the energy transfer is much more efficient for the B′ band than for the A′ band; this may be due to the fact that the B′ excited states are more diffuse than the A′ excited states.

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[12] By transfer luminescence we shall mean the luminescence at 428 nm excited by B′ band light.

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CONCLUSION

We have analyzed excitation and emission spectra of NaI(Tl) at high Tl concentrations as a function of temperature and concentration. The main result we have obtained is the evidence for an energy transfer from dimer centers to nearby monomer centers. This evidence consists of the behavior of the quantum efficiency of the transfer luminescence versus Tl concentration, of the coalescing of monomer and transfer luminescence peak positions and half-widths at LHeT, and finally of the essentially equal value of their decay times.

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Lattice Vibrations of Yttrium Vanadate*

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The lattice vibrations of YVO_4 have been analyzed group-theoretically, and symmetry coordinates for the vibrations have been constructed. The first-order Raman spectrum is reported in detail and preliminary results of infrared (IR) measurements are given. Six of the seven allowed IR-active modes and nine of the twelve allowed Raman-active modes have been observed. Symmetry assignments are given for all observed modes.

I. INTRODUCTION

YTTRIUM vanadate has recently emerged as a material of considerable interest as a host for phosphors and solid-state lasers as well as for the study of rare-earth ions in general. In this paper we present the results of an infrared and Raman study of the vibrational spectrum of YVO_4 and its interpretation in terms of symmetry coordinates in the YVO_4 lattice.

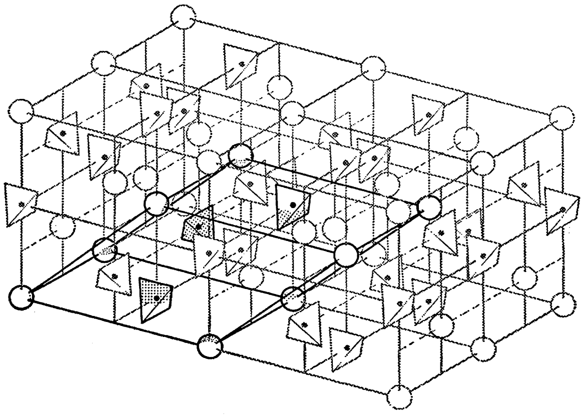

FIG. 1. The crystal structure of YVO_4. One choice for the primitive cell is shown in heavy lines with the part of each ion belonging to this cell shaded. Yttrium atoms are shown as circles and VO_4^{-3} ions as tetrahedrons.

YVO_4 crystallizes in the D_{4h}^{19} structure of zircon.[1] This structure is tetragonal with a c/a ratio of 0.883 and is not optically active. The primitive cell contains two molecules as shown schematically in Fig. 1.

A number of crystals with structure similar to YVO_4 have already been studied. In particular, we might cite Richman's Raman study[2] and Mooney and Toma's infrared work[3] on YPO_4. Analogous work on crystals of the scheelite (C_{4h}) structure has been reported by Russell and Loudon,[4] Porto and Scott,[5] and Barker.[6]

In the following sections we present a group-theoretical character analysis of the vibrational modes of YVO_4, showing how some of the lattice modes derive from the internal vibrations of the VO_4^{-3} complex. Symmetry coordinates are worked out for the allowed modes. The Raman and IR spectra of this material are described and in the final section we discuss the assignment of the observed modes to the various allowed symmetry species of the lattice.

II. GROUP THEORY

The two YVO_4 molecules per primitive cell in the D_{4h} zircon structure support $3\times2\times6=36$ modes of

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