with $\delta r/r>0$. For these reasons, we prefer so far the older analysis.[27]

However, work has to be continued along the lines marked out in Ref. 8. The Mössbauer literature, for all isotopes, has been dominated so far by rather primitive "atomic" descriptions; in the long run, better molecular, or crystalline, models must be devised to correlate the various measurements that can be made.

ACKNOWLEDGMENTS

We wish to acknowledge our debt to Dr. Michael Wilson for his considerable help in teaching us about SCF atomic calculations and to Dr. Gordon Goodman for a stimulating conversation with regard to chemical theory. Bruce Zabransky and James Tison made many contributions to this work in the laboratory.

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[27] As this work was in press, an important paper [J. P. Bocquet, Y. Y. Chu, O. C. Kistner, M. L. Perlman, and G. T. Emery, Phy. Rev. Letters, **17**, (1966) 809] was published which employed new experimental data on conversion electron intensities to deduce $\delta r/r=+3.1\times10^{-4}$. This result is strong support for positive fractional change of the nuclear charge radius. The remaining difference in numerical values can be traced to the following facts: After difficult unfoldings of complex spectra, they found that the conversion rate in the 5s shell decreased by 25% in going from β-tin to SnO$_2$. On the other hand, the analysis given here indicates (see Fig. 2) that a 75% decrease would have been more satisfactory.

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Energy Levels of Yb^{3+} in Gallium and Aluminum Garnets. I. Spectra

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The interpretation of the near infrared spectrum of ytterbium in the gallium and aluminum garnets is greatly simplified by the observation that a majority of the lines can be identified as vibronic by virtue of their symmetric pairing as summation and difference sidebands about the transition connecting the lowest $^2F_{7/2}$ and $^2F_{5/2}$ ytterbium levels. The few lines which cannot be so identified are readily assigned as electronic transitions connecting the remaining $^2F_{7/2}$ and $^2F_{5/2}$ levels. This procedure provides a complete identification of all the 4f-electron energy levels of trivalent ytterbium based on experimental evidence alone. It is found that the first excited $^2F_{7/2}$ level occurs above 540 cm^{-1} in the gallium garnets and above 600 cm^{-1} in the aluminum garnets. New assignments are made for the $^2F_{5/2}$ levels in the aluminum garnets, these assignments being more similar to those already made for the gallium garnets. No spectral evidence is found in the gallium garnets for ytterbium ions occupying other than normal sites. However, there is some indication in the aluminum garnets that a small percentage of the ytterbium ions occupy abnormal sites.

INTRODUCTION

The spectra of ytterbium in the garnets have been reported over the past seven years.[1] It may therefore seem presumptuous and redundant to treat anew the analysis of these spectra. In fact, despite the amount of effort expended, no unambiguous analysis has been achieved prior to this time. That this is so may seem surprising in light of the expected simplicity of the 4f-electron energy level scheme of ytterbium. Even taking into account the low (orthorhombic) symmetry of the site on which the rare earths occur in the garnets, only seven levels (three for the $^2F_{5/2}$ and four for the $^2F_{7/2}$ states) are to be expected. The spectrum, consisting of transitions between these two manifolds of levels, would therefore be presumed to be sparse and easily interpreted.

In contrast with expectation, the spectrum is complex. Many more lines than can be explained on the above basis are observed. In the assignments made to date, arbitrary criteria have been used for identifying the few *bona fide* electronic transitions, arbitrary assumptions have been made as to the nature of the crystal field, and certain lines have been discarded without adequate justification. No two sets of prior analyses agree, nor does any agree with the analysis to be presented here.

Ytterbium is one of the few ions for which an exact low-symmetry crystal-field calculation is possible. Ytterbium is furthermore of interest in that it is the one ion for which a reasonable amount of experimental data relating to exchange-field-induced effects in the iron garnets are also available. The exchange-field problem is impossible to pursue in any depth without an adequate solution of the crystal-field problem. In light of the small number of 4f-energy levels for ytterbium and the need to use them all in a low-symmetry calculation, the crystal field cannot be obtained without a complete and correct interpretation of the spectrum.

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[1] The majority of the prior studies are summarized by M. T. Hutchings and W. P. Wolf, J. Chem. Phys. **41**, 617 (1964) in connection with their treatment of the crystal-field problem. Certain specific references will be mentioned later in this paper as appropriate.

The purpose of this paper has been to lay a solid foundation for such an exact crystal-field calculation. The calculation itself is reported in the following paper,[2] hereafter referred to as II.

This complete analysis has been possible as the result of a very thorough empirical study of the vibronic portion of the absorption spectra and, where necessary, a detailed consideration of the emission spectra as well. The vibronic analysis, in turn, was made possible by the use of very thick samples of undiluted ytterbium garnets, and through a careful consideration of the temperature dependence of both line frequencies and intensities.

EXPERIMENTAL PROCEDURES

Single crystals of ytterbium gallium garnet (YbGaG) and ytterbium aluminum garnet (YbAlG), and of yttrium gallium garnet (YGaG) and yttrium aluminum garnet (YAlG) containing small percentages of ytterbium were grown by standard techniques from a lead oxide-lead fluoride flux. All starting material used were at least 99.99% pure, a purity more than adequate for the optical studies to be described.

Samples for the absorption study were cut and polished as slabs. The thickness of these slabs was varied sequentially from about 5 mm down to about 100 μ, with spectra being taken at selected thickness intervals. All spectra were taken on a Cary Model 14RI spectrophotometer, this instrument being designed for enhanced performance in the near infrared (relative to the standard Model 14). The effective resolving power of the instrument in the vicinity of 1 μ as calculated for slit widths used in the present study was between 5000 and 10 000, this being sufficient to resolve the spectral structure of interest.

The crystal samples were mounted on the cold finger of a low-temperature Dewar[3] designed to fit into the sample compartment of the Cary spectrophotometer. This Dewar, equipped with a single set of Infrasil (infrared-transmitting quartz) windows, can be operated with either liquid helium or liquid nitrogen as the coolant. Temperatures above equilibrium were obtained by allowing the coolant to boil away and the Dewar to warm slowly. Sample temperatures were measured by means of a copper-constantan thermocouple mounted on the cold finger adjacent to the sample.

For the luminescence study, samples were prepared by grinding garnet crystals containing 1 mole % ytterbium. The powder was washed thoroughly with dilute hydrochloric acid, dried, and then packed into a recessed copper sample holder using amyl acetate as a binder. The copper sample holder was mounted in contact with a liquid-nitrogen-cooled reservoir suspended in an evacuated chamber. Luminescence was excited by means of a 0.5- to 5-μA electron beam accelerated through a potential difference of approximately 10 kV. The electron-beam excitation unit, of which the vacuum chamber and cooled sample holder are a part, is designed to mount directly on the Model 14 in the conventional sample compartment position, with the emitting sample at the focus of the spectrophotometer optics. The use of this excitation scheme provides a number of advantages. These include greater efficiency of excitation of luminescence and improved optical coupling with the spectrometer through precise control of the location, size, and shape of the region of the sample excited. On the other hand, it is difficult to operate with this type of excitation at temperatures below that of liquid nitrogen, and even at this temperature caution must be used to avoid electron-beam heating of the sample.

In order to obtain better luminescent spectra, the sensitivity of the Model 14 at 1 μ was improved further by replacing the standard detectors by an RCA 7102 photomultiplier tube having an *S*-1 type response. This detector, supported in a Dewar so as to allow liquid-nitrogen cooling, was mounted directly on the back of the Model 14 in the normal photomultiplier compartment position as used in luminescence studies. The spectrophotometer was calibrated against a standard quartz iodine lamp[4] using both the cooled photomultiplier and the usual lead sulfide detector. The results of the calibration indicate that system sensitivity in the vicinity of 1 μ is improved with the cooled photomultiplier approximately two orders of magnitude as compared with the lead sulfide cell. This calibration was also used to correct raw spectra for system spectral

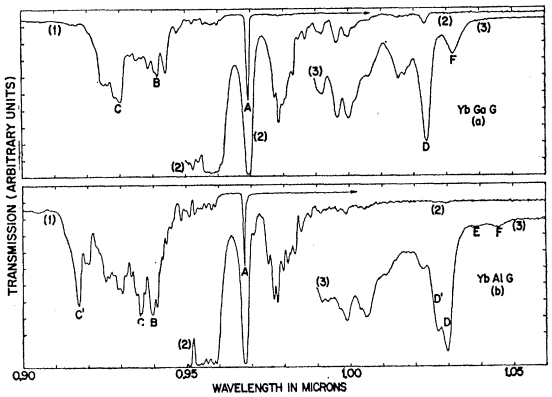

FIG. 1. Absorption spectra of ytterbium gallium and ytterbium aluminum garnets. (a) YbGaG; (1) thickness 72 μ, 77°K; (2) 2.9 mm, 77°K; (3) 2.9 mm, 115°K. (b) YbAlG; (1) 134 μ, 77°K; (2) 4.1 mm, 77°K; (3) 4.1 mm, 150°K.

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[2] J. J. Pearson, G. F. Herrmann, K. A. Wickersheim, and R. A. Buchanan, Phys. Rev. 159, 251 (1967).

[3] Except for minor modifications to the cold finger itself, this Dewar is identical with the commercial low-temperature accessory available for the Model 14. Its description and characteristics can be obtained from sales literature provided by Applied Physics Corporation, Monrovia, California.

[4] The standard lamp (Model P101), its calibration and power supply were obtained from Electro Optics Associates, Palo Alto, California.

response prior to calculating and replotting line intensities of interest in the present study.

BACKGROUND CONSIDERATIONS

Figure 1 shows the absorption spectra of YbGaG and YbAlG. Figure 2 shows the cathodoluminescent spectra of ytterbium in YGaG and YAlG. The first stage of the analysis of these spectra is to note, as in prior studies, that all absorption lines of wavelength longer than that of the lines marked *A* disappear when the samples are cooled below liquid nitrogen temperature. (Two minor lines near *A* in YbAlG are exceptions and will be discussed later.) This fact identifies *A* as the line corresponding to a transition from the lowest $^2F_{7/2}$ level to the lowest $^2F_{5/2}$ level of ytterbium. In addition, this fact indicates that all temperature-dependent lines of wavelength greater than *A* correspond to transitions originating on levels above the ground electronic level. As Wood has shown,[5] the temperature dependences of these lines demonstrate that they originate on a sequence of low-lying levels rather than on a single level, as had been presumed earlier. There are clearly many more lines observed than can be accounted for as electronic transitions alone. Contrary to Wood's assumption,[5] we have found it necessary to consider the possibility that the majority of these lines are in fact vibronic.

One expects to find for vibronic lines an essentially symmetric distribution about the more pronounced pure electronic transitions. That is, one expects to find to the low-frequency side of an electronic line those transitions (difference bands) starting on a vibrationally excited state and terminating on the pure electronic level of the ion, and to the high-frequency side those transitions (summation bands) starting on the pure electronic ground state and terminating on the electronic level plus the vibrationally excited level. In the case of a rare earth, where we do not expect the force constants between the ion and its neighbors to be noticeably dependent upon the states in which the 4*f* electrons find themselves, the result should be a symmetric distribution of sidebands about the pure electronic line with the separations from that line corresponding to the various vibrational frequencies adding to or subtracting from it.

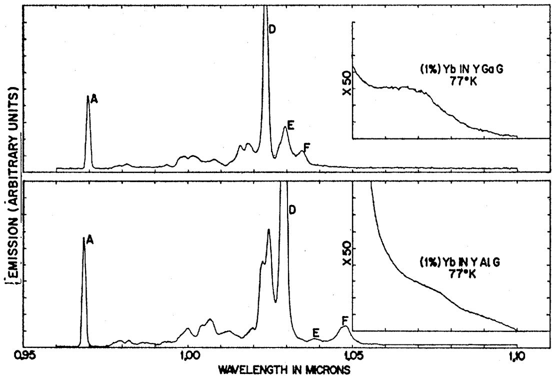

FIG. 2. Cathodoluminescent spectra of (1%) Yb^{3+} in (a) YGaG and (b) YAlG with sample temperature near 77°K. Insert has emission intensity scale expanded 50 times.

Accordingly, one would expect to find a symmetric distribution of vibronic lines about each electronic transition. As we show below, the vibronic lines comprising the majority of the ytterbium spectrum show up in combination with the transition from the lowest $^2F_{7/2}$ to lowest $^2F_{5/2}$ levels alone. This result, while unexplained is nonetheless fortunate, for otherwise the spectrum would be significantly more difficult to interpret.

The absorption spectra of the concentrated ytterbium garnets are to be preferred to those of the dilutely doped yttrium garnets for the vibronic analyses to be undertaken. The vibrational sidebands are better defined in the ytterbium garnets, probably because of the complete regularity of size and mass of the ions occurring on the rare-earth site. Also, the intensities of the lines for crystals of practical thickness are much greater. This is important to the observation of difference bands starting on the more energetic levels since these are weakly populated at the necessarily low working temperatures.

Since in the crystal-field calculations to follow, *g* tensors must be utilized in addition to energy levels, and since *g* tensors are available only for ytterbium in yttrium gallium and YAlG, we must also concern ourselves with the spectra of these dilute garnets. Although we cannot obtain good absorption spectra of the difference bands for these materials, we can in principle obtain much the same sort of information in somewhat less detail from luminescence data. Luminescence, conversely, cannot be excited in the concentrated garnets. However, once the vibronic nature of the majority of the lines has been established in the concentrated garnets, the comparison of luminescent and absorption spectra in the dilute garnets can be carried out in exactly the same way as the comparison of the summation and difference sidebands in the absorption spectra of the concentrated garnets, with the further correlation between the dilute and concentrated garnets also being possible at this point.

RESULTS AND DISCUSSIONS

In order to observe more directly the vibronic symmetry, the spectrum of YbGaG has been redrawn in Fig. 3 on a linear wavenumber scale and folded about line *A*. The coordinate scale is established by plotting the wave numbers of all lines relative to line *A* as the origin. For comparison purposes the intensities of all spectral lines of wavelength shorter than line *A* are plotted negatively. Note that the upper ordinate is the measured absorption coefficient $\alpha = (1/x)\ln(I_0/I)$, while the lower ordinate is the absorption coefficient divided

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[5] D. L. Wood, J. Chem. Phys. **39**, 1671 (1963).

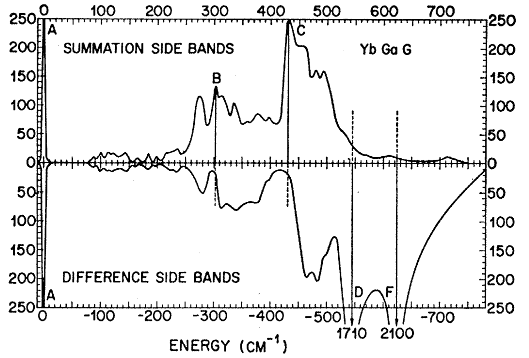


FIG. 3. Absorption spectrum of YbGaG folded about line A and plotted on a linear cm^{-1} scale relative to line A. The upper curve is a direct absorption coefficient plot, while the lower curve is the absorption coefficient divided by the Boltzmann factor.

by the Boltzmann factor. The purpose of this is to remove the temperature-dependent part of the absorption coefficient in order to compare intensities of difference bands with summation bands. On this plot, the vibronic lines coupling with A can easily be detected as coincidences between absorption peaks on the upper curve (summation bands) and on the lower curve (difference bands). Indeed, the frequency and intensity correlation between the summation and difference bands of A is very striking, with 18 pairs being closely recognizable. The degree of correlation between the summation and difference sidebands can be expressed by the root-mean-square of the differences between the frequencies of each assigned vibronic pair. Even without considering temperature corrections, this value is 3.7 cm^{-1} for the 18 pairs of vibronic lines observed in YbGaG. Surprisingly, almost the entire spectrum can be assigned as vibronic, these lines as noted earlier coupling *only* to line A.

Next, we consider those strong lines in Fig. 3 which have no correlation as sums and difference bands, the assumption being that these should be the remaining pure electronic transitions. Two lines should appear on the upper curve which correspond to transitions from the ground state to the two uppermost electronic states of $^2F_{5/2}$. There are only two strong lines which qualify. These are marked B and C. Three lines which have no counterpart on the upper curve should appear on the lower curve, these resulting from transitions originating on the three upper $^2F_{7/2}$ electronic levels and terminating on the lowest $^2F_{5/2}$ level. The two strongest lines in the lower spectrum, which are marked D and F, have no counterpart in the upper spectrum and are assigned as two of the expected transitions. The remaining $^2F_{7/2}$ level cannot lie below 500 cm^{-1} because *all* of the lines in this region have already been assigned as vibronic. The missing level therefore must either be nearly coincident with D or F, or lie well above 600 cm^{-1}.

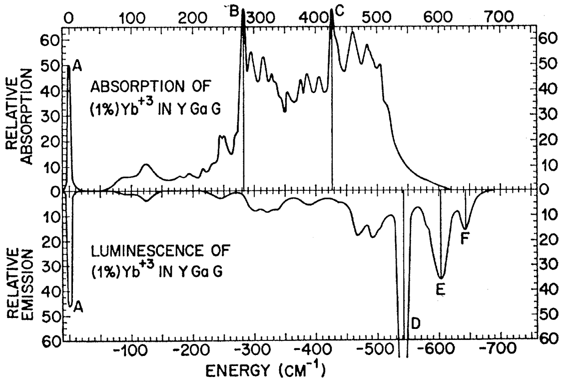


FIG. 4. Absorption and luminescence of (1%) Yb^{3+} in YGaG. The spectra have been redrawn on a linear wave-number scale and plotted relative to line A. The upper curve is the absorption spectrum of a 2.9-mm sample near 77°K. The lower curve is the luminescence spectrum of a powder sample near 77°K.

Figure 4 shows the luminescent and absorption spectra of YGaG containing 1% Yb^{3+} redrawn on a linear wave-number scale similar to Fig. 3. In Fig. 4 the emission spectrum (lower curve) has been corrected for the spectral response of the Cary 14 cooled photomultiplier system. The upper curve is the absorption spectrum. Although the luminescence spectrum of the dilute garnet does not exhibit the highly resolved structure observed in the absorption spectrum of the concentrated ytterbium garnet, there is a correlation of the emission peaks with peaks (or groups of peaks) in the absorption spectrum. In fact every emission peak out to 520 cm^{-1} can be correlated with vibronic peaks in the absorption spectrum. The two strongest peaks, marked B and C, in the absorption spectrum have no counterparts in the luminescence spectrum and must be the transitions from the ground state to the upper $^2F_{5/2}$ levels. The three strong peaks in the luminescence spectrum marked D, E, and F must likewise correspond to transitions terminating on the upper three $^2F_{7/2}$ levels since they obviously have no counterparts in the absorption spectrum.

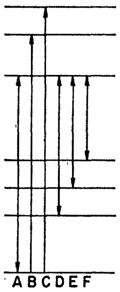
TABLE I. Summary of electronic transition frequencies of Yb^{3+} in gallium and aluminum garnets at 77°K. Values given in cm^{-1} in vacuum. a: absorption; f: fluorescence.

Line designation	(1%) Yb^{3+} in YGaG	YbGaG	(1%) Yb^{3+} in YAlG	YbAlG
A	10 309a 10 309f	10 313a	10 321a 10 321f	10 328a
B	10 592a	10 619a	10 620a	10 640a
C	10 739a	10 747a	10 674a	10 680a
D	9 766f	9 767a	9 710f	9 710a
E	9 710f		9 625f	9 627a
F	9 667f	9 689a	9 539f	9 562a

The frequencies assigned to electronic transitions for Yb^{3+} in YGaG and YbGaG are summarized in Table I and the energy levels deduced therefrom are shown in Fig. 5. Small differences between Yb^{3+} in YGaG and

YbGaG are observed because of the slightly different crystalline fields experienced by the rare-earth ions in the different hosts. It can now be seen by comparison of the ytterbium and doped YGaG spectra that the missing electronic line in the former spectrum must lie between lines *D* and *F*, thus accounting for the labeling sequence we have adopted.

We now proceed to an analysis of the aluminum garnet spectra. Figure 6 shows the spectrum of YbAlG redrawn on a linear wavenumber scale and folded about line *A* as the origin in the same manner as in Fig. 3. For reasons to be described, it was necessary to take into account the temperature dependences of line frequencies as well as line intensities. In the simpler gallium garnet spectra, the coincidences of vibronic pairs were easily recognized without detailed temperature corrections even though some of the difference spectra were of necessity taken at temperatures well above those at which the summation bands were obtained. In both the gallium and aluminum garnets, measurable frequency shifts occur over the temperature range of concern, and in interpreting the more detailed aluminum garnet spectra, correcting for these shifts has proven necessary. The corrections have been made in Fig. 6, all frequencies being those appropriate to liquid-nitrogen temperature and all intensities adjusted as in Fig. 3.



(1%) Yb IN YGaG	YbGaG	(1%) Yb IN YAlG	YbAlG	APPROX ERROR
10739	10747	10674	10680	±3
10592	10619	10620	10640	±3
10309	10313	10321	10328	±1
642	624	782	766	±7
599	(---)	696	701	±7
543	546	611	618	±4
0	0	0	0	

FIG. 5. Engery level diagram for Yb^{3+} in the yttrium and ytterbium garnets showing the transitions observed in this study. Values of the energy levels listed for the various garnets are in cm^{-1} in vacuum.

After the above-mentioned adjustments, 30 pairs of vibronic sidebands are found to be associated with line *A*, the root-mean-square of the discrepancy between deduced sum and difference frequencies being 2.9 cm^{-1}. The net conclusion, as for the gallium garnets, is that almost the entire spectrum is made up of vibronic lines, again coupling only with line *A*.

If, as before, we consider those lines which do not correlate adequately in terms of frequency and intensity, we must conclude that there are three candidates for the two electronic transitions expected on the summation side and that there are four candidates for the expected three transitions on the difference side.

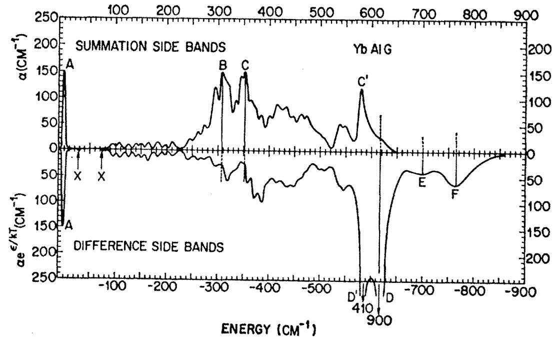


FIG. 6. Absorption spectrum of YbGaG folded over about line *A* and plotted on a linear cm^{-1} scale relative to line *A*. The upper curve is a direct absorption coefficient plot, while the lower curve is again corrected for Boltzmann distribution as in Fig. 3.

Lines *B* and *C* are clearly unrelated to lines *D*, *E*, and *F*. Lines *C'* and *D'* agree reasonably well in their separations from line *A*, but their intensities correlate poorly. Thus, while our immediate inclination would be to eliminate lines *C'* and *D'* as a vibronic pair, we cannot justify doing so without further evidence. We therefore turn to the temperature dependences of the lines in question as a further guide to their assignment.

In Fig. 7 we show the shifts in line frequency with temperature. Since the lattice constant of the crystal increases with temperature, we would expect the overall crystal-field splitting of each ^2F manifold to decrease with increasing temperature. This assumes that the primary effect depends on the change in the cubic part of the field rather than on the distortions from cubic. There should therefore be a net decrease with temperature of the frequency of all lines starting on the ground state and terminating on the $^2F_{5/2}$ levels. Lines

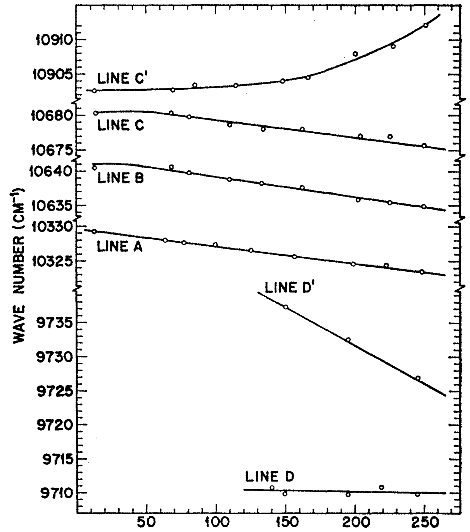


FIG. 7. Temperature dependence of certain absorption lines of the YbAlG spectrum. The labeling of the lines corresponds to that used in Fig. 1. Note thr broken ordinate scale used in this plot,

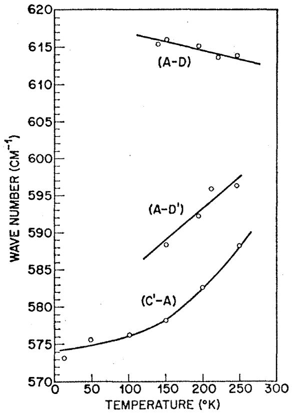


FIG. 8. Temperature dependence of the cm^{-1} differences of certain lines in the absorption spectrum of YbAlG. The labeling of the lines corresponds to that used in Figs. 1 and 7.

A, *B*, and *C* obey this prediction while *C'* clearly does not.

Going one step further, if *C'* is vibronic and if *D'* is its counterpart, then *C'* and *D'* should shift away from line *A* with temperature at the same rate. To test this possibility, we have plotted in Fig. 8 the difference frequencies (in wave numbers) of *C'* and *D'* relative to *A*. It can be seen that the two lines show the same type of behavior with temperature both as regards sign and slope. For comparison the temperature dependence of line *D*, a presumed electronic transition, relative to *A* is also plotted. As can be seen, the separation of *D* from *A* decreases with increasing temperature, as would be expected presuming this separation to correspond to a $^2F_{7/2}$ splitting. The temperature dependences of lines *E* and *F* could not be determined reliably because of the restricted temperature range over which they could be observed.

On the basis of the foregoing considerations, we assign lines *A*, *B*, and *C* as transitions from the lowest $^2F_{7/2}$ level to the three $^2F_{5/2}$ levels and lines *D*, *E*, and *F* as transitions from the remaining $^2F_{7/2}$ levels to the lowest $^2F_{5/2}$ level. Since all ytterbium levels are thus identified in YbAlG, the correspondence with the absorption and luminescence spectra of ytterbium-doped YAlG can be made directly. The frequencies and deduced level separations for the aluminum garnets are summarized with those of the gallium garnets in Table I and Fig. 5.

Although the $^2F_{7/2}$ crystal-field splittings are somewhat larger in the aluminum garnet than in the gallium garnet, the general correspondence of levels in the two hosts is clear. Once again we disagree with Wood[6,5] and Koningstein[7] on the $^2F_{7/2}$ assignments in that we find for the aluminum garnet no levels other than the ground state below 600 cm^{-1}. We also disagree with these workers on the location of the uppermost $^2F_{5/2}$ level. As can be seen from Fig. 5, the disposition of the $^2F_{5/2}$ levels in the aluminum and gallium garnets is made more similar by our assignment. The disagreement on the $^2F_{5/2}$ level assignment is directly related to whether line *C'* in the aluminum garnet spectrum is assigned as electronic or vibronic.

Koningstein has suggested[7] that there are "extra" lines in the ytterbium garnet spectra arising from Yb^{3+} ions occupying other than normal rare-earth sites. No evidence for any extra lines was observed in our gallium garnet spectra. However, two weak lines (marked *X* in Fig. 6) having no vibronic counterparts on the high-frequency side of *A* and persisting at liquid-helium temperature, were observed in the aluminum garnet spectrum. These seem likely to be spectra of Yb^{3+} ions either on abnormal sites or on regular sites but adjacent to some lattice defect. The integrated absorption intensity of these extra lines is approximately 1% of that of line *A*. If the ions giving rise to these spectra are on sites of substantially different symmetry, there is no reason to presume a transition probability for these satellite lines which is at all similar to that for transition *A*. Thus it is unsafe to draw from relative line intensities any conclusion as to the precise number of ytterbiums on abnormal sites. The best we can say is that the number must be a relatively small percentage of the ytterbiums on normal rare-earth sites.

Finally, we remark on the very weak luminescence observed[8] near 1.07 μ for Yb^{3+} in YGaG and near 1.075 μ for Yb^{3+} in YAlG. Although the origin of these emissions is not certain, it is our presumption at this time that they correspond to transitions from the lowest $^2F_{5/2}$ level to vibrational overtone levels near 975 cm^{-1} in YGaG and 1025 cm^{-1} in YAlG. The three most intense vibronic emission lines observed in the gallium garnet terminate on vibrational levels at 469, 491, and 501 cm^{-1} (average = 487 cm^{-1}). These vibrations would have first overtone levels near 974 cm^{-1} neglecting anharmonicity. The strongest vibronic emissions in YAlG terminate on levels near 547 and 566 cm^{-1} (average = 556 cm^{-1}). These vibrations would similarly have first overtones near 1112 cm^{-1}. While the correspondence between the frequency separations of these weak emissions from the lines *A* and the predicted vibrational overtones is not perfect, the agreement is sufficient to support qualitatively the interpretation given.

CONCLUSIONS

The interpretation of the complicated absorption spectrum of Yb^{3+} in the gallium and aluminum garnets can be greatly simplified by noting that the spectrum is composed primarily of vibronic sidebands coupling *only* to the electronic transition connecting the lowest $^2F_{7/2}$ and $^2F_{5/2}$ levels. Eighteen such pairs of vibronic

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[6] R. Pappalardo and D. L. Wood, J. Chem. Phys. **33**, 1734 (1960).

[7] J. A. Koningstein, Theoret. Chim. Acta **3**, 271 (1965).

[8] G. F. Herrmann, J. J. Pearson, K. A. Wickersheim, and R. A. Buchanan, J. Appl. Phys. **37**, 1312 (1966).

sidebands are observed in YbGaG and 30 pairs in YbAlG. The remaining lines which cannot be so paired are identified as the electronic transitions between levels of the $^2F_{7/2}$ and $^2F_{5/2}$ groups. Using this information together with luminescent data it has been possible to identify for Yb^{3+} all the $^2F_{7/2}$ and $^2F_{5/2}$ energy levels, as summarized in Fig. 5.

The assignments differ most notably from previous assignments in that no $^2F_{7/2}$ states except the ground state are observed below 540 cm^{-1} in the gallium garnets and 600 cm^{-1} in the aluminum garnets. The significance of this observation will become more apparent in the discussion of magnetic susceptibilities to follow in II. In anticipation of these discussions, we note that Van Vleck,[9] arguing from susceptibility data alone, has already questioned the existence of electronic levels below the limits just set.

While it has been suggested that some Yb^{3+} ions may occupy sites other than the normal rare-earth site, we see no evidence for this in our YbGaG spectrum. Two extra lines were observed, however, in the YbAlG spectrum and on the basis of their intensities we conclude that a small percentage of the Yb^{3+} ions do occupy other than normal rare-earth sites in our aluminum garnet crystals. This observation, too, has some bearing on the susceptibility problem and will be discussed further in II.

Very weak Yb^{3+} emissions have been observed near 1.07 μ in YGaG and near 1.075 μ in YAlG. These emissions are thought to be transitions from the lowest $^2F_{5/2}$ electronic state to vibrational (overtone) levels near 975 cm^{-1} in YGaG and 1025 cm^{-1} in YAlG.

In closing, it should be emphasized once again that the level analyses presented here are now complete, unique, and independent of prior assumptions as to the crystal field. As such they provide (with separately determined g values for two states) a firm and sufficient basis for the crystal-field calculations to follow. The calculations in turn provide, through the quality of the fit, an independent verification of the experimentally deduced energy-level scheme. Beyond this, the calculations provide an unambiguous labeling of levels which could *not* have been obtained through experiment alone.

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Energy Levels of Yb^{3+} in Gallium and Aluminum Garnets. II. Calculations

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Complete crystal-field calculations for Yb^{3+} in yttrium gallium and yttrium aluminum garnets have been performed. The energies and g values obtained in the ten-parameter fits agree well with experiment. The calculated crystal fields are predominantly cubic with important sixth-order contributions. A five-parameter fit to these data was also computed, using point-charge-model constraints derived by Hutchings and Wolf. Results indicate that the point-charge model is a useful first approximation, but too crude for quantitative predictions. On the basis of the derived wave functions, the susceptibility was calculated over a wide temperature range. For yttrium gallium garnet, results agree well with experiment, but for the aluminum garnet, the calculated temperature-independent susceptibility is appreciably below the reported value.

I. INTRODUCTION

In order to understand the magnetic properties of the rare-earth iron garnets on a microscopic basis it is helpful to be able to separate the effects on the rare-earth ion of the iron exchange and the diamagnetic lattice by replacing the latter with an effective crystal field. The parameters of this field can be obtained to a fair approximation from the energy levels of the rare-earth ion in structurally similar nonmagnetic garnets. The symmetry of the rare-earth site in the garnets is so low that no fewer than nine independent crystal-field parameters must be determined, and many pieces of experimental data are needed for an accurate calculation. An exact computer calculation is feasible, despite the low site symmetry, for a rare earth as electronically simple as trivalent ytterbium. Until now a complete calculation has not been carried out, partly because of the difficulty of the calculation and partly because of the scarcity of dependable experimental information. The paucity of f-electron energy levels for ytterbium forces the use of supplemental g-tensor information. Furthermore, the optical spectrum of ytterbium is surprisingly complicated, and an unambiguous assign-