rough estimate of the number of direct (000) excitons required to explain the magnitude of the observed $\Delta\chi$. If as many as one fourth of the excitons are in the $n=2$ state, then the χ will be dominated by $n=2$ (χ goes like n^4). Then a steady-state exciton population of approximately $10^{14}/\mathrm{cm}^3$ would be required for an exciting pair concentration of the order of $10^{15}/\mathrm{cm}^3$. This would yield, using the known photon flux, an effective lifetime of the order of 10 μsec. On the other hand, if $n=1$ is the dominant state of excitation, about equal numbers of excitons and pairs would be required, giving an effective exciton lifetime of about 100 μsec.

We wish to acknowledge helpful discussions with members of our theoretical group, and in particular M. A. Lampert. We have been greatly helped in specimen preparation and apparatus construction by B. E. Tompkins.

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[2] W. Shockley, Electrons and Holes in Semiconductors (D. Van Nostrand and Company, Inc., New York, 1950), p. 323.

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[4] Because of the anisotropic effective mass in the (111) minimum, and since the reduced mass is dominated by the electron effective mass, this equation would be somewhat more complicated for indirect (111) excitons. However, for order of magnitude calculations it is adequate here.

OPTICAL OBSERVATION OF EXCHANGE SPLITTING IN YTTERBIUM IRON GARNET

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Both ytterbium iron garnet (YbIG) and ytterbium aluminum garnet (YbAlG) exhibit complex absorption spectra in the region between 8500 A (11 760 cm^{-1}) and 10 500 A (9520 cm^{-1}) which are associated with electronic and vibronic transitions from the $^2F_{7/2}$ to the $^2F_{5/2}$ levels of the Yb^{+++} ion. When the spectrum of Yb^{+++} in the aluminum garnet is observed under medium resolution, one relatively isolated line near 9700 A stands out as uniquely sharp and intense. Low-temperature observations indicate that this line represents an electronic transition from the ground state to the lowest of the $J=5/2$ levels. The terminal levels involved are each Kramer's doublets degenerate in the absence of magnetic or exchange effects.

The corresponding transition in ytterbium iron garnet exhibits structure even under medium resolution. We have investigated this structure and conclude that it results from the splitting of the degenerate Yb^{+++} levels by the exchange field of the neighboring Fe^{+++} ions.

High-resolution spectra were obtained using a 21-footing grating spectrograph belonging to the UCLA Department of Physics. The reciprocal dispersion of this instrument is approximately 2.5 A/mm in the first order. The garnet samples were flat, polished sections prepared from single crystals. The aluminum garnets were grown by the flame fusion process, while the iron garnets were flux grown.

Under high resolution, the sharp Yb^{+++} transition of the aluminum garnet previously mentioned shows an unexpected fine structure. [See Fig. 1(a) and (b).] We do not have sufficient information at present to explain this structure. It is probably of the same origin as the fine structure observed by Hellwege[1] and Dieke[2] in other rare-earth compounds. The components sharpen

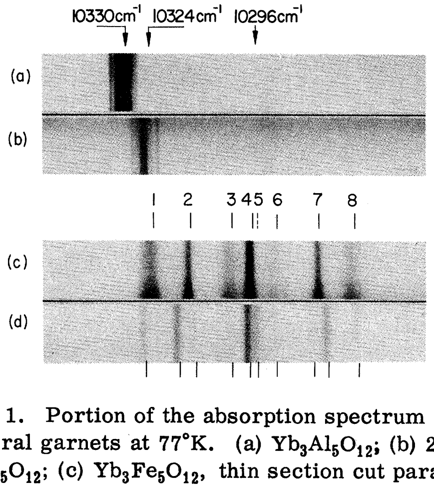

FIG. 1. Portion of the absorption spectrum of Yb^{+++} in several garnets at 77°K. (a) $Yb_3Al_5O_{12}$; (b) 2% Yb in $Y_3Al_5O_{12}$; (c) $Yb_3Fe_5O_{12}$, thin section cut parallel to a (211) plane, no external field; (d) same as (c), but with a 3000-gauss field along a [321] direction.

somewhat when the ytterbium is diluted heavily with yttrium, but the splittings remain essentially unaltered. This casts some doubt on any explanation involving exchange between neighboring ytterbium ions. Although a significant sharpening of spectral lines occurs upon cooling from 300°K to 77°K, there is almost no change in linewidths or intensities upon cooling the aluminum garnet from 77°K to 4°K.

Whatever the origin of the fine structure in the aluminum garnet, the splitting of the Yb^{+++} transition in the iron garnet is an order of magnitude larger [Fig. 1(c)] and presumably results from a distinctive overriding mechanism. In the absence of an external magnetic field, the pattern consists of four rather diffuse lines and three relatively sharp lines. Direct photometric measurements show that the total integrated intensity of the diffuse lines is approximately the same as that of the sharp lines. At 4°K only the four highest frequency lines (1, 2, 3, and 4) are seen.

The Yb^{+++} ions occupy six magnetically inequivalent sites in the garnet lattice. For the magnetic field along certain crystal directions of high symmetry, the inequivalence is greatly reduced. In particular, for a magnetic field along the crystal [111] direction the Yb^{+++} sites are equally divided into two inequivalent sets.

Because of magnetic anisotropy, the local direction of spontaneous magnetization in YbIG is along a crystal [111] direction in the absence of an external field; an applied field of 2000 to 3000 gauss is sufficient to overcome the magnetic anisotropy and move the magnetization (with its exchange fields) into any desired crystal direction. In agreement with these facts, we found that applying a magnetic field of 3000 gauss along a crystal [111] direction produced no perceptible shift or splitting of the field-free pattern (but did sharpen the lines slightly), whereas magnetic fields of comparable magnitude applied in certain other arbitrary crystal directions caused marked changes in the absorption spectrum producing generally a larger number of absorption lines spread over roughly the same total wavelength interval. The absorption with a 3000-gauss field along a crystal [321] direction in the sample plane is shown in Fig. 1(d). Application of a larger (12 000 gauss) field along the same direction did not change the character of the pattern but compressed the splittings measurably, in accord with the expectation that the external applied and exchange fields will be antiparallel.

In view of the above data, the structure of the observed optical transition in YbIG can be unambiguously assigned as arising from the splitting of Kramer's doublets for Yb^{+++} ions on magnetically inequivalent crystallographic sites through exchange interaction with the ferrimagnetically aligned Fe^{+++} ions. The energy-level diagram for the field-free (or small field in [111] direction) case is given in Fig. 2.

Polarized-light experiments with a 3000-gauss field along the [111] direction were also conducted. The outer lines (1, 2, 7, and 8) were stronger when the incident radiation was polarized such that E was perpendicular to H_{ext}; whereas the remaining lines were stronger when E was parallel to H_{ext}. These effects are suggestive of the ordinary Zeeman selection rules.

Two features of the exchange splitting are remarkable: (1) the large size of the splitting, and (2) the large anisotropy of the splitting. Although the incomplete state of our knowledge of the crystalline fields acting on the ytterbium ion (and determining its ground-state wave function) precludes quantitative calculation of the expected splitting, certain properties of that ground state are already known from paramagnetic resonance,[3] magnetic saturation,[4] and specific heat[5] data.

Meyer and Harris[5] observe a low-temperature peak in the specific heat of YbIG which can be

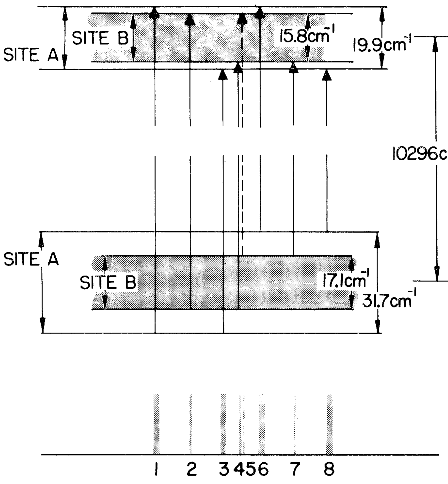

FIG. 2. Energy-level diagram for Yb^{+++} in YbIG indicating the transitions giving rise to the field-free spectrum shown in Fig. 1(c). (Transition 5 seems to be largely forbidden in the absence of a field, but appears on application of a magnetic field in the sample plane.)

fitted with an (isotropic) exchange splitting of 24.4 cm^{-1} of the lowest lying Kramer's doublet of the $J=7/2$ state. They also analyze Pauthenet's[4] data on saturation magnetization in YbIG to obtain a theoretical splitting of about 26 cm^{-1}. Our present results are in full accord with these observations, which represent in each case an average of the two inequivalent ground-state splittings distinguishable in the optical spectra. (See Fig. 2.) The exchange splitting is, however, two or three times larger than one would expect from extrapolation of the exchange coupling of gadolinium in the iron garnet as deduced from saturation magnetization or antiferromagnetic resonance data.[6] Corroborative information on the anomalously large exchange coupling of the Yb^{+++} ion is accumulating; for instance, differences in the vibrational spectrum of the crystal for the $J=5/2$ and $J=7/2$ states of the ytterbium ion indicate that the $4f$ electrons are participating perceptibly in the chemical bonding.

The large anisotropy of the exchange splitting is harder to understand. Paramagnetic resonance on Yb^{+++} in yttrium aluminum garnet and yttrium gallium garnet indicates that the g factor for the two inequivalent sites differs by only about 3% for H_{ext} in a [111] direction as compared with the 100% difference in exchange splitting observed here. A mapping of the exchange splitting in YbIG as a function of the crystallographic orientation of H_{ext} will be carried out as soon as experimentally feasible.

Theoretical calculations aimed at discovering the extent to which combined crystal field and exchange effects can break down the strong $\vec{L}\cdot\vec{S}$ coupling of this ion (destroying J as a "good" quantum number) are in progress. An analysis of the total optical spectrum of Yb^{+++} in the garnets to determine the crystal fields involved is also under way. It is further anticipated that a detailed investigation of the optical spectrum of other rare earth iron garnets will lead to the measurement of additional exchange splittings.

We wish to acknowledge the assistance of Dr. R. A. Lefever, who grew the single crystals used in this study. We also wish to thank Professor R. A. Satten and Mr. S. Pollack for allowing us to use the UCLA spectrograph and for assisting us with its operation.

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PARAMAGNETIC RESONANCE OF EXCHANGE-COUPLED Cr^{3+} PAIRS IN RUBY

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We have investigated the paramagnetic resonance spectrum of ruby (Cr-doped $\mathrm{Al_2O_3}$) crystals with concentrations of Cr^{3+} between 0.05 and 1.0% by weight. In addition to the Cr^{3+} lines, a very large number of weak lines are observed in the more concentrated samples. We believe that many of these weak lines arise from exchange coupling between neighboring chromium ion pairs.[1]

Measurements have been made at both 10 and 16 kMc/sec in various ruby samples. More detailed investigations were carried out using a crystal with 0.6% Cr^{3+} and a frequency of 15.74 kMc/sec. Comparison of the various crystals showed that the additional spectrum was strongly concentration dependent. Furthermore, the intensity of this additional spectrum was about what would be expected from Cr^{3+} ion pairs occupying neighboring lattice sites. The intensity of the lines reported below as measured in the 0.6% sample was ~ 1% of that of the isolated Cr^{3+}

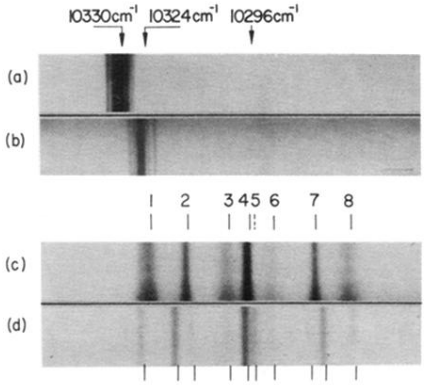

FIG. 1. Portion of the absorption spectrum of Yb^{+++} in several garnets at 77°K. (a) $Yb_3Al_5O_{12}$; (b) 2% Yb in $Y_3Al_5O_{12}$; (c) $Yb_3Fe_5O_{12}$, thin section cut parallel to a (211) plane, no external field; (d) same as (c), but with a 3000-gauss field along a [321] direction.