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Energy Transfer from Er^{3+} to Tm^{3+} and Ho^{3+} Ions in Crystals

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Energy transfer from Er^{3+} to Tm^{3+} and Ho^{3+} ions in crystals has been found to occur. Transfer proceeds from the $^4I_{13/2}$ state of Er^{3+} to the $^3H_4$ and $^5I_7$ emitted states of Tm^{3+} and Ho^{3+}, respectively. Phonon emission is required to conserve energy. The enhancement of infrared emission from Tm^{3+} and Ho^{3+} ions due to energy transfer from Er^{3+} results in a lowering of the threshold for maser oscillation of Tm^{3+} and Ho^{3+} ions in $CaMoO_4$. However, results indicate that greater benefit from energy transfer can be obtained in the garnets where Tm^{3+} and Ho^{3+} emission is strengthened by two orders of magnitude.

MANY examples of energy transfer between rare-earth ions are known to exist.[1] Energy absorbed by one rare-earth ion which would otherwise appear as fluorescence may be lost to the lattice through the intermediary of a second rare-earth ion.[2] On the other hand, energy gained by one rare-earth ion via transfer from a second may produce an enhancement of its emission. For example, the intensity of Eu^{3+} emission in tungstates and molybdates is strengthened by energy transfer from Tb^{3+} ions.[3–5] Similarly, Tm^{2+} absorption bands have been shown to pump Tm^{3+} fluorescence in CaF_2,[6] Tb^{3+} emission in CaF_2 may be pumped by Ce^{3+},[7] and Yb^{3+} emission by Nd^{3+}.[5]

This paper reports two additional cases of energy transfer between rare-earth ions: $Er^{3+}\rightarrow Tm^{3+}$ and $Er^{3+}\rightarrow Ho^{3+}$. In addition, the enhancement of infrared emission from Tm^{3+} and Ho^{3+} ions due to energy transfer from Er^{3+} is shown to result in a pronounced lowering of threshold for maser oscillation of Tm^{3+} and Ho^{3+} ions in $CaMoO_4$.

1. $Er^{3+}\rightarrow Tm^{3+}$ ENERGY TRANSFER

The absorption spectrum of $CaMoO_4$ containing both Er^{3+} (0.75% substitution for Ca^{2+}) and Tm^{3+} (0.5%) ions is shown in Fig. 1. Er^{3+} line absorption regions are designated by arrows. A comparison of Fig. 1 with the separate spectra of Er^{3+} and Tm^{3+} ions in $CaMoO_4$ reveals that Fig. 1 is merely a superposition of the individual absorption spectra for the two ions. Therefore, marked effects due to ion pairing, such as shifting of lines or the appearance of additional lines, do not exist.

Essentially all (>99%) of the fluorescence from Er^{3+} and Tm^{3+} ions in $CaMoO_4$ lies in the infrared (1.6 μ for Er^{3+} and 1.9 μ for Tm^{3+}). When both ions are present simultaneously in the same crystal, the spectral character of emission from Er^{3+} is unaffected by the presence of Tm^{3+}, and vice versa. However, the relative intensities are influenced markedly by energy transfer from Er^{3+} to Tm^{3+} ions. The infrared emission at 77°K from a crystal of $CaMoO_4$ containing both Er^{3+} (0.75%) and Tm^{3+} (0.25%) ions is shown in Figs. 2 and 3 (1% Nb^{5+} ions are added for charge compensation). The intensity scales are chosen to allow direct comparison of the strength of emission of one ion relative to the other. The existence of $Er^{3+}\rightarrow Tm^{3+}$ energy transfer is demonstrated by the excitation spectra for Tm^{3+} emission at 1.9 μ, shown in Figs. 4 (Tm^{3+} ions present only) and 5 (both Er^{3+} and Tm^{3+} present). Figure 4 shows the relative efficiency of the various Tm^{3+} absorption bands, indicated at the top of the figure, for producing Tm^{3+} emission at 1.9 μ. When Er^{3+} ions are present (Fig. 5) it is seen that Tm^{3+} emission is excited in two additional regions coinciding with Er^{3+} absorption (indicated by arrows). In particular, the most efficient band for producing Tm^{3+} emission at 1.9 μ is the Er^{3+} absorption band at 1.5 μ.

Comparing infrared emission intensities in this example of $Er^{3+}\rightarrow Tm^{3+}$ energy transfer we find that, under broadband excitation from a high pressure mercury arc, emission from Tm^{3+} (0.5 at.%) at ~1.9 μ is enhanced by a factor of about 2.5 when Er^{3+} (0.75%) is present. Correspondingly, Er^{3+} (0.75%) emission at ~1.6 μ is reduced by a factor of 2.5 when 0.5% Tm^{3+} is present. In these measurements using broadband excitation from a mercury lamp, we are comparing the effectiveness of $Er^{3+}\rightarrow Tm^{3+}$ energy transfer as a result of pumping into Er^{3+} absorption lines in the region 5200–5500 Å, and not taking advantage of the more efficient energy transfer band at 1.5 μ (Fig. 5).

2. $Er^{3+}\rightarrow Ho^{3+}$ ENERGY TRANSFER

The absorption spectrum of a single crystal of $CaMoO_4$ containing both Er^{3+} (0.25%) and Ho^{3+} (0.25%) is shown in Fig. 6. Er^{3+} absorption lines are indicated by arrows. Again each ion contributes independently of the other. The intensity scale for Ho^{3+} emission at ~2 μ (Fig. 7) is chosen to allow direct comparison with the strength of Er^{3+} emission of Fig. 2 when both are present at concentrations of 0.5% and

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[1] Perhaps the most elegant illustration of cooperative phenomena between rare-earth ions is the demonstration of ion-pair resonance by Varsanyi and Dieke [F. Varsanyi and G. H. Dieke, Phys. Rev. Letters **7**, 442 (1961)].

[2] L. G. Van Uitert and S. Iida, J. Chem. Phys. **37**, 986 (1962).

[3] L. G. Van Uitert and R. R. Soden, J. Chem. Phys. **36**, 1289 (1962).

[4] L. G. Van Uitert, J. Electrochem. Soc. **110**, 1 (1963).

[5] G. E. Peterson and P. M. Bridenbaugh, J. Opt. Soc. Am. **53**, 494 (1963).

[6] Z. J. Kiss, Phys. Rev. **127**, 718 (1962).

[7] C. G. B. Garrett and W. Kaiser (private communication).

0.75%, respectively. The existence of $Er^{3+} \rightarrow Ho^{3+}$ energy transfer is illustrated by the excitation spectra for Ho^{3+} emission at 2 μ shown in Fig. 8 (no Er^{3+} present) and Fig. 9 (0.75% Er^{3+} present). As in the case of Tm^{3+}, we find that the Er^{3+} absorption band at 1.5 μ is the most efficient band for producing Ho^{3+} emission at 2 μ, while the quantum efficiency at 5400 Å is strengthened by the presence of Er^{3+} absorption.

Under broadband mercury lamp excitation we find Ho^{3+} (0.5%) emission at 2 μ is increased by about a factor of two when Er^{3+} (0.75%) is present, where again we are comparing the effectiveness of $Er^{3+} \rightarrow Ho^{3+}$ energy transfer due to pumping into Er^{3+} absorption lines in the range 5200–5500 Å, and not utilizing the more efficient band at 1.5 μ. Due to the fact that Ho^{3+} also has absorption lines at 5400 Å (and Tm^{3+} does not) the presence of Er^{3+} is less effective in enhancing emission from Ho^{3+} than from Tm^{3+}.

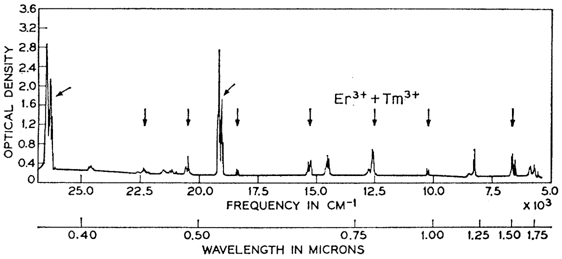

FIG. 1. Absorption spectrum of $CaMoO_4$ containing both Er^{3+} (0.75%) and Tm^{3+} (0.5%) ions. (77°K). The arrows designate regions of Er^{3+} absorption.

3. MECHANISM OF $Er^{3+} \rightarrow Tm^{3+}$, $Er^{3+} \rightarrow Ho^{3+}$ ENERGY TRANSFER

The process by which Er^{3+} transfers energy to Tm^{3+} or Ho^{3+} ions is believed to be as follows (see Fig. 10).[8–10]

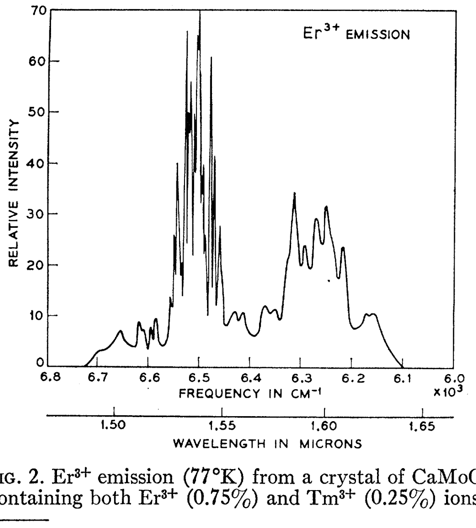

FIG. 2. Er^{3+} emission (77°K) from a crystal of $CaMoO_4$ containing both Er^{3+} (0.75%) and Tm^{3+} (0.25%) ions.

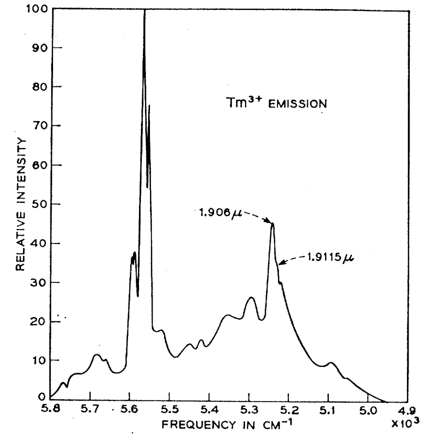

FIG. 3. Tm^{3+} emission (77°K) from $CaMoO_4$ containing both Er^{3+} (0.75%) and Tm^{3+} (0.25%) ions. The intensity scale permits comparison with the strength of Er^{3+} emission shown in Fig. 2.

First of all, consider Er^{3+} absorption at 6500 cm^{-1} (1.5 μ). Resonance exchange between the two ions is ruled out since the Er^{3+} band lies about 1000 cm^{-1} above the respective $^3H_4$ and $^5I_7$ emitting states of Tm^{3+} and Ho^{3+}. Therefore, the energy transfer step proceeding from the $^4I_{13/2}$ state of Er^{3+} requires phonon emission to conserve energy. Since the $^4I_{13/2}$ state of Er^{3+} and the $^3H_4$ state of Tm^{3+} lie at about 6500 and 5600 cm^{-1}, respectively, an energy of 900 cm^{-1} must be dissipated to the lattice.

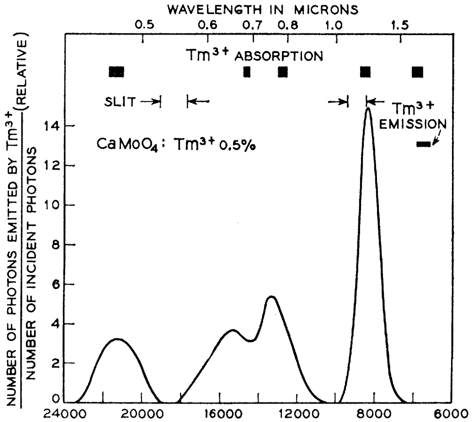

FIG. 4. Excitation spectrum for Tm^{3+} emission at 1.9 μ in $CaMoO_4$. Tm^{3+} absorption bands are indicated at the top of the figure.

The $^5I_7$ emitting state of Ho^{3+} lies at about 5100 cm^{-1}, and the corresponding energy difference is 1400 cm^{-1}. These energies could be taken up quite easily by the MoO_4^{2-} anion since the fundamental vibrational frequency of this ion is approximately 850 cm^{-1}.[11,12]

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[8] G. H. Dieke, *Advances in Quantum Electronics*, edited by J. R. Singer (Columbia University Press, New York, 1961), p. 170.

[9] F. Varsanyi and G. H. Dieke, J. Chem. Phys. **36**, 835 (1962).

[10] J. B. Gruber and J. G. Conway, J. Chem. Phys. **32**, 1178 (1960).

[11] C. L. Schafer and F. Matosii, *Das Ultrarot Spektrum* (Julius Springer-Verlag, Berlin, 1930), p. 334.

[12] H. M. Heaton and H. Moore, J. Soc. Glass Tech. **41**, 3 (1957).

Next, consider Er^{3+} absorption at 19 000 cm^{-1} (5300 Å). Again, the energy transfer step most probably proceeds from the $^4I_{13/2}$ state of Er^{3+}. This follows because energy absorbed by Er^{3+} cascades very rapidly via nonradiative transitions to the $^4I_{13/2}$ state (greater than 99% of Er^{3+} emission arises from $^4I_{13/2}$ transitions to the ground state). However, in this case we cannot definitely rule out the possibility that energy transfer might occur between higher states of the two ions, for example, at some point in the cascade of Er^{3+} where near coincidence exists between the levels of Er^{3+} and Tm^{3+} or Er^{3+} and Ho^{3+}.

The probability that the MoO_4^{2-} ion functions as the intermediary for $Er^{3+} \rightarrow Tm^{3+}$ and $Er^{3+} \rightarrow Ho^{3+}$ energy transfer is supported by the fact that the spectral character of absorption and emission for two ions is merely the sum of the spectra of independent ions, i.e., the ions are not coupled together in nearest neighbor sites. It should be remarked further that phonon participation may be noted in the emission spectra of Figs. 2, 3, and 7 to the extent that transitions to lower components of the ground states of the three ions (on the high-energy side of the figures) are sharper than those to higher components. The latter lines are broadened by lattice vibrations which assist rapid depopulation of these states in subsequent nonradiative transitions.

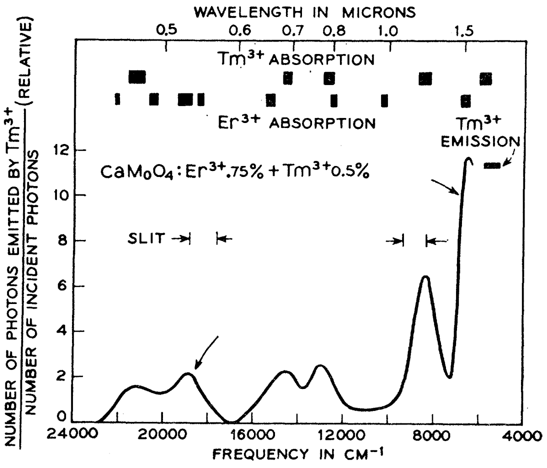

FIG. 5. Excitation spectrum for Tm^{3+} emission at 1.9 μ in $CaMoO_4$ containing both Er^{3+} (0.75%) and Tm^{3+} (0.5%) ions. Tm^{3+} and Er^{3+} absorption bands are indicated at the top of the figure. Two $Er^{3+} \rightarrow Tm^{3+}$ energy transfer bands are designated by arrows.

4. OPTICAL MASER EFFECTS

Maser oscillation from Tm^{3+} and Ho^{3+} ions in $CaWO_4$ has been reported previously.[13–15] In $CaMoO_4$ stimulated emission is observed in two lines of the $^3H_4 \rightarrow {}^3H_6$ emission from Tm^{3+} (see Fig. 3) and in three lines of the $^5I_7 \rightarrow {}^5I_8$ emission from Ho^{3+} (see Fig. 7).

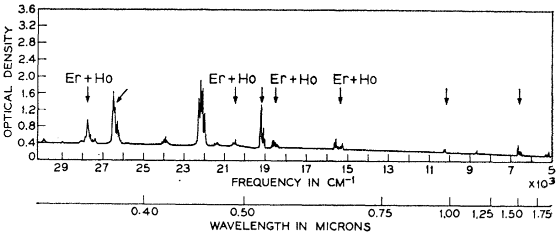

FIG. 6. Absorption spectrum of $CaMoO_4$ containing both Er^{3+} (0.25%) and Ho^{3+} (0.25%) ions. (77°K). The arrows designate regions of Er^{3+} absorption. Regions of overlap are designated Er+Ho.

By virtue of $Er^{3+} \rightarrow Tm^{3+}$ energy transfer, the presence of Er^{3+} to the extent of 0.75 at.% reduces the threshold for Tm^{3+}(0.5%) oscillation in $CaMoO_4$ by better than a factor of 3 (under pulse illumination from an FT-524 xenon lamp). At 77°K, the lowest threshold observed corresponds to about 20 J of electrical energy into the lamp; at 20°K the threshold is lower by about 20%. The fluorescence lifetime for 1.9 μ emission from Tm^{3+} (with Er^{3+} present), as inferred from the time delay before the onset of maser oscillation, is $\geq$900 μsec at both 77 and 20°K.

As a result of $Er^{3+} \rightarrow Ho^{3+}$ energy transfer, the presence of Er^{3+} (0.75%) reduces the threshold for Ho^{3+} (0.5%) oscillation by about a factor of 2 under pulse illumination from a xenon lamp. At 77°K, the lowest threshold observed corresponds to about 100 J of energy into the lamp; at 20°K, the threshold is reduced to 45 J. From the time delay before maser oscillation, the lifetime for 2 μ emission from Ho^{3+} (with or without Er^{3+} present) is $\geq$1300 μsec at 77 and 20°K.

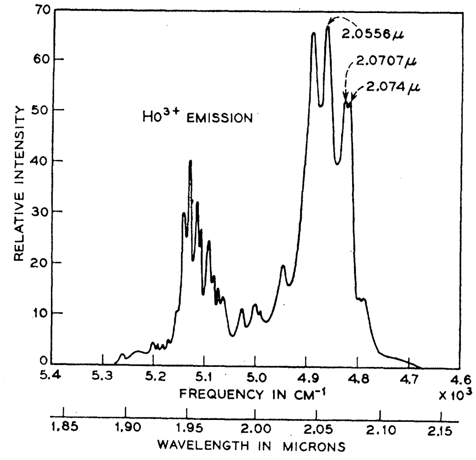

FIG. 7. Ho^{3+} emission (77°K) from $CaMoO_4$ containing both Er^{3+} (0.75%) and Ho^{3+} (0.5%) ions. The intensity scale permits comparison with the strength of Er^{3+} emission shown in Fig. 2.

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[13] L. F. Johnson, G. D. Boyd, and K. Nassau, Proc. I.R.E. **50**, 86 (1962).

[14] L. F. Johnson, G. D. Boyd, and K. Nassau, Proc. I.R.E. **50**, 87 (1962).

[15] L. F. Johnson, J. Appl. Phys. **34**, 897 (1963).

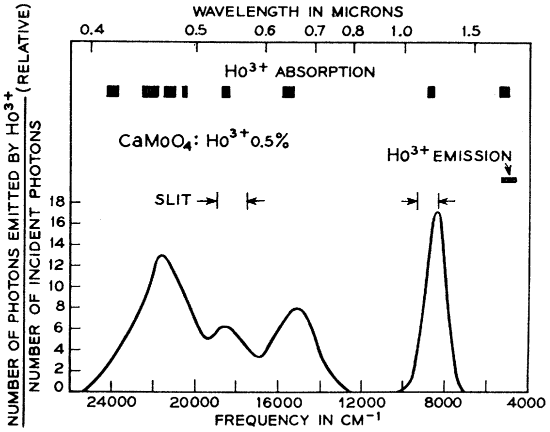

FIG. 8. Excitation spectrum for Ho^{3+} emission at 2 μ in $CaMoO_4$. Ho^{3+} absorption bands are indicated at the top of the figure.

A summary of the optical maser characteristics of Tm^{3+} and Ho^{3+} ions in $CaMoO_4$ resulting from Er^{3+} energy transfer is shown in Table I. Although maser oscillation has been observed from Er^{3+} ions in $CaWO_4$,[16] oscillation has not been obtained from Er^{3+} in $CaMoO_4$, even without Tm^{3+} and Ho^{3+} ions present. While a notable improvement in threshold for Tm^{3+} and Ho^{3+} maser oscillation has been obtained as a result of Er^{3+} energy transfer, continuous operation has not yet been attained.

TABLE I. Summary of optical maser characteristics of Tm^{3+} and Ho^{3+} ions in $CaMoO_4$ aided by Er^{3+} energy transfer.

Rare-earth ion	Temperature (°K)	Maser wavelength (μ)	ν (cm^{-1})	Threshold FT 524 (J)
Tm^{3+}	77	1.9115	5232	19
		1.9060	5247	20
Ho^{3+}	77	2.0740	4822	107
		2.0707	4829	170
		2.0556	4865	310

5. COMMENTS ON $Er^{3+} \rightarrow Tm^{3+}$ AND $Er^{3+} \rightarrow Ho^{3+}$ ENERGY TRANSFER

To maximize the effectiveness of Er^{3+} energy transfer, one would like to employ higher concentrations of Er^{3+} ions to increase the fraction of Tm^{3+} (or Ho^{3+}) ions which receive energy from Er^{3+}. It has, in fact, been found that in small flux-grown crystals of $Na_{0.5}\,Er_{0.49}\,WO_4$ containing 1% Tm^{3+} or Ho^{3+} ions, essentially no 1.6-μ emission is produced by Er^{3+}, and emission from Tm^{3+} and Ho^{3+} is very strong. However, large crystals of this compound have not been grown, and it is difficult to prepare crystals of $CaMoO_4$ of good optical quality when the total rare-earth ion concentration exceeds 1.5%.

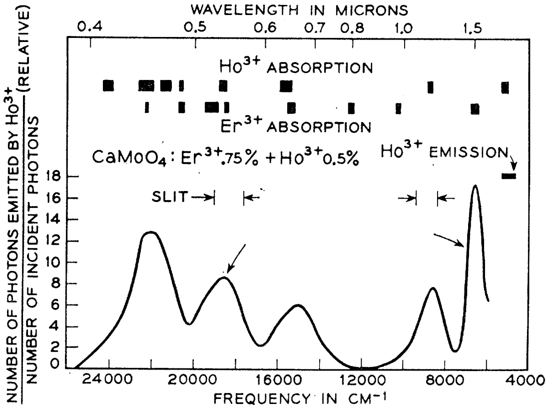

FIG. 9 Excitation spectrum for Ho^{3+} emission at 2 μ in $CaMoO_4$ containing both Er^{3+} (0.75%) and Ho^{3+} (0.5%) ions. Ho^{3+} and Er^{3+} absorption bands are indicated at the top of the figure. The excitation band at 1.5 μ is due to $Er^{3+} \rightarrow Ho^{3+}$ energy transfer, while the band at 5400 Å has been strengthened by energy transfer.

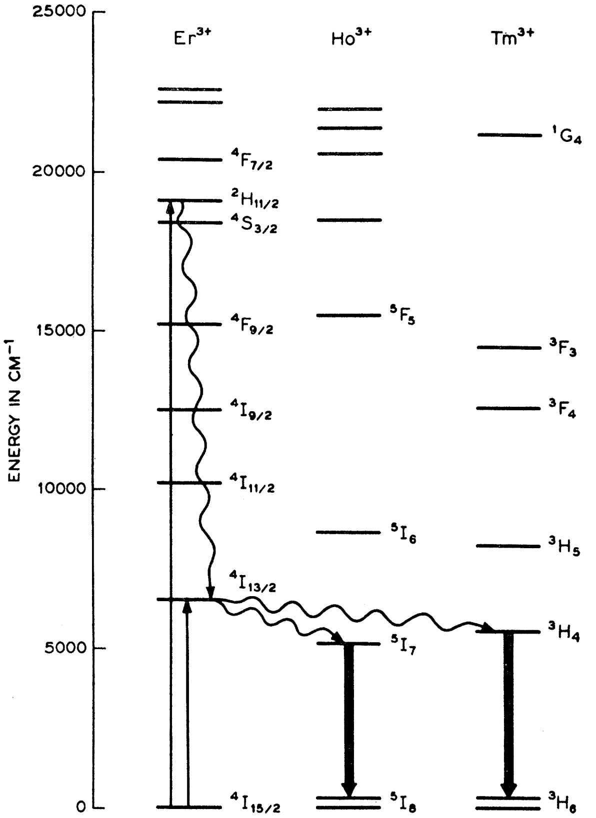

FIG. 10. Energy levels of Er^{3+}, Ho^{3+}, and Tm^{3+} ions in $CaMoO_4$ and the mechanism of $Er^{3+} \rightarrow Ho^{3+}$ and $Er^{3+} \rightarrow Tm^{3+}$ energy transfer. Nonradiative transitions are designated by wavy arrows; maser transitions by heavy arrows. The term assignments for Er^{3+}, Ho^{3+}, and Tm^{3+} are taken from Refs. 8–10, respectively.

A group of compounds in which maximum benefit may be obtained from energy transfer between rare-earth ions are the garnets. In addition to the general

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[16] Z. J. Kiss and R. C. Duncan, Jr., Proc. I.R.E. **50**, 1531 (1962).

property of preserving the sharp line fluorescence of rare-earth ions (typically <1 cm^{-1} wide at 77°K), the transfer agent may be incorporated in high concentration. For example, it was found that emission from 1% Tm^{3+} ions in the aluminum garnet $(Er_{0.5}Y_{0.5})_3Al_5O_{12}$ is 100 times stronger than in $Y_3Al_5O_{12}$. Similarly, Ho^{3+} (1%) emission is 40 times stronger in the erbium substituted compound. However, the full merit of these systems as optical masers can only be realized when larger crystals are available.

ACKNOWLEDGMENTS

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Excited States of Cesium Halide Crystals

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A model of the conduction band structure of cesium halide crystals is suggested. It combines the features of two earlier electron-transfer models by Fischer and Hilsch and by Klick and Kabler into one which, in the language of effective mass theory, amounts to requiring several, but at least three, separate conduction bands having a splitting of the order of 0.1 eV. On the basis of this model, both the fine structure of the cesium halide *F* bands and the unusually high multiplicity of cesium halide exciton bands can be consistently understood. Further implications of the model are discussed.

I. INTRODUCTION

In contrast with most alkali halides, the cesium halides show marked structure in absorption bands attributed to *F* centers.[1,2] As is well known, the *F* center is composed of an electron bound to a negative ion vacancy, a model well verified in the noncesium alkali halides and one which seems most reasonable to associate with the *F* bands seen in the cesium halides. Except for CsF, the cesium halides possess simple cubic Bravais lattices, so it appeared possible,[1] at least, that the *F*-band splitting in CsCl and CsBr was a consequence of the different local structure of the *F* center. The discovery of similar structure in CsF, a face-centered cubic crystal, eliminated this possibility,[2] while experiments on simple cubic phases of normally fcc alkali halides also failed to reveal structure-induced splitting in rubidium halide *F* centers.[3] Consequently, the blame seemed to fall on cesium itself, and Suffczynski[4] computed the spin-orbit splitting expected in a certain localized effective mass state in a cesium halide. His results indicated that the splitting should be negligible, again opening the entire issue to speculation.

It is our belief that spin-orbit effects do produce at least part of the *F*-band splitting, but in a more indirect way than that considered by Suffczynski. We propose that there are three conduction-band branches in the cesium halide crystal which display a splitting appropriate to that seen in the *F* band. This contention is supported by the existence of a similar unusual structure in the exciton bands of the cesium halides, which are, therefore, also to be understood on a many-branch conduction-band model.

II. THEORY

In Fig. 1 we present three hypothetical band structures of alkali halides. It is Fig. 1 (a) which we suggest represents the band structure of alkali halides not containing cesium, and Fig. 1 (b) which we suggest represents that of the cesium halides. Figure 1 (c) shows an

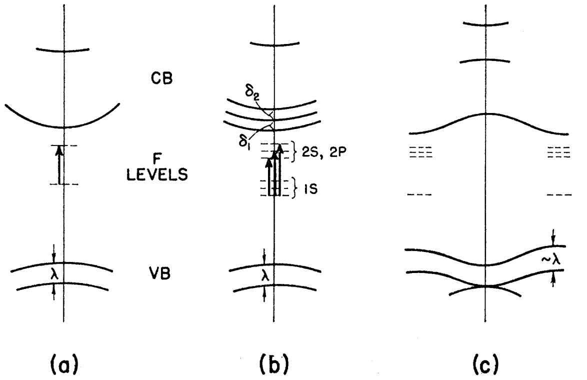

FIG. 1. Schematic band structures for alkali halide crystals. (a) Bands for crystals not containing cesium. (b) Proposed bands in cesium halides. (c) Possible bands in the cesium halides (see text). In all cases, λ is the spin-orbit splitting of the valence band.

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[1] H. Rabin and J. H. Schulman, Phys. Rev. Letters **4**, 280 (1961); Phys. Rev. **125**, 1584 (1962) (for CsCl, CsBr).

[2] F. Hughes and H. Rabin, J. Phys. Chem. Solids **24**, 586 (1963) (for CsF).

[3] D. Fitchen, Thesis, University of Illinois, 1962 (unpublished).

[4] M. Suffczynski, J. Chem. Phys. **38**, 1558 (1963).