sistivity) are thought to be consequences of improved sample purity, it would seem advisable to investigate the magnetic susceptibility of this sample over the temperature region in question. A temperature hysteresis effect was noted in the resistivity; that is, later runs on the same sample gave lower resistivity values at the same temperatures.

Figure 3 shows the behavior of the low-temperature resistivity of neodymium. The inset is a blow-up of the region from 0°K to 30°K showing more clearly the two jumps in the resistivity at 5°K and 20°K. Measurements of magnetic susceptibility,[5,7] thermoelectric power[8] and heat capacity[6] also indicate abnormal behavior near these temperatures. Lock[5] suggests that neodymium undergoes a magnetic transition near 7°K, being antiferromagnetic below this temperature.

The resistivity of samarium (Fig. 4) shows a knee at 14°K and a sharp change in slope at 106°K. Measure-

ments of specific heat[9] and thermoelectric power[8] show abnormal behavior near the higher temperature; maxima have been reported in the specific heat[10] and magnetic susceptibility[5] curves near 14°K. The suggestion has been made[5] that samarium is also antiferromagnetic below 14°K.

From a comparison of the results reported here with those reported earlier, it appears that the low-temperature resistivity of a rare-earth metal is very sensitive to the presence of impurities. The rare earths are very effective "getters" for negative impurities such as oxygen, carbon, nitrogen, and hydrogen; it is believed that very small amounts of these materials in the earlier samples drastically affected their resistivities.

ACKNOWLEDGMENTS

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Visible Luminescence of Rare-Earth Yttrium Gallium Garnets

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Yttrium gallium garnet ($Y_3Ga_5O_{12}$) has been prepared with small percentages of different rare earths substituted for yttrium. Garnets activated with Pr, Sm, Eu, Tb, Dy, Ho, Er, and Tm are all luminescent. The emission and excitation spectra of the samples have been measured at 77°K. The data have been analyzed in terms of the atomic energy levels of the impurity ions and the effects of crystalline field and of phonon interactions. Wherever possible, comments are made about whether the crystal field can be treated as possessing cubic or lower symmetry.

I. INTRODUCTION

IN previous works[1,2] we have reported on visible fluorescent emissions of SrS and $BaTiO_3$ singly activated with rare-earth ions. We analyzed the data in terms of the energy levels of the rare earths and the perturbations effected by the crystalline field potential. Because of the present widespread interest in garnet materials and because of the possibility of observing interesting magnetic interactions in iron garnets, we undertook a similar fluorescent investigation of these materials.

Previous data indicate that the rare earth has a free ion structure and that the crystal field potential effects a small perturbation on it. This is indicated by the similarity of optical data for different materials containing the same rare earth species. The similarity is especially

evident for short wavelength data involving transitions of $4f$ electrons, which are well shielded from the lattice by filled $5s$ and $5p$ orbitals. Lest it be thought that all materials containing rare earths possess the same optical properties, it must be pointed out that excitation spectra[3] can be very different for different materials.

In order to measure emissions from rare earth sites, there must be an energetic excitation of the site. There are two simple and important mechanisms for getting energy to the site. One mechanism involves an excitation of the host lattice by means of the creation of an electron hole pair. The free electron and hole can then recombine at a rare-earth site thus imparting energy to the rare earth, exciting it, and causing fluorescent emissions. For such a mechanism the excitation spectrum should be indicative of the host lattice and should

[1] S. P. Keller and G. D. Pettit, J. Chem. Phys. 30, 434 (1959).
[2] S. P. Keller and G. D. Pettit, J. Chem. Phys. 31, 1272 (1959).

[3] An excitation spectrum is defined as the dependence of the intensity of emitted light on the wavelength of the incident light.

show a broad peak characteristic of the absorption band of the host material. If the lifetime τ or the mobility μ of the charge carriers of the host material is unfavorable, the exciting energy may never arrive at the rare earth and hence exciting energy must be pumped directly into the rare earth from the incident radiation. In this second mechanism an excitation spectrum would be characteristic of the rare earth and would consist of multistructured peaks and bands. The first mechanism is found in materials like SrS and in relatively good photoconductors with appropriately good values of τ and μ. The second mechanism is found in materials with either short lifetimes, very low mobilities, or generally in poor photoconductors, like $BaTiO_3$ and, in the present case, $Y_3Ga_5O_{12}$.

With either mechanism of excitation the fluorescence results from optical transitions between excited states and lower states, including the ground state, of the activator. The gross structure of the fluorescence can be correlated with energy level spacings of the rare earths, whereas the fine structure can be correlated with Stark splitting of certain levels due to the internal crystal field. The magnitude of the splitting is, of course, related to the strength of the field, and the number of Stark components is related to the symmetry of the field surrounding the ion. A further complication may arise from phonon interactions as will be discussed later.

In summary, we can derive from optical data of rare earth activated materials, the following:

(a) the "goodness" or "badness" of a photoconductor from its excitation spectrum, (b) the probable symmetry of a site, (c) likely term signatures of various states of one or more configurations, (d) energy level spacings of rare earth ions, and (e) phonon interactions.

The present work describes and discusses data obtained from yttrium gallium garnet activated with a particular rare-earth ion. We have been able to obtain fluorescent samples with trivalent Pr, Sm, Eu, Tb, Dy, Ho, Er, and Tm ions. The excitation and fluorescent spectra contain a large number of structures. The major importance of the paper consists of the data which may be of value to various workers. At this point interpretations are rather conjectural and measurements obtained at other temperatures are necessary in order to remove this conjecture. We have tried to correlate the gross data with energy levels characteristic of the particular ion. The validity of the correlation can be determined by comparison with the results of many other workers in the field. In some cases we have been able to make the correlation with little ambiguity. On the other hand often the fine structure presents complications in interpretations due to phonon interactions and effects due to Stark components of excited states. In most cases we could make conjectures about certain fine structures and their possible causes. However, their origin is unresolved and for definitive answers we shall have to await data obtained at temperatures other than 77°K, the temperature of the present measurements.

The chemical preparations and the instrumentation are described in Sec. II. The data, discussion, and conclusions are presented in Sec. III, under separately marked subsections for each ion. Section IV contains certain over-all conclusions.

II. CHEMICAL PREPARATION AND INSTRUMENTATION

"Five nines pure" Ga_2O_3 was obtained from Eagle-Picher and "five nines pure" Y_2O_3 was obtained from Lindsay Chemical Company. The materials were intimately mixed in appropriate amounts with solutions of rare-earth oxides of spectroscopic purity obtained from Johnson Mathey. The mixture was fired in air for 1.5 hr in a quartz boat, at 1300°C. The concentration of the activators was varied from 0.02 to 2.0 molar %. The fluorescence spectrum did not change in structure but it did in intensity, in that the higher percentages resulted in more intense emissions. All data reported here are for 2.0 M % concentrations. Samples were prepared with each of the 13 rare earths. The eight reported on here were the only ones that were visibly luminescent. We do not know the reasons for our inability to obtain luminescent samples with the other five rare-earth ions. It is assumed that in each sample the rare-earth ions occupy only the yttrium site. It is possible that small percentages actually occupy gallium sites, or even interstitial positions which might explain certain aspects of the data. We shall continue with this assumption until we understand the data to such a degree that we have reason to doubt its validity.

The data were obtained at 77°K by means of a glass Dewar described elsewhere.[1] A Cary spectrometer, model 14, was used in all of the measurements. The spectral resolution is 1 A in the visible and ultraviolet region of the spectrum. The reproducibility is 0.5 A and the wavelength calibration is accurate to 4 A.

For the fluorescence measurements, the sample was excited by light focused onto it from a Bausch & Lomb grating spectrometer with a high-pressure dc Osram Xe lamp as the light source. The fluorescent emission was focused into the entrance slit of the Cary spectrometer and accordingly analyzed. For the excitation measurements, the Cary was operated in the single beam manner, the Xe lamp was placed at the entrance slit, and the sample was placed in the monochromatic beam near the 1P28 photomultiplier tube. The fluorescent emission from the sample was focused into the photomultiplier tube while the exciting light was eliminated by means of filters.

Fluorescent emissions for different wavelengths of exciting light and excitation spectra for different wavelengths of emitted light were determined. There were no quantitative differences in the various data. We were able to determine long wavelength excitation peaks by observing long wavelength emission peaks. In this way we were able to minimize problems arising due to reflected light. The fluorescence data presented here were
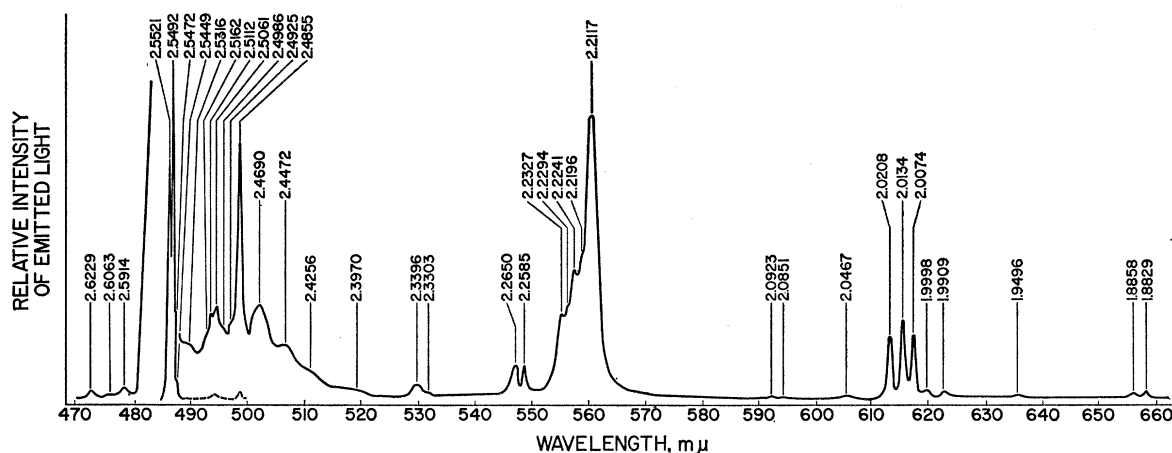
FIG. 1. Fluorescence spectrum for Pr^{3+}. The wavelength scale is in millimicrons and the numbers written above the structures denote the energy in electron volts.

excited with those wavelengths that gave the most intense emissions.

III. EXPERIMENTAL RESULTS AND DISCUSSION

If we assume validity of term signatures we can assign to any state a total angular momentum. As is well known the application of a crystalline field perturbation can remove some of the degeneracies associated with a particular state and various separated Stark components of that level will result. Group theory enables us easily to predict how many Stark levels are derivable from a state of a given angular momentum if the symmetry of the crystal field is known. In particular, if we assume that the ground state is obtained by means of Hund's rules and if we know that the final state of a particular optical transition is the ground state, then we may be able to determine what the predominant symmetry of the field is. The local symmetry around the yttrium is known to be orthorhombic. Some people have treated the problem as if the field were cubic and others have treated it as if the field were orthorhombic. The potentials derived from these symmetries would effect different splittings, and hence an analysis of the data as to the dominant symmetry of the field may prove useful. In the following sections, the data and discussions for each rare-earth ion will be presented separately together with the electron configuration, the Hund ground state, and the number of levels expected from cubic symmetry or less than cubic symmetry.

Certain general comments can be made about the excitation and fluorescence spectra. In the case of the former, if the ground state is separated from its nearest lying level by more than kT, the excitation spectrum should be indicative only of the excited state spacings. There may be regularly spaced structure to the long or short wavelength side of major peaks due to an absorption or emission of a phonon during the transition. The former should be quenched at low temperature. If there

are states lying close to the ground state and if more than one level is occupied, the excitation spectrum should indicate this multiplicity.

In the case of the fluorescence spectrum, if the spacings of the excited levels are small, one expects rapid thermal equilibration by means of phonon interactions. Hence, the fluorescence would be due to transitions from a single excited state (or several Stark components, if present, and if their energy separation is less than kT to ensure occupation) to various lower levels. (The energy of the transition from this excited state to the lowest lying state should show up in the excitation spectrum. This is not seen due to the fact that reflected light problems do not allow us to go to the long wavelengths in the excitation spectrum. Ideally, one should view a certain wavelength emission and seek the longest wavelength excitation that would excite this emission, but reflected light prevents this.) If the spacings of excited levels are such that thermal equilibration cannot ensue, then one should see identical emission bands displaced from each other in energy due to transitions from several excited states to the same set of low-lying levels. The emissions may be complicated by an absorption or an emission of phonons during the transition resulting in subsidiary structures to the short and long wavelength sides of the emission peak, respectively. The former should be quenched at low temperatures. If various structures on emission peaks are due to Stark splitting of excited states, then occupation of these states is temperature dependent. The same is true for the excitation spectrum where structure may be due to occupation of Stark components of a ground state. Hence, measurements at various temperatures can be definitive.

The excitation data will not be presented because they are too lengthy and involved and in most cases somewhat unrewarding. Instead, there will be a description of the pertinent facts obtainable from the data.

1. Pr³⁺

The ground state is $^3H_4$ with a $4f^2$ electron configuration. This ion has been investigated by a number of other workers.[4] If the field possesses predominantly cubic symmetry, four Stark levels would be expected and lower symmetry can result in nine levels. Figure 1 presents the fluorescence spectrum. The wavelength scale is millimicrons and the numbers written above the structures denote the energy in electron volts. (This is true for all spectra in the paper.) The break in Fig. 1 at around 4800 A indicates a change in the intensity scale.

The emission and excitation spectra are rather complicated and not too definitive. The emission spectrum has a strong doublet at 2.5521 and 2.5492 ev which is very close to an excitation spectrum doublet at 2.5524 and 2.5497 ev. Since this is on the short wavelength side of the fluorescence spectrum, it may well involve the ground state and hence the doublet can be due to either two Stark components of the ground level or of an excited state. Since the doublet energy spacing is less than kT and since the excitation spectrum does not show this structure throughout, this doublet must be due to Stark components of an excited state. The short wavelength peak is down in intensity by an amount that
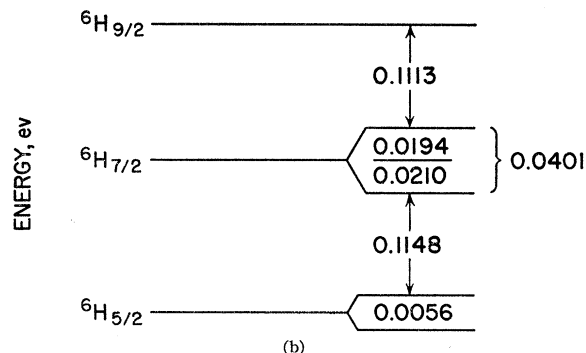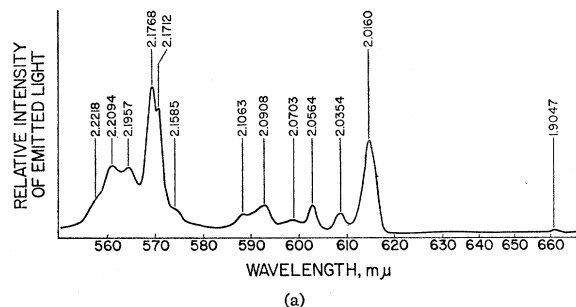

FIG. 2. (a) Fluorescence spectrum for Sm³⁺. The wavelength scale is in millimicrons and the numbers written above the structures denote the energy in electron volts. (b) Energy level diagram for the ground ^6H multiplet. The spacings are not to scale.

would be expected considering the Boltzmann population of the two excited states.

The emission peak around 2.55 ev is almost certainly due to a transition between the $^3P_2$ and one of the $^3H_{4,5,6}$ levels. The region between 2.6229 and 2.3970 ev in Fig. 1 undoubtedly contains peaks due to other transitions from the ^3P to the ^3H levels. The small structure near 2.33 ev may be due to $^3P_1 \leftrightarrow ^3H_5$ transitions as reported in the work cited in footnote 2. Probably the origin of the structures around 2.22 ev are the $^3P_0 \leftrightarrow ^3H_5$ transition, the 2.09 and 2.08 ev peaks are the $^1D_2 \leftrightarrow ^3H_4$ transition, and the peaks at 2.01 ev are the $^3P_0 \leftrightarrow ^3H_6$ transition, as reported in the work cited in footnote 2.

In neither the emission nor the excitation spectrum can we say much about phonon interactions. Measurements at temperatures other than 77°K are needed to distinguish between different effects. The data presented were obtained with the exciting radiation, from the Bausch & Lomb, peaked at 4.46 ev. Excitation at 3.37 ev resulted in the same fluorescence. These two energies were two of many peaks in the excitation spectrum. In all runs, exciting wavelengths were similarly determined from excitation spectra.

In an earlier work,[5] we reported on short wavelength emission for Pr³⁺. These results have not been made consistent with data reported here and in the works cited in footnotes 2 and 4.

2. Sm³⁺

The ground state is $^6H_{\frac{5}{2}}$ with a $4f^5$ electron configuration. There have been several investigations of this ion by other workers.[6] For a cubic field one expects two resultant levels and for a field of less than cubic symmetry three Kramers doublets could result. The excitation spectrum is rather complicated and not consistent with the energy level scheme that Dieke and Hall present. It appears that there are repeated energy separations of about 0.0053, 0.0066, and 0.0130 ev. However, the separated peaks do not have proper relative heights, they do not appear in wavelength regions where they might be expected and they are not repeated sufficiently to be definitively due to either phonons or Stark splittings of various levels. The 0.0053-ev spacing often seems to lie on the long wavelength side of major peaks. If this structure is due to phonon interactions, then a phonon must be emitted to the lattice in the transition. This situation would be expected to be independent of the temperature of the lattice and hence the measurements will have to be made at He and at room tempera-

[4] J. Brochard and K. H. Hellwege, Z. Physik 135, 620 (1953); C. B. Ellis, Phys. Rev. 49, 875 (1936); F. H. Spedding, Phys. Rev. 58, 255 (1940); E. V. Sayre, K. M. Sancier, and S. Freed, J. Chem. Phys. 23, 2066 (1955); B. R. Judd, Proc. Roy. Soc. (London) A241, 414 (1957); G. H. Dieke and R. Sarup, J. Chem. Phys. 29,

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[5] S. P. Keller and G. D. Pettit, Phys. Rev. 113, 785 (1959).
[6] A. Benton and E. L. Kinsey, Phys. Rev. 75, 888 (1949); S. Freed and J. G. Harwell, J. Am. Chem. Soc. 55, 54 (1933); F. H. Spedding and R. S. Bear, Phys. Rev. 46, 308, 979 (1932); G. H. Dieke and L. A. Hall, J. Chem. Phys. 27, 465 (1957); K. Oshima, S. Hayakawa, H. Nagano, and M. Nagusa, J. Chem. Phys. 24, 903 (1956).

FIG. 3. Fluorescence spectrum for Eu^{3+}. The wavelength scale is in millimicrons and the numbers written above the structures denote the energy in electron volts.
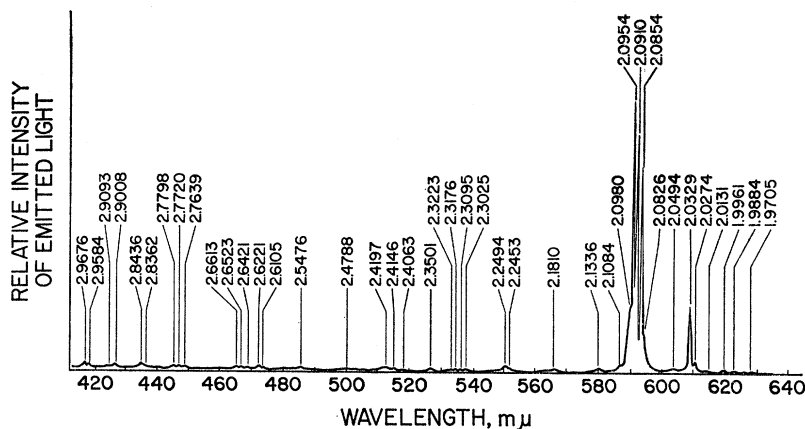
tures to decide its nature. The over-all spacings in the excitation spectrum are small enough that one would expect rapid thermal equilibration to prevail. If this is the case, the emission spectrum should be due to transitions from a single excited state to multiple lower states. But as we shall see, this is apparently not true.

If we examine the fluorescence spectrum, shown in Fig. 2(a), we see that the short wavelength emission has too much structure to be due to transitions from a single excited state to components of the $^6H_{\frac{5}{2}}$ state of which there can be at most three. The spacings and intensities are such that the data cannnot be explained as transitions from Stark components of an excited state. It is concluded that some of the peaks are due to these transitions, and the remaining structures are due to transitions from some higher excited state to various lower states. One can divide the sharp emission peaks into groups (2.1768 and 2.1712 ev), (2.0564, 2.0354, and 2.0160 ev), and (1.9047 ev). These are probably due to transitions from a single excited state to two Stark components of the $^6H_{\frac{5}{2}}$ level, three components of the $^6H_{7/2}$ level, and a single level of the $^6H_{9/2}$ level. These conclusions are summarized in Fig. 2(b). The spacings are consistent with what others have reported[1,2,6] (except for the work of Oshima et al.). There remain the broad and short peaks to account for. As already stated these can be due to transitions from different excited states to various lower states belying the idea of thermal equilibration of excited states. The splittings are consistent with a field of cubic symmetry. The data presented in Fig. 2(a) were obtained with the exciting radiation peaked at 3.05 ev. Excitation with 3.41-ev and 3.28-ev radiation gave the same emission spectrum.

3. Eu^{3+}

The ground state is $^7F_0$ with a $4f^6$ electron configuration. Since it is a nondegenerate state, there will be no splitting by any field. The excitation spectrum is rather complicated with no striking periodicity, although there appears to be an energy separation of about 0.0080 ev that is rather prevalent. Since the ground state is non-

degenerate, the excitation spectrum cannot show periodicity due to Stark components of the ground state. As will be seen, the $^7F_1$ state lies well above the $^7F_0$, compared to kT, and hence there will be no contributions to the excitation spectrum from this state. The separation of the peaks in the excitation spectrum are small and hence one would expect thermal equilibration among the excited states.

The fluorescence is presented in Fig. 3, in which the bands at 590 and 610 mμ are probably due to transitions from the $^5D_1$ and from the $^5D_0$ levels to the $^7F_1$ level, respectively. The first set of transitions would exhibit nine lines and the latter three, if the field were of low symmetry. The data show five or six for the former and two for the latter. This would lead one to believe that the $^7F_1$ is split into at least two levels. It may well be that there are actually three levels with all degeneracy removed. The energies of the transitions are consistent with the data of Dieke and Hall.[6]

The data obtained in Fig. 3 were obtained with exciting radiation peaked at 4.94 ev. Irradiation with 3.42-ev or 3.14-ev light gave the same emission spectra.

4. Tb^{3+}

The ground state is $^7F_6$ with a $4f^8$ electron configuration. The data presented here are similar to what has been reported earlier[1] and more involved than that reported by Dieke and Hall.[6] A cubic field would split the ground state into six levels and a field of lower symmetry could split it into 13 levels. The excitation spectrum is involved and shows no repetitive spacings or structures to enable us to say anything about fine structures.

The emission data are presented in Figs. 4(a) through 4(f). The intensities of the peaks of Figs. 4(d) and 4(e) are about five times those in the other regions. The spectra are fairly involved but certain conclusions can be offered. One is tempted to associate the emission between 380 and 390 mμ with transitions to the ground $^7F_6$ state in which case the 12 observed structures are consistent with a complete removal of degeneracy, the

(a)

RELATIVE INTENSITY OF EMITTED LIGHT

3.2786 3.2726 3.2678 3.2634 3.2560 3.2449 3.2387 3.2330 3.2165 3.2104 3.2041 3.1986

WAVELENGTH, mμ

380   390

(b)

RELATIVE INTENSITY OF EMITTED LIGHT

3.0283 3.0213 3.0100 3.0016 2.9898 2.9818 2.9727 2.9624 2.9601 2.9398 2.9324

WAVELENGTH, mμ

410   420

(c)

RELATIVE INTENSITY OF EMITTED LIGHT

2.8691 2.8570 2.8493 2.8447 2.8423 2.8329 2.8293 2.8191 2.8103 2.7974 2.7707 2.7550 2.7101 2.7061 2.6918 2.6799 2.6304

WAVELENGTH, mμ

430   440   450   460   470

(d)

RELATIVE INTENSITY OF EMITTED LIGHT

2.5851 2.5780 2.5695 2.5625 2.5533 2.5493 2.5440 2.5394 2.5379 2.5336 2.5298 2.5220 2.5164 2.5107 2.5083 2.5035 2.4978 2.4921 2.4677
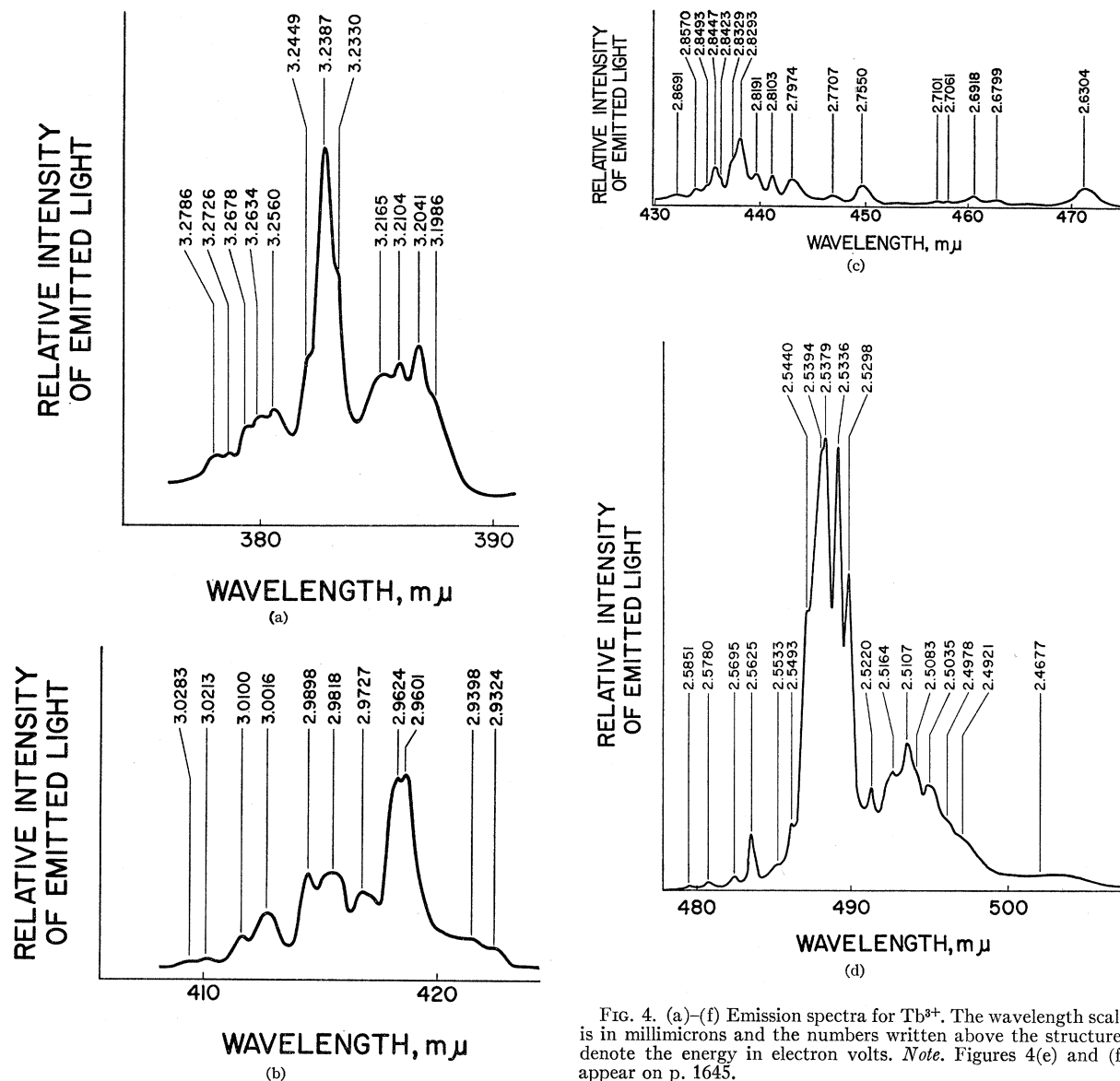
WAVELENGTH, mμ

480   490   500

Fig. 4. (a)–(f) Emission spectra for Tb^{3+}. The wavelength scale is in millimicrons and the numbers written above the structures denote the energy in electron volts. *Note.* Figures 4(e) and (f) appear on p. 1645.

thirteenth peak being unresolved. The two lowest levels are separated by 0.0060 ev, which is approximately equal to kT and hence might give rise to doublet structures on excitation peaks. This is not seen, nor is there any clear-cut association of this emission band with bands in the excitation spectrum. The spacing of about 0.0060 ev is common in this band as in other emission bands. This is also true of spacings of 0.0019, 0.0028, and 0.0057 ev. As a result one is tempted to associate these spacings with phonon interactions or with Stark components of excited states. The spacings are not that widespread nor are the intensities of various structures proper to be consistently amenable to such explanations. As in other cases, further temperature measurements are needed.

Continuing with the emission spectrum, one can con-jecture that the band around 415 mμ of Fig. 4(b) is due to transitions from the same excited state to the Stark components of the $^7F_5$ level. This leads to a separation between the $^7F_5$ and $^7F_6$ states of about 0.29 ev, which agrees with an earlier work[1] and with Dieke and Hall.[6] The number of structures seen is 11, which is consistent with the assumption of a low symmetry resulting in the removal of all the degeneracy.

The emission peaks between 430 and 470 mμ of Fig. 4(c) are numerous and probably due to transitions from the same excited state, as mentioned above, to the $^7F_4$ and the higher $^7F_{3,2,1}$ levels. The spacing between the $^7F_4$ and $^7F_5$ levels is about 0.16 ev which again agrees with previous work.

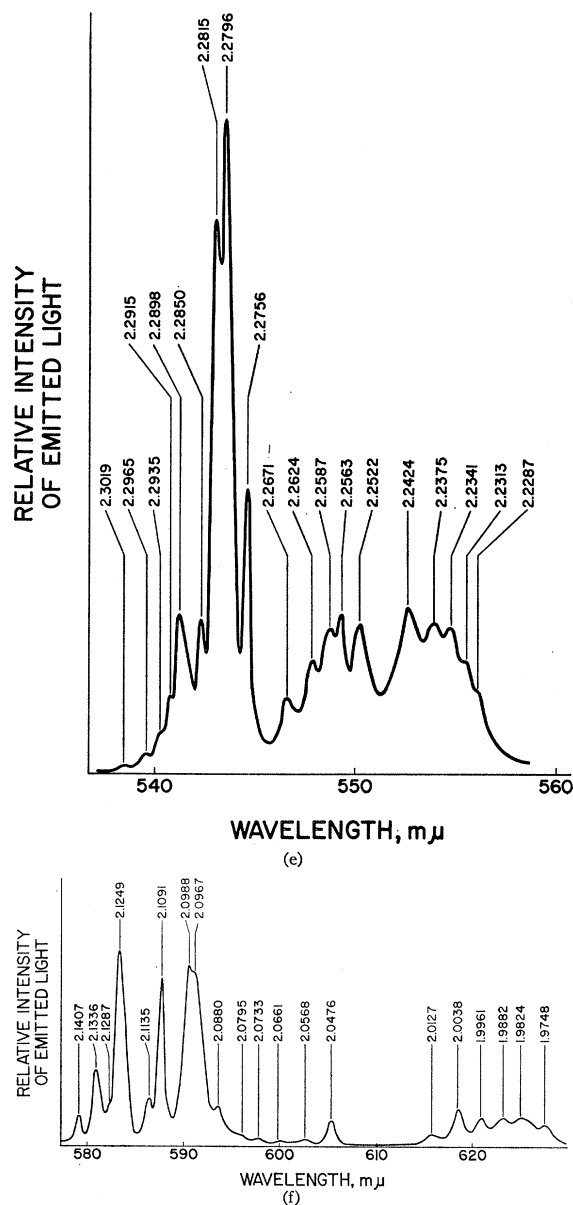Continuing, the structure around 490 mμ of Fig. 4(d), is probably due to transitions from a lower excited state

FIG. 4. *Continued* from p. 1644.

to the $^7F_6$ level. There are too many structures and hence there must be phonon interactions and/or several excited states. The similarity of this spectrum to that shown in Fig. 4(a) is not what one would expect if the end states of the transitions were the same. The emission around 545 mμ, in Fig. 4(e), is perhaps due to transitions to the $^7F_5$ level, but again the similarity between this spectrum and that in Fig. 4(b) is not what it should be. The widths of the bands around 380 and 490 mμ agree, but those of the bands at 545 and 415 mμ do not. The energy difference between the former pair is about 0.700 ev and the energy difference between the latter pair is about 0.715 ev, which is not a tremendous discrepancy.

The emission between 580 and 630 mμ in Fig. 4(f) is similar to that in Fig. 4(c), in numbers of peaks, complexity, and over-all groupings, but not in detailed structure. The energy difference between the two spectra is about 0.720 ev and so perhaps these are also transitions from the same lower excited state to various levels in the ^7F multiplet.

The data presented in Figs. 4(d), (e), and (f), may be due to the presence of a Tb^{3+} site inequivalent to the one responsible for the spectra presented in Figs. 4(a), (b), and (c). The inequivalence of the sites can easily result from crystal imperfection.

Independent of the explanations it is undoubtedly true that the symmetry is lower than cubic. It is also true that there are certainly phonon interactions in that there are shifts of energy between the excitations and the emissions, as in the case of the other ions. Again, measurements at other temperatures will shed further light on this problem.

The data presented in Figs. 4(a)–(f) were obtained with the exciting radiation peaked at 3.40 ev. When 3.27-ev exciting radiation was used, the fluorescence was the same with the exception that the emission bands shown in Figs. 4(a) and (b) were not present.

5. Dy^{3+}

The ground state is $^6H_{15/2}$ with a $4f^9$ electron configuration. As in the case of the others, this ion has been studied extensively.[7] A cubic field would split this level into five states and a field of lower symmetry can result in eight Kramers doublets. The excitation spectrum shows no repetitive short or long wavelength subsidiary structures, although spacings of about 0.0038 and 0.0063 ev are common, as in the case of other ions.

The fluorescence spectrum is presented in Fig. 5 and it is seen that the two shortest wavelength peaks are separated by an energy greater than kT. If these two peaks are due to transitions to ground-state levels, only the lowest will be appreciably occupied at 77°K. As a result the excitation spectrum results from transitions only from this lowest level and should be indicative of excited state spacings. The spacings in the excitation spectrum are rather close and one would expect thermal equilibration to prevail, so that only one excited state or several Stark components of it will be the initial states for the fluorescence transitions. As a result the fluorescence should be somewhat uncomplicated and it is seen to be so. Dieke and Singh measured Stark components of the $^6F_{11/2}$ excited state separated by 0.0096 and 0.0152 ev. A splitting of the latter magnitude would not be observable in an emission spectrum since it would not be appreciably occupied at 77°K.

Even though the fluorescence data in Fig. 5 contain

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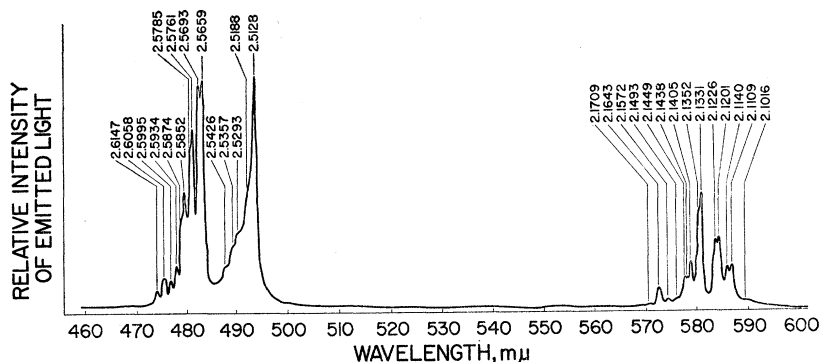
FIG. 5. Fluorescence spectrum for Dy^{3+}. The wavelength scale is in millimicrons and the numbers written above the structures denote the energy in electron volts.

considerable fine structure there is little doubt that the band around 480 mμ is due to transitions to the Stark components of the $^6H_{15/2}$ level and the band around 580 mμ is due to transitions to the Stark components of the $^6H_{13/2}$ level. The measured spacings between these multiplet states is consistent with Dieke and Singh and with Ford and Williams. There is present less structure than was reported in the work cited in footnote 1, but the present data are consistent with those in the work cited in footnote 2. The $^6H_{15/2}$ level and the $^6H_{13/2}$ level should lead to 8 and 7 Kramers doublets, respectively, if the field is of low symmetry. We see that the 480 mμ band has 15 peaks and the 580 mμ band has 14 peaks. Undoubtedly, all of the allowable degeneracy has been removed by the crystal field and the extra lines seen may be due to two Stark components of an excited state, probably the $^6F_{11/2}$ state. The data show 0.0060 ev as a repeated energy separation, as in the case of other ions. However, the data are not definite enough to allow this as a definite proof of two Stark levels of an excited state separated by this energy. It is also possible that this separation is caused by phonon interactions but again the data are not substantiative enough for a definite conclusion. There seems to be short rather than long wavelength structure on the sides of prominent peaks. If anything, one would expect long wavelength structure at this temperature, since the major process would be an emission of a phonon rather than an absorption of one. If the 0.0060-ev energy separation is due to two Stark components of an excited state, then
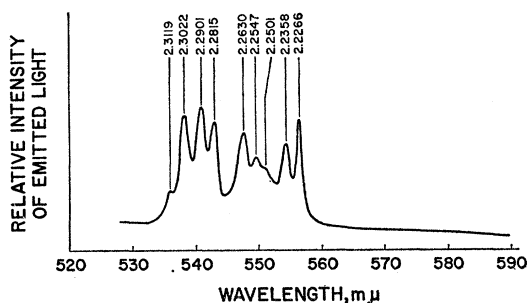
since $\Delta E/kT \sim 1$ the ratio of short wavelength to long wavelength peaks of the doublets should be approximately $\frac{1}{2}$. This is almost borne out with many of the peaks. Again, measurements at other temperatures are needed to shed more light on the general problem of phonons versus Stark components.

The data presented in Fig. 5 were obtained using exciting radiation peaked at 3.39 ev. Other excitation spectra were obtained using radiation peaked at 3.80 ev, 3.52 ev, and 3.21 ev. The resultant emissions were all similar.

6. Ho^{3+}

The ground state is $^5I_8$ with a $4f^{10}$ electron configuration. A cubic field would result in a splitting of this level into 7 states, whereas a complete removal of degeneracy is possible with lower symmetry resulting in 17 states. The excitation data are very detailed and involved. There are two short wavelength peaks separated by 0.0097 ev for which $e^{-E/kT} \sim 0.2$ and hence the second lowest level is not greatly populated. If one assumes these to be due to a doublet in the ground level then one might expect to see doublet structure in the excitation spectrum with the long wavelength structure down in intensity by the factor of 0.2 which would be difficult to observe. In fact, no such structure is seen. In the excitation spectrum the spacing of about 0.0035 ev is fairly widespread but not enough to be supportive of phonon interactions. This same spacing has been observed with other ions. The spacings between major excitation peaks are sufficiently small so that thermal equilibration can be attained via phonon interactions and one would expect the fluorescence to be due to transitions from a single excited state to lower levels. The simplicity of the fluorescence bears this out.

The fluorescence, shown in Fig. 6, has no structure that can be associated with phonons or Stark components of excited states. According to reference 1, the end state in this transition is not the $^5I_8$ state, but rather the $^5I_5$ state. According to Dieke and Hall in reference 6, the energy is too small for the $^5I_8$ ground state to be the end state in the transition and so it is likely to be the $^5I_5$ state, which should be split into 4 levels for a cubic field and 11 for one lower than cubic.

FIG. 6. Fluorescence spectrum for Ho^{3+}. The wavelength scale is in millimicrons and the numbers written above the structures denote the energy in electron volts.

The data in Fig. 6 were obtained with exciting radiation peaked at 3.44 ev. Other excitations were obtained with 2.96 ev and 2.73 ev as the exciting radiation, but the resultant emissions were all similar.

7. Er³⁺

The ground state is $^4I_{15/2}$ with a $4f^{11}$ electron configuration. A cubic field would split this state into 5 levels, whereas a field of lower symmetry could remove all but the Kramers degeneracy and could result in 8 levels. The excitation spectrum is quite complex, but shows no obvious repetitive structure that can be ascribed to either phonon interactions or occupation of several Stark components of the ground state. The spacings of about 0.0035 and 0.0050 ev seem prevalent as in other ions, but not so prevalent that they can be explained, with any certainty, as due to phonons. The spacings between levels are sufficiently small that one would expect appreciable interactions with phonons such that thermal equilibration would ensue. The fluorescence is uncomplicated and supports this conclusion.

The fluorescent data are shown in Fig. 7 and they are not sufficiently definitive so that we can say anything concrete about them. Again, a spacing of about 0.0050 ev is fairly common. This fact together with the fact that the same spacing is common in the excitation spectrum supports the idea of phonon structure, but the support is far from satisfying or adequate. Other temperature measurements are necessary.

Based upon earlier work[1,2] the peaks at 2.2855, 2.2812, and 2.2760 ev are probably due to transitions from an excited state to the split $^4I_{11/2}$ level and the peaks at 2.2329, 2.2289, and 2.2174 ev are probably due to transitions to the split $^4I_{9/2}$ level. The remaining structure is too much for field splitting of these levels.

Fluorescence spectra were obtained with exciting radiation peaked at 3.41 ev, 3.29 ev, and 3.25 ev. The spectra were all similar and Fig. 7 presents the one obtained with the 3.25-ev excitation.

8. Tm³⁺

The ground state is $^3H_6$ with a $4f^{12}$ electron configuration. This ion has been investigated by other workers.[8] A cubic field would split this ground level into six levels and a field of lower symmetry could split it into 13 levels. In the excitation spectrum there is no periodicity of the levels nor repetition of spacings. Long wavelength energy spacings are small enough that thermal equilibration among these states probably ensues. This is not necessarily true for the levels associated with short wavelength excitations. An excitation band shows up around 3.45 ev that bears good agreement with the

[8] H. A. Bethe and F. H. Spedding, Phys. Rev. **52**, 454 (1937); F. H. Spedding Phys. Rev. **58**, 255 (1940); J. B. Gruber and J. G. Conway (private communication); U. Johnsen, Z. Physik **152**, 454 (1958).
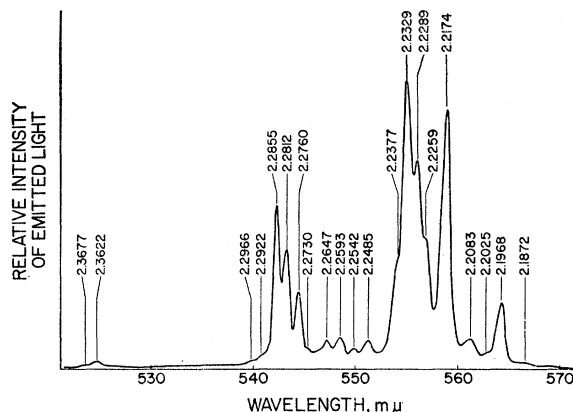

FIG. 7. Fluorescence spectrum for Er³⁺. The wavelength scale is in millimicrons and the numbers written above the structures denote the energy in electron volts.

spacing proposed by Spedding and Gruber and Conway,[8] which they attributed to the $^1I_6$ level. Spedding lists this as 3.43 ev above the ground state, which compares with our value. The excitation band we see is split into 6 structures with an over-all separation of 0.0353 ev. The splitting Spedding reports is 0.02 ev (for the hydrated sulfate). The significant aspect is that the splitting indicates six levels which is what is expected if the field were predominantly cubic. The remainder of our excitation spectrum bears no obvious relationship to Spedding's data.

The fluorescence spectrum is presented in Fig. 8. The energies of the emission peaks do not agree with that of Keller and Pettit,[1] but they do with Dieke and Hall[6] and are in fair agreement with the data of Spedding.[8] If the short wavelength structures are associated with the lowest lying levels, then the energy separation between the two lowest levels is appreciably greater than kT and hence the excitation spectrum would be uncomplicated by doublet structures, which turns out to be true. The long wavelength structure at 2.5586 ev is too far removed from the other emission peaks to be a Stark component of the ground level and it is rather close to be an adjoining multiplet level. (It perhaps is due to a transition from the pronounced $^1I_6$ level to one of the higher levels of the ^3H multiplet. According to Spedding the $^3H_5$ level lies 1.02 ev above the $^3H_6$ level.
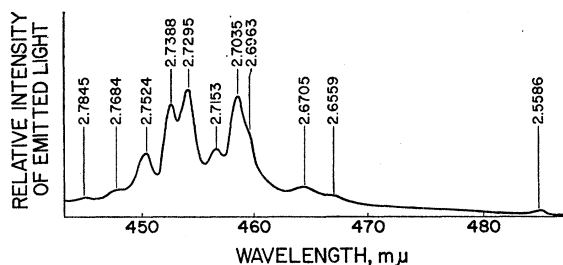

FIG. 8. Fluorescence spectrum for Tm³⁺. The wavelength scale is in millimicrons and the numbers written above the structures denote the energy in electron volts.

The $^1I_6$ level lies 0.80 ev above the $^1G_4$ level. If we assume the main emission located near 2.73 ev is due to transitions from the $^1G_4$ level to components of the $^3H_6$ level, then a transition from the $^1I_6$ level to the $^3H_5$ level would be shifted to longer wavelengths by 0.22 ev. We see that the 2.5586-ev peak is shifted by 0.18 ev and so this assignment is not unreasonable based upon energy spacings.)

There is no obvious phonon structure in the fluorescent spectrum. Since there are undoubtedly such interactions with excited states, one would expect to see phonon structure on the emission curve.

If one assumes a field of cubic symmetry, then the location of six levels derivable from Fig. 8 cannot be made to check with the spacings derived in the work of White and Andelin[9] in the limit of $a=0$. (The results of White and Andelin are unapplicable to the other ions mostly due to the fact that they appear to possess less than cubic symmetry whereas White and Andelin assumed cubic symmetry.)

As in the case of other ions, data are needed at other temperatures.

The fluorescence shown in Fig. 8 was obtained with exciting radiation peaked at 3.45 ev.

IV. CONCLUSION

The excitation spectra of the various samples have indicated to us that the rare earths must be directly excited and that energy transfer from the garnet lattice is inefficient. The fluorescent emissions, in many cases, can be related grossly to energy level assignments. The fine structure on the spectra pose quite different prob-

lems. We have tried to analyze them in terms of crystal field splittings of ground and of excited states. We have also invoked phonon interactions in that the rare earth could absorb or emit phonons coincident with a transition. Many conclusions can at best be conjectural and it must be remembered by the reader that the major contributions of this paper are the experimental data and the potentiality of the line of investigation. More work must be done in order to obtain definitive results. We plan to undertake measurements at room and at He temperatures in order to determine more about crystal field effects and phonon interactions, which are at present somewhat obscure.

We have assumed that the rare-earth ions occupy substitutional positions in place of the yttrium sites. Some of the fine structure might be due to the invalidity of this assumption in that a small percentage of the rare earth might be in gallium sites. Under the confines of our assumption, we have analyzed the data with a goal of determining whether a simple cubic field or one of lesser symmetry (e.g., orthorhombic) is the better approximation to the predominant symmetry of the site. The results indicate that simple cubic symmetry applies to Sm and Tm whereas less than simple cubic symmetry is necessary to explain the data for Pr, Eu, Tb, Dy, Ho, and Er. Why there is this difference remains an unanswered question.

There are further questions about the data which shall have to await their answers in additional data; e.g., why don't the same phonon interactions occur for all rare earths over a broader wavelength region?

ACKNOWLEDGMENT

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[9] R. L. White and J. P. Andelin, Jr., Phys. Rev. 115, 1435 (1959).