PHYSICAL REVIEW B VOLUME 35, NUMBER 16 1 JUNE 1987

Spectroscopic studies of excited Tm^{3+} ions in alkaline-earth fluorides

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(Received 1 December 1986)

The vacuum-ultraviolet absorption of CaF_2, SrF_2, and BaF_2 crystals doped with Tm^{3+} and illuminated with infrared radiation was investigated. Transitions involving the absorption of two successive photons were observed. The lifetime in the $^3H_4$ multiplet of Tm^{3+} ions present in clusters in these hosts was investigated as a function of temperature.

INTRODUCTION

In a recent publication,[1] we have studied the vacuum-ultraviolet (VUV) absorption of CaF_2:Tm^{3+} crystals illuminated with infrared (IR) radiation. Transitions involving the absorption of two successive photons were observed. The first excites the ion within the $4f^{12}$ configuration while the second promotes an electron into the $5d$ shell.

It became evident that under suitable conditions a transition from an excited state of the $4f^n$ configuration to one of the $4f^{n-1}5d$ configuration is amenable to observation via optical absorption. The study yielded a lifetime of 140 ms at liquid-nitrogen temperature in the $^3H_4$ multiplet of Tm^{3+} ions present in clusters in the CaF_2 host. (We, as most authors[2] do, call the first excited state of thulium $^3H_4$ in spite of the fact that the eigenvector contains only 7% squared amplitude of this component but 65% $^3F_4$.) Our work also led to the conclusion that it is the final $4f^{11}5d$ state that interacts with the lattice giving rise to the local phonon frequency.

The present work is an extension of the work reported in Ref. 1, in three different ways. First, we expanded the studies of the excited Tm^{3+} ion in CaF_2 to include measurements at liquid-helium temperature. Second, we extended our studies to involve SrF_2 and BaF_2 as hosts for the Tm^{3+} ion. The three constitute a complete series of hosts with the calcite structure in which Re^{3+} ions can be investigated in VUV. A comparison of the results in the different hosts helps clarify the role of the lattice in determining the frequency of the local phonon mode. Third, in our work we determined the temperature dependence of the lifetime in the $^3H_4$ multiplet of Tm^{3+} in either of the three hosts. The results help elucidate the possible relaxation mechanisms from the $^3H_4$ to the $^3H_6$ ground multiplet. In spite of the great complexity of the spectra under study, we are able to contribute to the understanding of the electron-phonon interactions in these systems.

EXPERIMENTAL

Crystals used in this work were grown and supplied by Optovac Inc. Those were randomly oriented and were used as received except that samples of the proper dimensions were prepared by either cleaving or cutting and subsequent polishing. Impurity concentration values are given in atomic percentage present in the growth melt.

The experimental setups and procedures were essentially the same as in Ref. 1. In the course of the present work only a few modifications were introduced. In a brief summary, the Tm^{3+} ions were excited using infrared (IR) radiation produced by a 200-W tungsten halogen lamp with a gold-coated reflector. The IR light was chopped with a frequency of 0.5 Hz. The spectral range of the IR light extended from about 1.05 μm, the switch-on wavelength of the cryostat silicon window (0.25 mm), up to about 3.5 μm, the cutoff wavelength of the quartz envelope of the halogen lamp. The sample ($5\times5\times10$ mm^3) was sandwiched between a cooled sapphire plate and the crystal holder in order to secure an adequate cooling of the crystal sample even under strong IR illumination. The cryostat itself was specially designed for work in the full range between liquid helium and room temperatures. It was mounted in front of the exit slit of a McPherson model No. 225 vacuum monochromator. A home-built microwave xenon-gas lamp served as a source of the VUV radiation. The temperature was monitored using a Ge thermometer. The monochromatic VUV beam transmitted by the sample was detected by a solar-blind, Hamamatsu model No. R1460 photomultiplier. This was followed by electronics operated in a single-photon-counting mode. The resulting counts were accumulated during many periods of the IR chopping using a multichannel analyzer (Nuclear Data model No. 2400) until a sufficient signal-to-noise ratio was attained. The main source of noise was the slight instability in the VUV lamp. The time evolution of the VUV light transmitted by the sample was analyzed resulting in the determination of lifetime values.

The VUV spectrum of the excited Tm^{3+} ion was determined as a function of the wavelength (point by point) using two photon counters (Ortec model No. 3315) gated synchronously with the chopper. The first count of the VUV photons was when the IR radiation was on, while the other when it was off. The transmittance of the sample at a particular wavelength was calculated as a ratio of counts registered by these two counters. In order to increase the accuracy, counts were integrated over 60 chopper periods. The final content of each counter was of the order of 10^7 counts. Thus an accuracy of better than 0.1% was achieved.

RESULTS

Figures 1(a) and 1(b) correspond to the lowest energy $4f^{12}$-$4f^{11}5d$ transitions from the ground states in SrF_2:Tm^{3+} and BaF_2:Tm^{3+}, respectively. The spectra were recorded with the crystals near liquid-helium temperature (5 K). The impurity concentration in the 2-mm-thick crystals is 0.01%. The different absorption peaks are numbered for identification purposes. It is worth noting that the two spectra bear a great deal of similarity to each other except that peak 5 is missing in the BaF_2:Tm^{3+} case, and the spectra are shifted by about 400 cm^{-1} with respect to each other.

Figures 2(a) and 2(b) are the VUV absorption spectra of 5-mm-thick IR-excited SrF_2:Tm^{3+} and BaF_2:Tm^{3+} crystals with an impurity concentration of 1 at. % taken at 77 K. Note the presence in each of two prominent (zero-phonon) peaks *A* and *B* in addition to two less pronounced (local-phonon) ones separated by 420 cm^{-1} in the case of the SrF_2 host and 400 cm^{-1} in the case of BaF_2, from their parent peaks. Figures 3(a)–3(c) depict the same spectra as in Fig. 2 except that they were taken at 8 K and they include a curve [3(a)] corresponding to CaF_2:Tm^{3+}. The difference of temperature between the IR excited and the ground-state VUV spectra (Fig. 1) is caused by the intense IR illumination in the former case which is absent in the latter.

Figure 4(a) 4(b), and 4(c) represent the near-IR absorption spectra of Tm^{3+} in CaF_2, SrF_2, and BaF_2, respectively. Spectra were taken at 8 K and crystal samples were the same as in Figs. 2 and 3. The absorption in these is attributed to $4f^{12}$-$4f^{12}$ transitions between multiplets ${}^3H_6$-${}^3H_4$. We indicate on the figures specific wavelengths such as *A*1, *B*2, etc. The designation corresponds to the possible spectral position of the level from which the IR excited transition (shown in Figs. 2 or 3) originates.

Figure 5 shows the temperature dependence of the lifetime in the ${}^3H_4$ multiplet of the Tm^{3+} ions in each of the

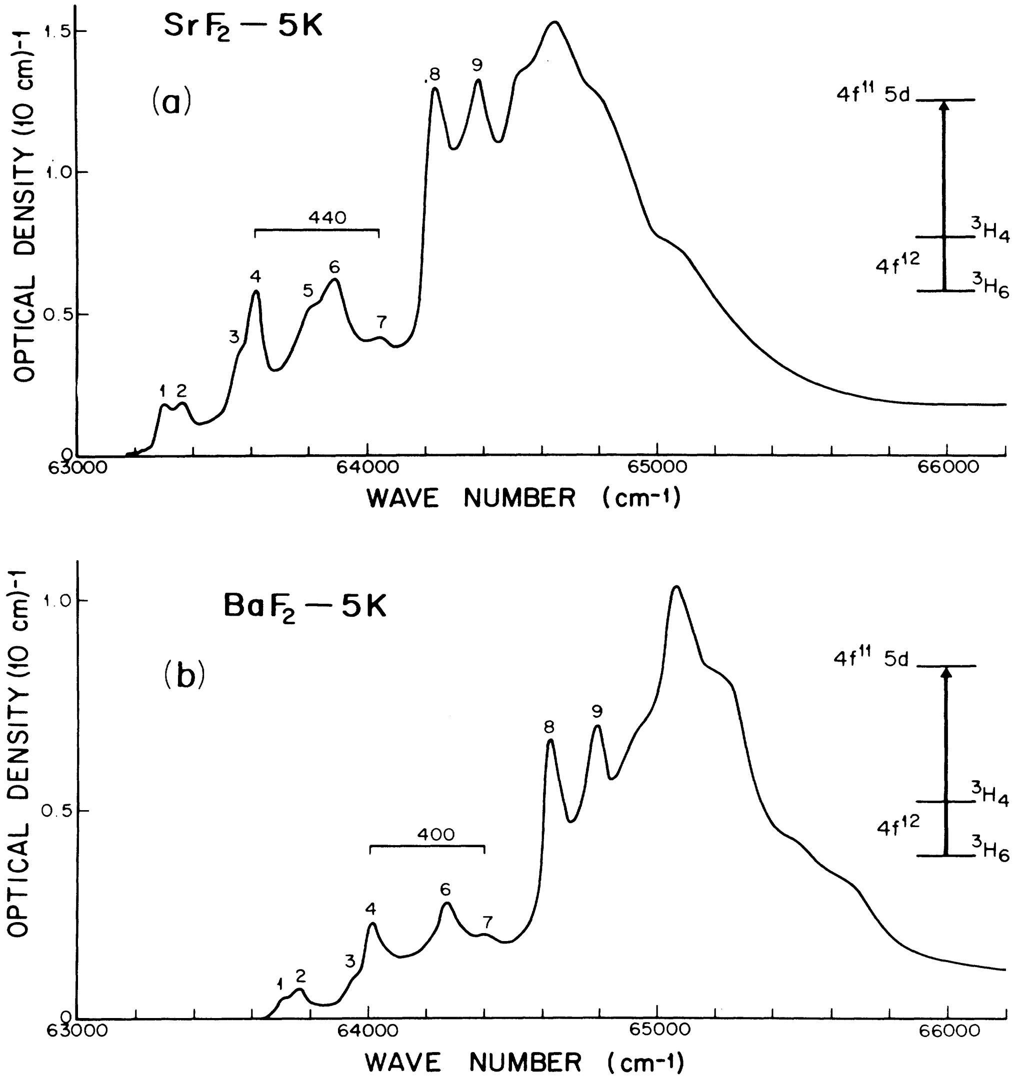

FIG. 1. Vacuum-ultraviolet absorption spectrum at 5 K of (a) SrF_2:Tm^{3+}; (b) BaF_2:Tm^{3+}. Impurity concentration of 0.01 at. % and sample thickness of 2 mm.

hosts CaF_2, SrF_2, and BaF_2. The lifetime was determined using the absorption peaks designated A in either Figs. 2 or 3. Actually, using peaks B yielded in each case an identical value, as did using essentially any part of those absorption spectra.

DISCUSSION

As stated previously,[1] the spectra presented in Fig. 1 are attributed to the lowest $4f^{12}(^3H_6)$-$4f^{11}5d$ transitions in the Tm^{3+} ions in the corresponding host. Due to the complexity and mutual close proximity of the component peaks, it is difficult to reliably identify zero-phonon lines and their phonon sidebands as was possible to some extent in the parallel case of the CaF_2 host. It is, however, plausible to associate peaks 4 and 7 with such an identification. The separation between the two in the case of SrF_2 [Fig. 1(a)] is ~ 440 cm^{-1}. In the case of BaF_2 [Fig. 1(b)], it is ~ 400 cm^{-1}. Both values agree well with the corresponding local phonon frequencies[3] in these hosts.

The spectra presented in Fig. 2 correspond to the transition $4f^{12}(^3H_4)$-$4f^{11}5d$ in the Tm^{3+} ion in the corresponding host. In both cases, SrF_2:Tm^{3+} [Fig. 2(a)] and BaF_2:Tm^{3+} [Fig. 2(b)], it is possible to identify two zero-phonon lines (peaks A and B) and their accompanying ~ 420 and ~ 400-cm^{-1} phonon sidebands, respectively. Figure 3, which is the same as Fig. 2, except for the crystal sample temperature, includes data [Fig. 3(a)] for the CaF_2 host as well.

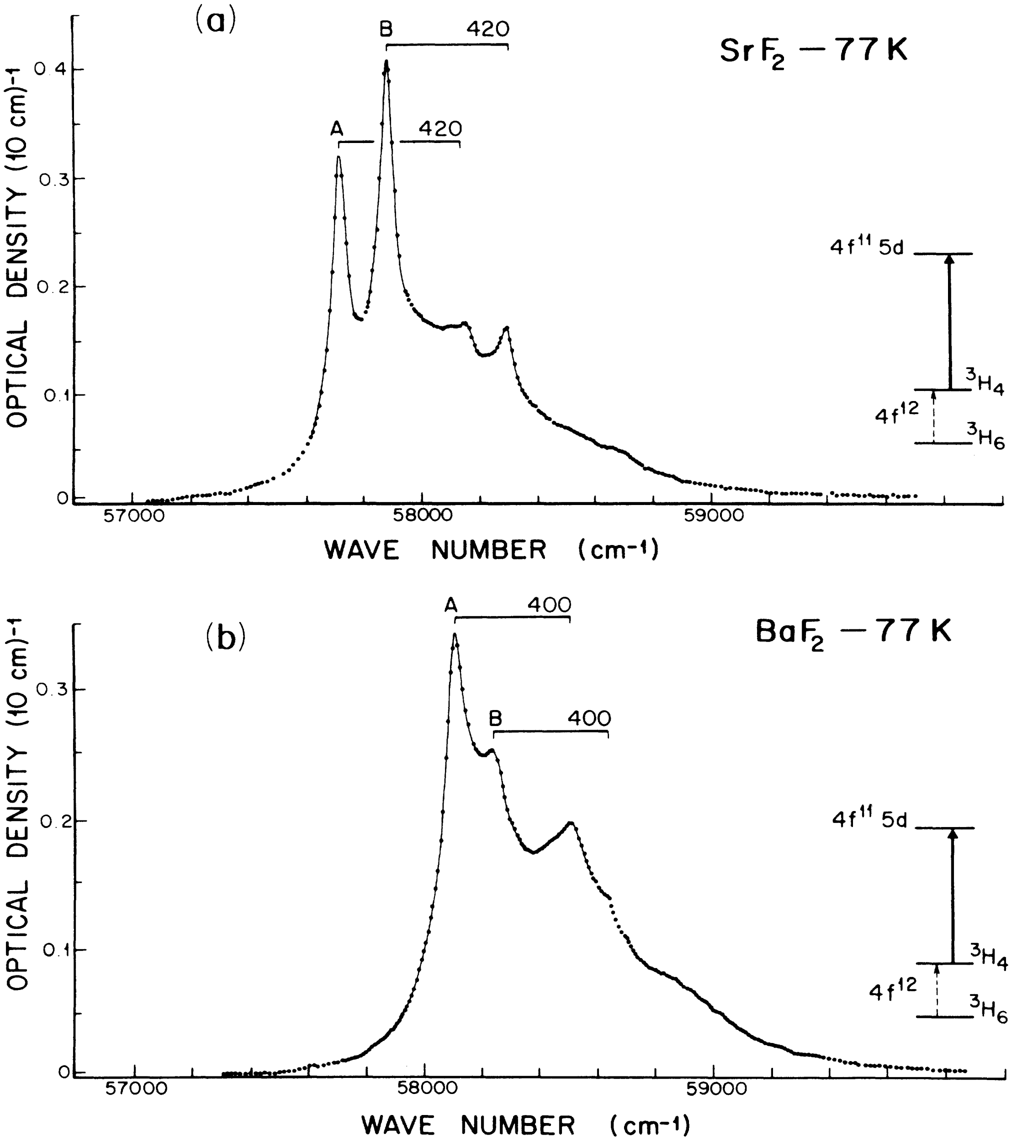

FIG. 2. Vacuum-ultraviolet absorption spectrum at 77 K of infrared illuminated crystals. (a) SrF_2:Tm^{3+}; (b) BaF_2:Tm^{3+}. Impurity concentration of 1 at. % and sample thickness of 5 mm. Note the energy values of the prominent spectral features as follows. (a): $A = 57\,710$ cm^{-1}; $B = 57\,875$ cm^{-1}. (b): $A = 58\,110$ cm^{-1}; $B = 58\,258$ cm^{-1}.

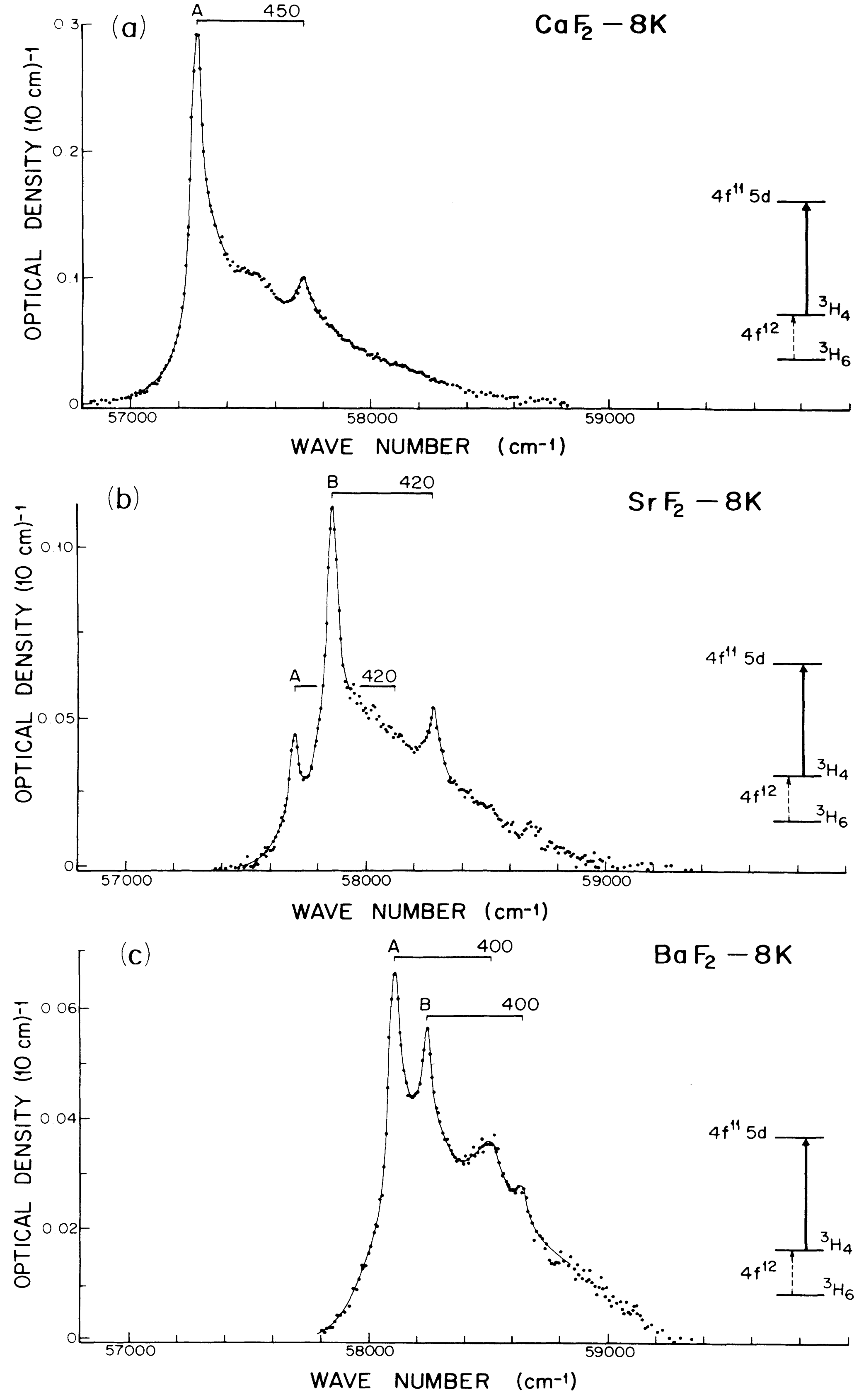

FIG. 3. Same as Fig. 2 except spectra taken at 8 K. (a) CaF$_2$:Tm^{3+}; (b) SrF$_2$:Tm^{3+}; (c) BaF$_2$:Tm^{3+}.

The spectra in these cases correspond to samples with high impurity concentrations (1 at. %). Previous results[1,4] show that in the case of relatively high impurity concentration, a tendency toward dopant clustering develops. As a result, a change in local mode frequency can be expected. In the case of CaF_2 the change from $\sim$480 to $\sim$450 cm^{-1} for the present (Tm^{3+}) ion is in excellent agreement with those observed[5] for Eu^{3+} and Pr^{3+} clusters. In the case of the SrF_2 host, the change is from $\sim$440 to $\sim$420 cm^{-1}. For the BaF_2 host the value of $\sim$400 cm^{-1} seems not to change. This fact may be explained by assuming that the Tm^{3+} dopants start to cluster in the BaF_2 lattice at low concentrations. Indeed Loh *et al.*[5] have noted a similarity between the $4f^2$-$4f5d\,|\,e_g\rangle$ absorption of BaF_2:Pr^{3+} (0.005%) and that of CaF_2:Pr^{3+} (0.5%). A similarity was also noted above between Figs. 1(a) and 1(b). Both these curves represent the same transitions in the Tm^{3+} ion, and since in both hosts (SrF_2 and BaF_2) we assume the presence of dopant clustering, the similarity is to be expected.

A careful comparison between Figs. 2(a) and 2(b) [also Fig. 3(b) of Ref. 1] and Figs. 3(a)–3(c) reveals some temperature-dependent effects in the absorption spectrum of the IR excited samples. In the CaF_2 host only one prominent component, line *A*, and its vibronic component are evident in the spectrum and no major changes occur as a result of passing from 77 to 8 K except that the spectrum is better resolved. [Compare Fig. 3(b) of Ref. 1 and Fig. 3(a) of the present work.] In the case of the SrF_2 and BaF_2 hosts, there are two prominent components (lines *A*

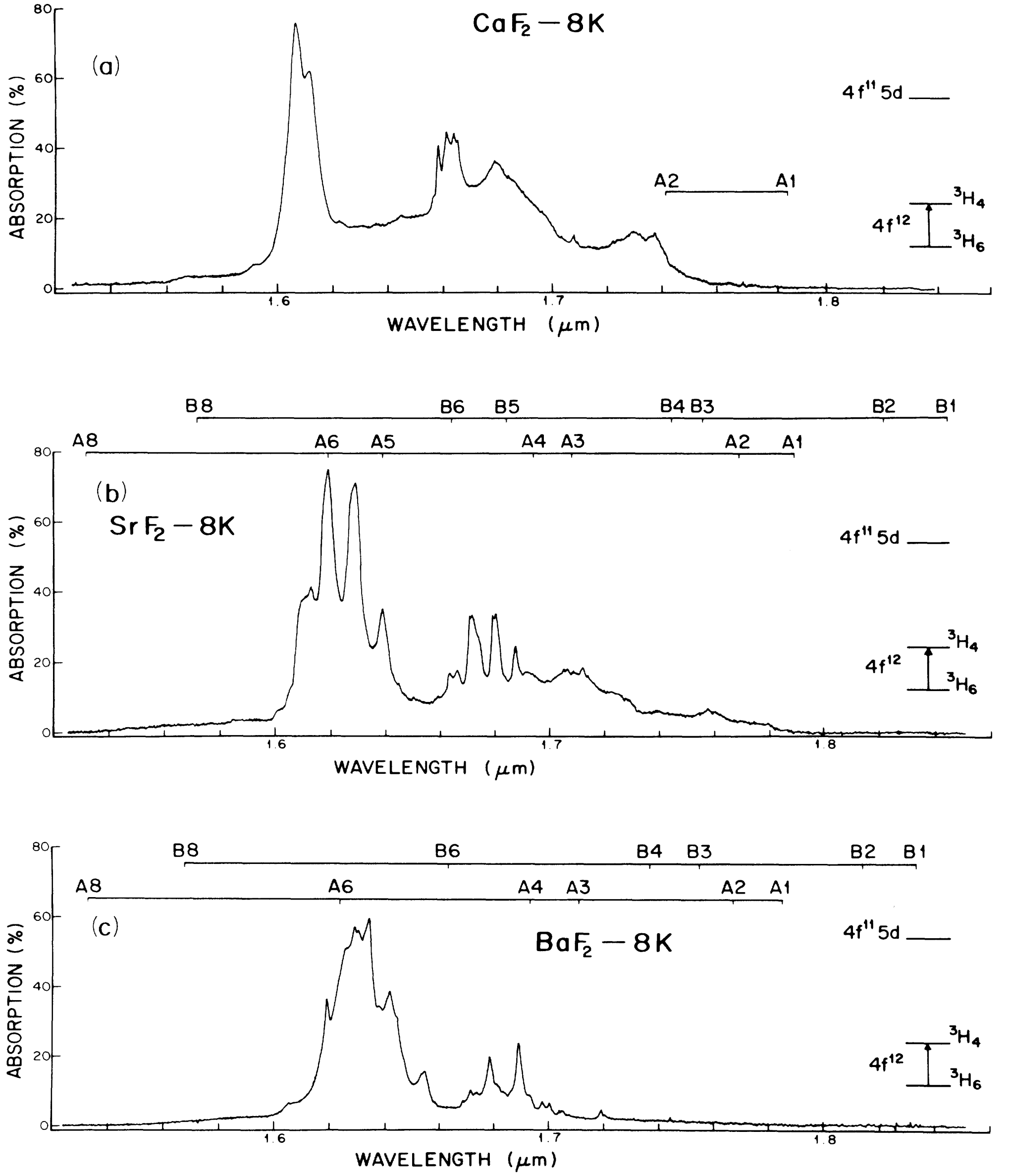

FIG. 4. Near-infrared absorption spectra at 8 K of crystals corresponding to Fig. 3. (a) CaF_2:Tm^{3+}; (b) SrF_2:Tm^{3+}; (c) BaF_2:Tm^{3+}.

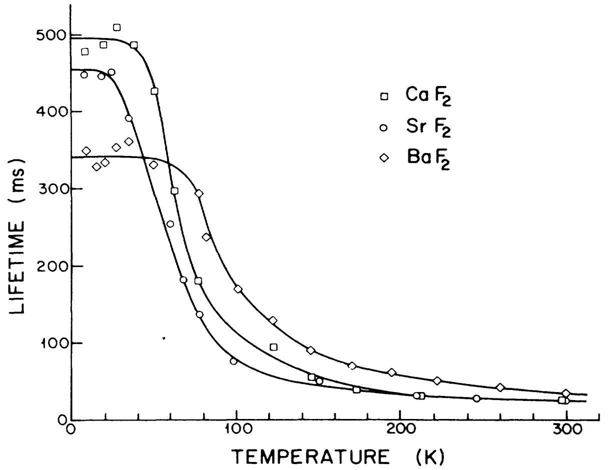

FIG. 5. Temperature dependence of lifetimes in the $^3H_4$ multiplet of Tm^{3+} in the hosts as indicated.

and *B*) and their respective vibronic components. In the SrF_2 host, cooling to 8 K results in the diminishing of component *A* (and its vibronic). This lends strong support to associating the two features in our manner [compare Figs. 2(a) and 3(b)]. In the BaF_2 host, the two components and their vibronics survive the cooling to 8 K [compare Figs. 2(b) and 3(c)]. The two components, we propose, represent the same ionic transition except possibly that of Tm^{3+} occupying two different sites. This could come about by the charge-compensating F^- ion hopping between two positions. In BaF_2, the openness of the larger BaF_2 lattice may allow hopping even at 8 K, whereas the smaller CaF_2 lattice does not allow it even at 77 K. In SrF_2 at a sufficiently low temperature, the contraction of the lattice freezes out one of the two possible sites.

The simultaneous presence of different impurity sites is to be expected.[6] What we observe here, however, is a new type of temperature dependent site symmetry, i.e., a site whose characteristic spectrum does not exist or is much diminished *below* a given temperature.

In each of the three hosts, the IR absorption spectrum exhibits some 20 absorption features while no more than 9 in the $^3H_4$ multiplet for any single ionic site can be expected. This indicates also that we are dealing with a number of sites present in our crystals.

Due to very fast relaxation within the $^3H_4$ multiplet,[7,8] only the lowest Stark component of each site at low temperature is populated. Therefore, the excited state (or states) from which the VUV absorption originates is expected to be located in the region of the long-wavelength limit of the IR absorption spectrum.

An attempt can also be made to spectrally locate the excited states using the VUV spectra. In the case of SrF_2, the zero-phonon peaks 1–9 (except 7) shown in Fig. 1(a) which are due to transitions from the ground state, determine the lowest $4f^{11}5d$ energy levels of SrF_2:Tm^{3+}. Subtracting from each of these energy values the amount absorbed in the excited state, i.e., the energy corresponding to the lines *A* and *B* [Fig. 2(a)], yields the possible locations of the excited states indicated in Fig. 4(b). Labels $A1, A2, \ldots, B1, B2, \ldots$ indicate which absorption peaks are involved. Locations *A*8 and *B*8 should be excluded because they are above the energy of the IR photons absorbed. If locations *A*1 and *A*2 are also excluded because of the low intensity of lines 1 and 2 and thus the low concentration of specific centers, the remaining positions fit well within the general IR absorption band.

The same procedure applied to BaF_2:Tm^{3+} and to CaF_2:Tm^{3+} yields similar results [see Figs. 4(a) and 4(c)]. In the case of the SrF_2 host, no two lines could be found in the ground-state spectrum [Fig. 1(a)] separated by the same amount of energy as the *A*-*B* separation in the excited-state spectrum [Fig. 2(a)]. Therefore, a single excited level is not sufficient to explain the observed excited-state spectrum. This supports the assumption that the two suggested ionic sites are such as to have different excited states. The same applies to the BaF_2 host.

The extremely long lifetime of the excited state may very well mean that the coefficient of spontaneous emission is very low, which in turn, according to the Fuchtbauer-Ladenburg formula,[2] means that the intensity of the absorption line should be very low. Therefore only the weakest lines (if any at all) in the IR absorption spectrum should be associated with the locations of the excited states. This makes a precise determination very difficult.

In Fig. 5, the temperature dependence of the lifetime values, as indicated in the preceding section, are given. The relatively high lifetime values[1] were attributed by us in the case of CaF_2:Tm^{3+} to the effects of impurity ion clustering. In other words these unusually long lifetimes (in all three hosts) come about through a series of resonance energy transfers among members of clusters. The partial or complete trapping of resonance radiation lengthens the apparent lifetimes of states which radiate to the ground state ($^3H_6$) of the ion. This requires that "true" lifetime measurements be made at low impurity concentrations where accuracy would suffer due to weak signals and poor statistics.

The probability for energy transfer involving deexcitation of an ion and excitation of another is given by

$$P_{1,2}=\frac{1}{\hbar^2}\,|H_{1,2}|^2\int g_1(\bar{\nu})g_2(\bar{\nu})d\bar{\nu}\ , \qquad (1)$$

where $g_1(\bar{\nu})$ are normalized line-shape functions associated with the two (absorption, emission) transitions and $H_{1,2}$ is the ion-ion interaction Hamiltonian. The different possible transitions and relaxation paths are dependent upon lattice temperature. Thus temperature-dependent lifetimes can be expected to occur as a result of the following.

(1) Phonon-assisted radiative transitions.

(2) Single and/or multiphonon nonradiative decay.

(3) Thermal population of nearby levels which have different decay rates.

(4) Decreased radiation trapping caused by changes in the emission and absorption line shapes or line shifts [see expression (1)].

If energy transfer due to ion-ion coupling is present, as one may except in case of clusters, the relaxation rate may be temperature sensitive as a result of the following.

(5) One or both (emission-absorption) transitions are phonon assisted.

(6) Thermal population of levels changes the number and rate of possible transitions.

(7) The integral in Eq. (1) decreases because of line broadening and/or shifting.

In view of the very long lifetimes involved, we believe that points 4–7 might be most suitably used in an effort to interpret Fig. 5.

ACKNOWLEDGMENT

This research was supported by the Natural Sciences and Engineering Research Council of Canada.

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