PHYSICAL REVIEW B VOLUME 60, NUMBER 2 1 JULY 1999-II

Selective laser excitation of the Ho^{3+}-La^{3+} dimer center in CaF_2 crystals

Marjorie Mujaji*
Department of Physics, University of Zimbabwe, Box MP 167, Mount Pleasant, Harare, Zimbabwe

J. D. Comins†
Department of Physics, University of the Witwatersrand, Johannesburg, Wits 2050, South Africa

(Received 15 June 1998; revised manuscript received 1 April 1999)

A single heterogeneous dimer center occurs in CaF_2 crystals double doped with 0.45 mol % La^{3+} and 0.005 mol % Ho^{3+} ions. The center exhibits up-conversion fluorescence. The crystal-field energy levels derived for each of the four multiplets of this center lie lower than those of the Ho^{3+} C_{4v}-symmetry center but higher than corresponding levels of the homogeneous dimer center. The center's fluorescence lifetime for the D multiplet is comparable to that for the homogeneous dimer center. [S0163-1829(99)06225-6]

I. INTRODUCTION

Dielectric relaxation studies show that a variety of homogeneous trivalent rare-earth ion cluster centers occur in CaF_2 crystals.[1–5] Relaxation peaks associated with cluster centers are apparent for rare-earth ion concentrations above 0.01 mol % and they grow in intensity with rare-earth concentration.[4,5]

In optical studies, cluster centers have been reported in CaF_2 crystals for several trivalent rare-earth elements, including Er^{3+},[6–8] Ho^{3+},[9,10] Eu^{3+},[11,12] and Pr^{3+}.[13] For CaF_2:0.2% Er^{3+},[7] a total of 16 centers with two or more Er^{3+} ions per center were reported. The Er^{3+} cluster centers were characterized by shorter fluorescence lifetimes compared to the single Er^{3+} ion centers and by up-conversion fluorescence. In contrast, only three cluster centers were observed in CaF_2:Ho^{3+} crystals for both 0.1 and 0.2 mol % Ho^{3+} concentrations.[9,10] Mujaji and Comins[10] assigned all three cluster centers as Ho^{3+} dimer centers arising from aggregation of either C_{4v} or C_{3v} symmetry monomer centers, with possible rearrangement of lattice F^- ions or additional interstitial F^- ions. Hamers, Wietfeldt, and Wright[11] identified only two Eu^{3+} cluster centers in CaF_2:0.1% Eu^{3+} crystals. From a subsequent study, Cirillo-Penn and Wright[12] concluded that the two Eu^{3+} cluster centers were associated with a dimer and a trimer aggregation of Eu^{3+} ions. Meanwhile some 20 cluster centers were observed in CaF_2:0.1% Pr^{3+} crystals.[13]

In both optical measurements[6,8,14] and statistical calculations,[14,15] dimerization is found to precede trimer and higher-order clustering; dimer centers occur extensively for trivalent rare-earth ion concentrations in the range 0.01–0.5 mol % while centers with at least three trivalent rare-earth ions per center become dominant above 0.25 mol %.[6,8,14]

Dimer centers comprising heterogeneous trivalent rare-earth ions occur readily in double-doped CaF_2 crystals.[9,11,13,16–20] Such centers are of particular interest in the study of ion-pair relaxation processes. In these studies, the laser is set to excite one of the constituent ions' absorption transitions while the fluorescence spectra and temporal transients of the other ion are measured. Models for the relaxations of the coupled heterogeneous ions and possible mechanisms for energy transfer can then be deduced.

The results presented here are from a laser selective excitation study of the heterogeneous Ho^{3+}-La^{3+} dimer center present in CaF_2:0.45% La^{3+}:0.005% Ho^{3+} crystals. Incorporation of the La^{3+} ions is ensured by the higher concentration. Since the La^{3+} ion has the xenon-core structure, it is optically inactive and therefore not suitable for study of ion-pair relaxation processes. The ion is, however, ideal for studying the effects of changes in the crystal field induced by one dopant ion at the codopant ion site. For the present case, any interaction between the La^{3+} ion and the Ho^{3+} ion would be apparent as energy shifts, on the Ho^{3+} crystal-field levels, induced by a changed crystal field at the Ho^{3+} ion site.

The spectral appearance and temporal behavior of the Ho^{3+}-La^{3+} center are found to be similar to those for the homogeneous Ho^{3+}-Ho^{3+} C center,[10] though the transition energies and intensity distributions are distinctly different. The center exhibits some up-conversion fluorescence. Given the low Ho^{3+} content (0.005 mol %) in the crystal, the La^{3+} ion must facilitate some strong coupling between relatively distant Ho^{3+} ions resulting in the observed up-conversion fluorescence. None of the centers in the pure CaF_2:0.005% Ho^{3+} crystals[21] exhibit any up-conversion fluorescence. Crystal-field energy levels for four multiplets of the Ho^{3+}-La^{3+} center are derived. The energy-level positions are compared with those of the Ho^{3+} C_{4v} symmetry (A) center and the homogeneous Ho^{3+} dimer C center.

II. EXPERIMENT

The CaF_2:0.45% La^{3+}:0.005% Ho^{3+} crystal was provided by Dr. G. D. Jones, Dr. R. J. Reeves, and Dr. J. P. R. Wells of the University of Canterbury, New Zealand. The crystal was grown in an oxygen-free atmosphere.

The equipment for selective laser excitation comprised a Spectra-Physics 375 dye laser pumped by the 514.5-nm laser radiation from a Spectra-Physics 171 argon-ion laser. The Rhodamine 640 (perchlorate) dye used for this work is appropriate for exciting the $Z(^5I_8)\rightarrow D(^5F_5)$ transitions of the Ho^{3+} ion.

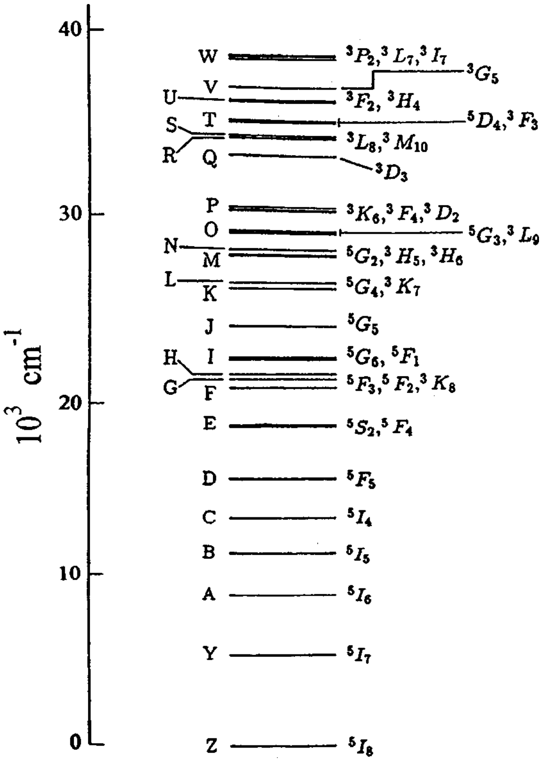

FIG. 1. The free-ion energy-level structure of the Ho^{3+} ion (from Ref. 22).

The sample was mounted onto the sample holder of an Oxford CF1204 dynamic exchange gas cryostat through which a regulated flow of liquid helium was maintained. The measurements were done at temperatures of 10 and 77 K. The temperature at the sample was monitored by a resistance sensor and a thermocouple, and regulated via an Oxford ITC4 temperature controller.

Fluorescence from the sample was collected and analyzed using a Jarrell-Ash 1-m double Czerny-Turner model 25-100 scanning spectrometer. The spectrometer is equipped with a thermoelectrically cooled Burle C31034-02 photomultiplier tube, an EG&G Princeton Applied Research Model 1121A preamplifier/discriminator and a Model 1112 photon counter.

The fluorescence lifetime of the *D* multiplet was measured in the Physics Department of the University of Canterbury, New Zealand. The equipment comprised a PRA LN107 dye laser pumped by a PRA LN1000 pulsed nitrogen laser, a Spex 1700 monochromator, and a VC 6275 digital storage oscilloscope. All wavelengths and energies reported here are in nm and cm^{-1} in air, respectively.

III. SPECTROSCOPY OF THE Ho^{3+}-La^{3+} CENTER IN CaF_2 CRYSTALS

The free-ion energy level structure of the Ho^{3+} ion[22] is shown in Fig. 1. The energy separations between neighboring free-ion energy levels (LSJ multiplets) are ~3 000 cm^{-1}. When the rare-earth ion is introduced into the fluorite lattice, each of the free-ion energy levels is split by the crystal field into crystal-field energy levels (Stark levels). The crystal field in this case arises from the combined effects of the ligand ions and the charge compensating interstitial F^- ions at the Ho^{3+} ion site and is further modified by the co-dopant La^{3+} ions, for some of the Ho^{3+} ion sites. Although the extent to which the energy level structure is modified depends on the strength of the crystal-field effects, no major changes occur due to the shielding of the $4f$ electrons by the outer-lying $5s$ and $5p$ orbital electrons.[23] The energy separations between intra-multiplet crystal-field energy levels are therefore much less than the intermultiplet separations, being typically 100 cm^{-1} or less. The overall spread in the crystal-field energy levels is no more than 500 cm^{-1} for each multiplet.

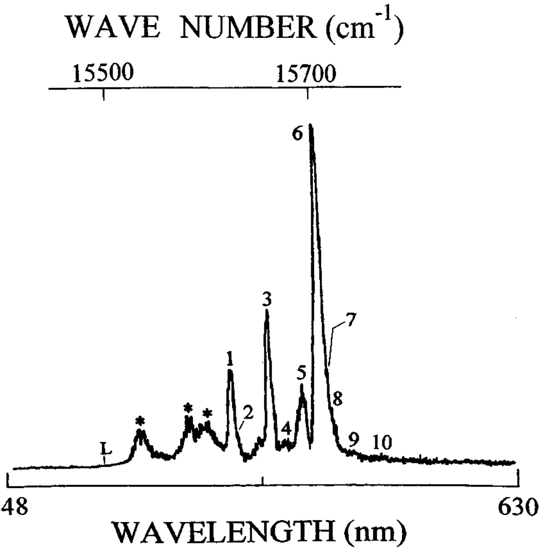

FIG. 2. Excitation spectrum of the *D* ($^5F_5$) multiplet of the Ho^{3+}-La^{3+} dimer center in CaF_2:0.45% La^{3+}:0.005% Ho^{3+} crystals as measured at 10 K, monitoring the $D_1 \rightarrow Z_9$ transition at 15 497.0 cm^{-1}. The transitions originating from the ground state (Z_1) are identified by numerical labels for energy levels of the *D* multiplet. The transition being monitored is shown by *L*. Transitions marked * do not belong to this center.

Since Ho^{3+} is a non-Kramers ion, each Ho^{3+}-based center has $2J+1$ crystal-field energy levels per LSJ multiplet.[23] The symmetry properties of these crystal-field levels are determined by the symmetry of the ion site. For the Ho^{3+} ion in a C_s-symmetry site such as in the Ho^{3+}-La^{3+} center described in this work, none of the crystal-field energy levels are degenerate and intermultiplet transitions are allowed between any pair of levels.[24]

With the monochromator set to monitor all fluorescence transitions above 650 nm, the dye laser was scanned across the 630–648-nm range to record a broadband excitation spectrum for all the centers present. Although excitation transitions for the already documented *A* and *B* monomer centers[21] dominate the spectrum, some weaker unidentified transitions are also apparent. Employing the now well established technique of laser selective excitation[7–13,16,17,21] all the as yet unassigned absorption features were found to belong to a single center. This center, which is absent in single-doped CaF_2:0.005% Ho^{3+} crystals, is associated with the presence of the La^{3+} ions and is henceforth labeled the Ho^{3+}-La^{3+} center. Figure 2 shows the site-selective excitation spectrum for this Ho^{3+}-La^{3+} center, obtained with the monochromator set to monitor the center's $D_1 \rightarrow Z_9$ transition at 15 497.0 cm^{-1} (645.3 nm). The homogeneous cluster

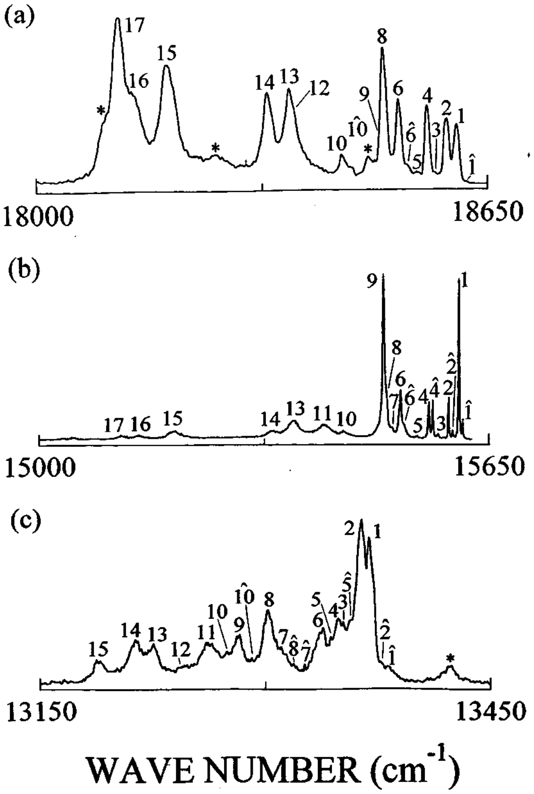

FIG. 3. Fluorescence spectra of the Ho^{3+}-La^{3+} dimer center in CaF$_2$:0.45% La^{3+}:0.005% Ho^{3+} crystals as measured at 10 K, with excitation of the $Z_1 \rightarrow D_6$ transition at 15 714.1 cm^{-1}. (a) $E \rightarrow Z$ transitions, (b) $D \rightarrow Z$ transitions, and (c) $E \rightarrow Y$ transitions. Transitions are identified by numerical labels for energy levels of the terminating multiplet. Transitions originating from the higher energy E_2 and D_2 levels are identified by ˆ. Transitions marked * do not belong to this center.

(*C, D,* and *E*) centers[9,10] are absent.

The direct $D \rightarrow Z$ and up-conversion $E \rightarrow Z,Y$ fluorescence spectra of the Ho^{3+}-La^{3+} center are shown in Fig. 3. The spectra were obtained at 10 K, with the laser tuned to the $Z_1 \rightarrow D_6$ transition at 15 714.1 cm^{-1} (636.4 nm). The up-conversion fluorescence from the F($^5F_3$) multiplet was too weak to measure.

The $D \rightarrow Z$ fluorescence spectrum of the Ho^{3+}-La^{3+} center recorded at 77 K is shown in Fig. 4. The $D_1 \rightarrow Z$ transitions are much weaker than at 10 K [Fig. 3(b)] while transitions from higher energy levels of the *D* multiplet are now apparent.

Transitions of the C_{4v}-symmetry *A* and the C_{3v}-symmetry *B* centers maintain the energy positions in the single-doped CaF$_2$:Ho^{3+} crystals.

A fluorescence lifetime of 113±2 μs was obtained for the *D* multiplet of the Ho^{3+}-La^{3+} center. This lifetime is comparable to the corresponding lifetime for the Ho^{3+}-Ho^{3+} *C* center in CaF$_2$:0.1% Ho^{3+}.[10]

IV. DISCUSSION OF RESULTS

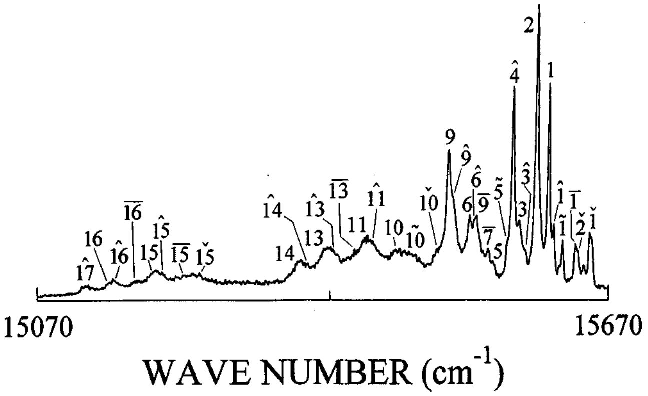

FIG. 4. Fluorescence spectrum of the $D \rightarrow Z$ transitions of the Ho^{3+}-La^{3+} dimer center in CaF$_2$:0.45% La^{3+}:0.005% Ho^{3+} crystals as measured at 77 K, with excitation of the $Z_1 \rightarrow D_6$ transition. Transitions are identified by numerical labels for energy levels of the *Z* multiplet. Transitions originating from the higher energy D_2, D_3, D_4, and D_5 levels are identified by ˆ ,˜ ,¯ , and ˇ , respectively.

The crystal-field energy levels derived for the *Z, Y, D,* and *E* multiplets (Fig. 1) of the Ho^{3+}-La^{3+} center are presented in Table I. In Fig. 5, the relative positions of the crystal-field energy levels of the *Z* multiplet of the Ho^{3+}-La^{3+} center are compared with those of both the parent C_{4v}-symmetry (*A*) center and the Ho^{3+}-Ho^{3+} dimer (*C*) center. The data for the *A* and *C* centers are from Refs. 21 and 10, respectively.

The Z_1-Z_2 energy level separation of 14.8 cm^{-1} for the Ho^{3+}-La^{3+} center is much larger than the 1.9 cm^{-1} for the *A* center. The formerly doublet (γ_5) levels under C_{4v} symmetry show splittings of between 6.0 and 24.0 cm^{-1} for the Ho^{3+}-La^{3+} center. Except for Z_2, all the crystal-field energy levels of the ground (*Z*) multiplet of the Ho^{3+}-La^{3+} center are shifted to lower energies compared to those for the *A* center (Fig. 5). Similar trends are apparent for the *Y* and *D*

TABLE I. Crystal-field energy levels for the $Z(^5I_8)$, $Y(^5I_7)$, $D(^5F_5)$, and $E(^5S_2)$ multiplets of the Ho^{3+}-La^{3+} dimer center identified in CaF$_2$:0.45% La^{3+}:0.005% Ho^{3+} crystals. The energies are in cm^{-1} in air.

Level	$Z(^5I_8)$	$Y(^5I_7)$	$D(^5F_5)$	$E(^5S_2)$
1	0.0	5 236.4	15 606.1	18 605.5
2	14.8	5 241.1	15 611.9	18 618.1
3	30.6	5 253.7	15 619.9	
4	44.0	5 256.1	15 633.5	
5	60.1	5 262.0	15 654.7	
6	84.5	5 267.1	15 714.1	
7	95.5	5 295.0	15 729.5	
8	103.3	5 304.0	15 739.1	
9	109.1	5 323.5	15 759.0	
10	165.5	5 331.1	15 790.3	
11	193.7	5 343.0		
12	232.3	5 359.5		
13	238.5	5 380.5		
14	269.5	5 392.0		
15	410.9	5 417.5		
16	462.4			
17	485.9			

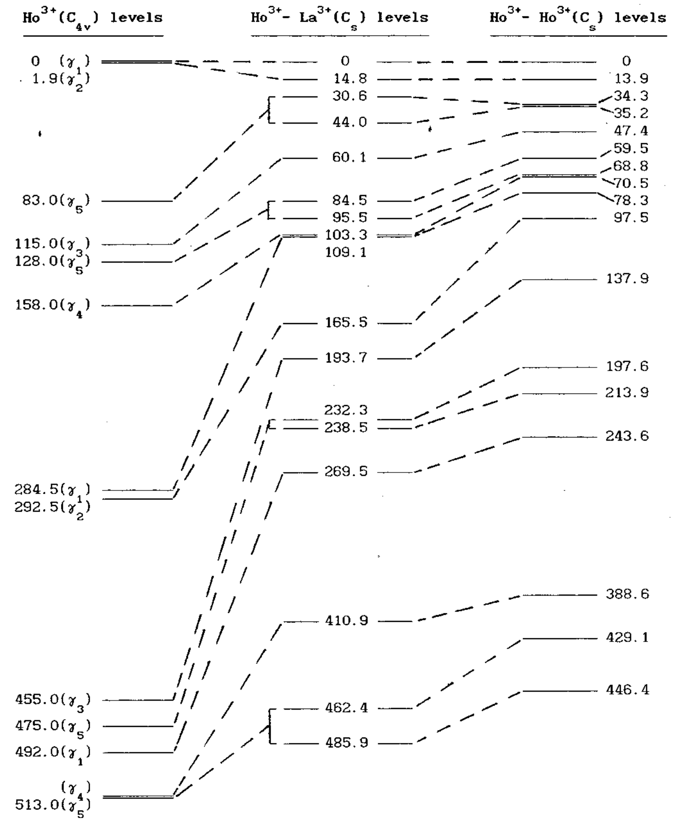

FIG. 5. Comparison of the crystal-field energy level positions for the ground (Z) multiplets of the C_{4v}-symmetry single Ho^{3+} (A) center, the Ho^{3+}-La^{3+} center, and the Ho^{3+}-Ho^{3+} C center. The data for the A and C centers are from Refs. 21 and 10, respectively.

multiplet energy levels (Table I and Ref. 21).

Although the fluorescence spectra of the Ho^{3+}-La^{3+} center (Fig. 3) have the same general appearance as those of the Ho^{3+}-Ho^{3+} C center, transitions for the heterogeneous dimer center are broader (particularly for the up-conversion fluorescence) and their energy positions are shifted significantly from those of the C center. The first excited states are at comparable positions being 14.8 and 13.9 cm^{-1} above their respective ground states. However, all the other Z multiplet levels occur at higher energies for the Ho^{3+}-La^{3+} center than for the Ho^{3+}-Ho^{3+} C center (Fig. 5). The crystal-field energy levels for the Y, D, and E multiplets of the heterogeneous dimer center also lie higher than those for the homogeneous dimer center (Table I and Ref. 10). The differences in transition and energy level positions between the Ho^{3+}-La^{3+} and Ho^{3+}-Ho^{3+} dimer centers are more profound than reported for Er^{3+} ions[16] in the Er^{3+}-Yb^{3+} and Er^{3+}-Er^{3+} dimer centers. However, large shifts were reported by Tissue and Wright[13] for Pr^{3+} ions in the Pr^{3+}-Gd^{3+} and Pr^{3+}-Y^{3+} dimer centers compared to those of the Pr^{3+}-Pr^{3+} dimer center.

Since the La^{3+} ion does not have any optically active energy levels, no energy transfer processes can occur with the Ho^{3+} ion. Accordingly, we examine possible mechanisms for the up-conversion fluorescence. Since the Ho^{3+} concentration is so low, we first consider a sequential two-photon excitation of the Ho^{3+} ion in the isolated Ho^{3+}-La^{3+} center. Such excitation would result in the occupation of energy levels of the P multiplet (Fig. 1) at ~31 400 cm^{-1} (twice the excitation energy). Multiplets of lower energy would be populated by nonradiative relaxation; fluorescence could therefore be observed from some of the lower-lying multiplets. A thorough search did not reveal any of the fluorescence transition groups expected in the energy range from 21 000 to 30 000 cm^{-1}. Phonon assisted decay by ~10 000 cm^{-1} from the P multiplet to the F and E multiplets (Fig. 1) is not at all possible. In general, up conversion by sequential excitation is markedly less efficient compared to ion-ion energy transfer (the quantum efficiencies are $\sim 10^{-5}$ cm^2/W and $\sim 10^{-3}$ cm^2/W, respectively) and can only be observed in the absence of the latter.[19] Furthermore, as discussed in the Introduction, no up-conversion fluorescence is observed in the CaF$_2$:0.005% Ho^{3+} crystal.[21] Thus the collective experimental observations do not support the presence of two-photon absorption as a satisfactory explanation of the results presented here.

Hence, in spite of the low Ho^{3+} concentration, we need to consider some form of coupling with another separated Ho^{3+} ion to account for the up-conversion fluorescence associated with the Ho^{3+}-La^{3+} center. As ion-ion interactions leading to up conversion are significant only when the optically active ions occur in close proximity,[18–20] we consider two possible configurations:

(i) Some lattice distortion is likely to occur in the vicinity of a Ho^{3+}-La^{3+} dimer due to the different sizes of the Ho^{3+} and the La^{3+} ions. As a result of this distortion, it might be favorable for an additional isolated Ho^{3+} ion to occupy one of the Ca^{2+} sites in the neighborhood of the dimer. It is apparent that the two Ho^{3+} ions in this configuration would be in sites of different symmetries. As such, the hybrid center ought to yield more than the $2J+1$ crystal-field energy levels expected for Ho^{3+} ions in similar low-symmetry sites. We do not find any evidence for such a configuration in the current work. However, it is possible that any small splittings arising from this asymmetrical Ho^{3+}-La^{3+}-Ho^{3+} configuration could have been masked by the rather large linewidths associated with the transitions observed here (Fig. 3).

(ii) Alternatively, some pairs of Ho^{3+}-La^{3+} dimer centers may occur in close proximity resulting in significant interaction between the Ho^{3+} ions of neighboring centers. In such a case, the Ho^{3+} ions would be in sites of identical symmetry and would yield exactly the same transitions and crystal-field energy levels, as observed in the work presented here. Also, we observe the same $Z \rightarrow D$ excitation transitions when a transition of either the direct or the up-conversion fluorescence is monitored. This further supports this latter configuration. The intercenter interaction would account for the rather large linewidths associated with transitions of the up-conversion fluorescence observed in this work.

It therefore appears that the up-conversion fluorescence observed in this study can be explained in a self-consistent manner by mechanism (ii), i.e., intercenter interaction between pairs of similarly excited Ho^{3+} ions. The Ho^{3+}-La^{3+} center shows the same spectral and temporal characteristics, with respect to the C_{4v}-symmetry (A) center, as the Ho^{3+}-Ho^{3+} C center. It is likely that this Ho^{3+}-La^{3+} center has the same rhombic configuration proposed for the C center.

V. CONCLUSIONS

The crystal-field energy levels for a given multiplet of the Ho^{3+}-La^{3+} center in double-doped CaF_2 crystals are shifted to lower energies compared to those of the parent C_{4v}-symmetry center, but still lie higher than corresponding levels for the Ho^{3+}-Ho^{3+} C center. The up-conversion fluorescence exhibited by the center suggests some interaction between the Ho^{3+} ions at the relatively low Ho^{3+} concentration of 0.005 mol %, as up conversion does not occur in single-doped CaF_2:0.005% Ho^{3+} crystals. Computational work is under way to investigate the stability of the proposed Ho^{3+}-La^{3+} dimer configuration as well as the possibility that pair aggregation of such dimers would be favorable. The fluorescence lifetime of the D multiplet for the Ho^{3+}-La^{3+} center is comparable to that for the Ho^{3+}-Ho^{3+} C center.

ACKNOWLEDGMENTS

This research was supported by the University of the Witwatersrand, Johannesburg and by the Foundation for Research Development, Pretoria. The work was carried out in the Laser Spectroscopy Laboratory of the Physics Department, University of the Witwatersrand. We are grateful to G. D. Jones, R. J. Reeves, and J. P. R. Wells of the University of Canterbury, New Zealand for the crystal and for allowing M.M. access to facilities for fluorescence lifetime measurements, and to the Abdus Salam ICTP, Italy for granting M.M. access to their computer facilities and financial support from SIDA. We are also grateful to P. R. Stoddart for useful suggestions and to W. Hayes for fruitful discussions.

---

*Electronic address: mujajim@compcentre.uz.ac.zw
†Electronic address: comins@physnet.phys.wits.ac.za

[1] C. Andeen, D. Link, and J. Fontanella, Phys. Rev. B **16**, 3762 (1977).

[2] J. Fontanella, C. Andeen, and D. Schuele, Phys. Rev. B **17**, 3429 (1978).

[3] C. G. Andeen, J. J. Fontanella, M. C. Wintersgill, P. J. Welcher, R. J. Kimble, Jr., and G. E. Matthews, Jr., J. Phys. C **14**, 3557 (1981).

[4] J. Fontanella and C. Andeen, J. Phys. C **9**, 1055 (1976).

[5] J. Fontanella, D. J. Treacy, and C. Andeen, J. Chem. Phys. **72**, 2235 (1980).

[6] J. B. Fenn Jr., J. C. Wright, and F. K. Fong, J. Chem. Phys. **59**, 5591 (1973).

[7] D. R. Tallant and J. C. Wright, J. Chem. Phys. **63**, 2074 (1975).

[8] D. R. Tallant, D. S. Moore, and J. C. Wright, J. Chem. Phys. **67**, 2897 (1977).

[9] M. B. Seelbinder and J. C. Wright, Phys. Rev. B **20**, 4308 (1979).

[10] M. Mujaji and J. D. Comins, Phys. Rev. B **59**, 6092 (1999).

[11] R. J. Hamers, J. R. Wietfeldt, and J. C. Wright, J. Chem. Phys. **77**, 683 (1982).

[12] K. M. Cirillo-Penn and J. C. Wright, Phys. Rev. B **41**, 10 799 (1990).

[13] B. M. Tissue and J. C. Wright, Phys. Rev. B **36**, 9781 (1987).

[14] F. K. Fong, J. Chem. Phys. **64**, 4243 (1976).

[15] V. V. Osiko, Fiz. Tverd. Tela (Leningrad) **7**, 1294 (1965) [Sov. Phys. Solid State **7**, 1047 (1965)].

[16] D. R. Tallant, M. P. Miller, and J. C. Wright, J. Chem. Phys. **65**, 510 (1976).

[17] J. P. R. Wells, G. D. Jones, and R. J. Reeves, J. Lumin. **72-74**, 977 (1997).

[18] J. C. Wright, in *Radiationless Processes in Molecules and Condensed Phases*, edited by F. K. Fong, Topics in Applied Physics Vol. 15 (Springer, Berlin, 1976), Chap. 4.

[19] F. Auzel, J. Lumin. **45**, 341 (1990).

[20] L. A. Riseberg and M. J. Weber, in *Progress in Optics*, edited by E. Wolf (North-Holland, Amsterdam, 1976), Vol. XIV, Chap. III.

[21] M. Mujaji, G. D. Jones, and R. W. G. Syme, Phys. Rev. B **46**, 14 398 (1992).

[22] G. H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals* (Interscience, New York, 1968).

[23] B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience, New York, 1964).

[24] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (M.I.T. Press, Cambridge, MA, 1963).