Magnetic Susceptibility and Crystalline Field Levels of Ytterbium Gallium Garnet*

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The paramagnetic susceptibility of YbGaG is measured over the interval 4–1000°K, primarily in order to obtain information on the location of the Γ_6 level, which, unlike Γ_8, does not combine magnetically with the ground Γ_7 state, and so is not detectable in the usual magnetic experiments at low temperatures. From our measurements it is inferred that the Γ_6 level is about 800 cm^{-1} above Γ_7. High precision cannot be claimed for this estimate, as our analysis of the magnetic data is made on the assumption of a perfectly cubic crystalline field, whereas the local symmetry at an individual lattice site is known to be but approximately cubic. In any case, the conclusion seems warranted that any low-lying levels at 100 cm^{-1} or so deduced from optical absorption data are of a vibrational rather than electronic nature.

THE energy levels associated with the crystalline field splitting of the rare-earth ion in ytterbium gallium garnet have been studied in various laboratories by measurements of magnetic susceptibilities[1–4] and by optical spectroscopy.[5] As a first approximation the crystalline field can be taken as being cubic, and the ground manifold of $Yb^{3+}(^2F_{7/2})$ splits into three components, Γ_7 (ground state), Γ_8, and Γ_6.[3,5] The magnetic measurements made by Ball, Garton, Leask, and Wolf[3] at low temperatures indicate that the spacing, $\Gamma_8-\Gamma_7$, between the ground and the first excited crystalline Stark level is 570 cm^{-1}. Similar results were also obtained by Ayant, Thomas, Cohen, and Ducloz.[4] More recently, from the study of the dependence of the intensity of the optical transitions on temperature, Wood[6] has reported two low-lying levels at 112 cm^{-1} and 308 cm^{-1} in addition to the one at 570 cm^{-1}. In this paper we shall present some measurements made at the University of Oklahoma of the paramagnetic susceptibility of ytterbium gallium garnet over the temperature range of 4–1000°K from which the crystalline field splittings of the $^2F_{7/2}$ manifold of the Yb^{3+} are determined. The main feature of the present work is that it extends to higher temperatures than previous investigations and so yields information on the location of the Γ_6 level which does not combine magnetically with the ground state, and so does not enter at low temperatures. Up to room temperatures, these measurements were made by the Faraday balance used in our previous work.[7] For higher temperatures, the cryostat assembly was replaced by a furnace similar to that of Garber, Henry, and Hoeve.[8] The accuracy of the susceptibility data is estimated to be about 1.5%. The measurements of temperature are accurate to 0.6% at temperatures below 750°K and to 3% for $T>750$°K.

Table I shows the experimental results above 29°. The susceptibilities given there have been corrected for the diamagnetism of the crystals. We do not include in the Table our measurements below 29° which were made on yttrium gallium garnet containing 10% Yb^{3+} impurity, as at the lower temperatures there are no appreciable deviations from the relation $\chi=(C/T)+\alpha$

TABLE I. Magnetic susceptibilities (cgs-emu/g-ion of Yb^{3+}) of YbGaG.

T	$\chi\times10^3$	T	$\chi\times10^3$
29.3	41.1	218	8.70
38.6	32.2	252	7.94
44.5	28.1	295	7.11
45.9	27.8	326	6.59
46.3	27.4	384	5.82
47.9	26.2	452	5.12
48.3	26.1	526	4.59
51.2	24.9	568	4.28
53.8	24.1	611	4.10
57.2	23.0	639	3.92
68.7	19.6	658	3.81
69.8	19.3	684	3.67
70.8	19.2	724	3.50
77.3	18.1	776	3.28
89.0	16.4	814	3.15
102.5	14.6	866	2.98
111	13.7	907	2.86
113	13.5	928	2.83
129	12.5	967	2.69
141	11.8	998	2.60
162	10.6	1038	2.50
181	9.92	1069	2.45
197	9.36	1109	2.37

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with the choice of constants that we give later. Our measurements do not extend to low enough temperatures to reveal the anomalies at $T\sim0.2°K$ which were reported by Ball *et al.*[3] and which are presumably caused by interionic coupling. The diamagnetic contribution was estimated by measuring the magnetic susceptibility of the pure yttrium gallium garnet which gives -85×10^{-6} cgs-emu per g-ion of the yttrium ion. The diamagnetic susceptibility of Yb^{3+}, however, differs slightly from that of Y^{3+} (by 6×10^{-6} per g-ion).[9] Thus, the diamagnetic correction of YbGaG is taken as -91×10^{-6} cgs-emu per g-ion of Yb^{3+}. The results are displayed graphically in Figs. 1 and 2. From these graphs it is seen that, below 150°K, the magnetic susceptibilities fit very well to the equation

$$\chi=(C/T)+\alpha, \qquad (1)$$

with $C=1.082$ and $\alpha=0.00397$ which is in fairly good agreement with Wolf's results[3] of $C=1.116$ and $\alpha=0.00358$ (probably without diamagnetic correction) and with the theoretical value of $C=1.096$ calculated from the g factors of the electron spin resonance data.[10] The discrepancies are more likely caused by differing amounts of chemical purity than by differences in the magnetic measurements *per se*.

As pointed out by Wolf,[3] α is affected only by the Γ_8 levels but not by the Γ_6. Using our value of α and assuming that the crystalline field is completely cubic, we obtain $\Gamma_8-\Gamma_7=515$ cm^{-1}. From the magnitude of α and the linear behavior of χ versus $1/T$ at low temperature, one may conclude that there are no crystalline Stark levels of Yb^{3+} below 515 cm^{-1}. The low-lying energy levels reported by Wood, therefore, should be attributed presumably to such effects as vibrational structure which have no appreciable effect on the magnetic properties. This interpretation is also

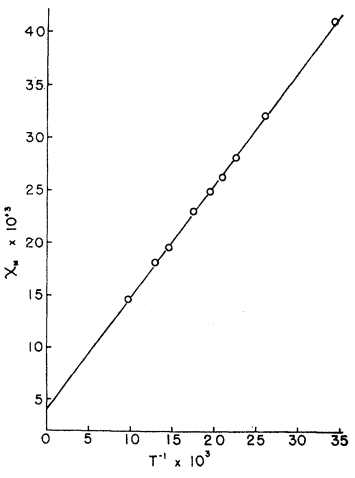

FIG. 1. Magnetic susceptibility versus $1/T$ from 30–100°K. The circles denote the experimental points and the solid curve gives the theoretical values according to Eq. (1).

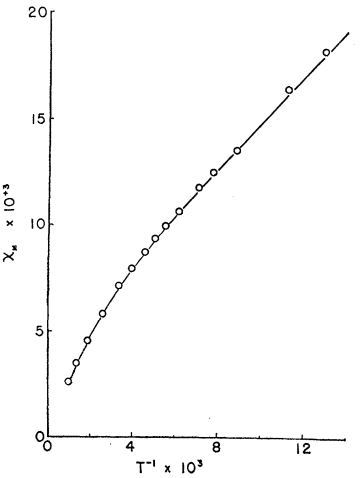

FIG. 2. Similar graph for the interval 77–1000°K. Theoretical values calculated from Eq. (2).

supported by the fact that Tinkham[11] has recently observed absorptions at 111 cm^{-1} for YbGaG and at 114 cm^{-1} for ErGaG which are identified as phonon transitions.

The magnetic data at high temperature may be used to determine the position of the Γ_6 level according to the formula

$$\chi=B\left\{\frac{4.0849}{\Delta_8}+\frac{2.164}{T}+\exp\left(\frac{-\Delta_8}{kT}\right)\left(\frac{3.5374}{T}+\frac{5.2952}{\Delta_6-\Delta_8}-\frac{4.0849}{\Delta_8}\right)+\exp\left(\frac{-\Delta_6}{kT}\right)\left(\frac{1.3333}{T}-\frac{5.2952}{\Delta_6-\Delta_8}\right)\right\}, \qquad (2)$$

where

$$B^{-1}=2+4\exp(-\Delta_8/kT)+2\exp(-\Delta_6/kT),$$

and Δ_8 and Δ_6 stand for the energy differences $\Gamma_8-\Gamma_7$ and $\Gamma_6-\Gamma_7$ (in units of cm^{-1}), respectively, and $k=1/1.44$. However, calculations show that χ is not very sensitive to $\Gamma_6-\Gamma_7$; a satisfactory fit to the experimental data can be achieved by taking $\Gamma_6-\Gamma_7$ anywhere between 700 and 900 cm^{-1}. The calculated susceptibilities obtained by using $\Gamma_6-\Gamma_7$ 800 cm^{-1} are shown in Figs. 1 and 2 (solid curves). The position of the Γ_6 level will change further if one includes the effects of the crystalline fields of lower symmetry in the susceptibility formula. However, in the absence of detailed information concerning the crystalline field, this point will not be pursued.

With the positions of the Γ_8 and Γ_6 levels, it is possible, in principle, to determine the two crystalline field parameters. Following the notation of Pappalardo and Wood,[5] we have

$$\mathcal{P}=22.5-27.8\text{ cm}^{-1}, \quad \mathcal{R}\sim+0.4--0.2, \qquad (3)$$

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which indicates that the parameter associated with $\langle r^6\rangle$ has much less effect on the level splittings than the one with $\langle r^4\rangle$. It is interesting to see if the relation $\mathcal{R}\ll\mathcal{P}$ is borne out by the point-charge picture. Using Eq. (7) of Ref. 5, we write

$$\mathcal{P}/\mathcal{R}=-11.7R^2\alpha_s\langle r^4\rangle/\alpha_s'\langle r^6\rangle\,, \qquad (4)$$

where R is the distance between Yb^{3+} and its nearest neighbors, α_s and α_s' are two screening factors as defined by Eqs. (2)–(6) of Ref. 5. An estimate of Eq. (4) can be made if we use the values of $\langle r^4\rangle$ and $\langle r^6\rangle$ calculated by Freeman and Watson[12] and set $\alpha_s=\alpha_s'$. This gives $\mathcal{P}/\mathcal{R}=-74$. The ratio of $\mathcal{P}$ to $\mathcal{R}$ as calculated from the point-charge picture is, therefore, in qualitative agreement with the experimental results.

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Dynamic Polarization by Thermal Mixing between Two Spin Systems

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A new dynamic nuclear polarization method is described, producing polarizations larger than the maximum polarization arising from a "solid effect." The main effect is a cooling of a spin system I in zero applied or effective field, where its Hamiltonian consists of its dipolar spin-spin interactions only; this cooling is followed by an adiabatic magnetization which produces the polarization. The cooling of the spin system I results from its thermal mixing with a second spin system S, having a large quadrupole interaction. Two types of experiments are considered: In zero applied field the thermal mixing is achieved in a frame rotating with respect to spins S and fixed with respect to spins I, by irradiating the sample with an rf field of frequency close to the quadrupole frequency of the spins S. When a dc field is applied, the mixing takes place in a frame rotating at different frequencies with respect to spins I and S, by using two rf fields of frequencies close, respectively, to the resonance frequency of each spin system. The theory is based entirely upon the concept of spin temperature, both in laboratory and rotating frames. Experiments performed on paradichlorobenzene confirm the main features of the theory and provide a further verification of the spin-temperature hypothesis. A maximum proton polarization eight times larger than the polarization arising from a full solid effect has been obtained.

I. INTRODUCTION

CONTACT between two spin systems in solids has been achieved in the past in various magnetic resonance experiments, where the magnetization of one spin system was influenced by the magnetization of the second one.

Among these are the nuclear calorimetry experiments in lithium fluoride,[1,2] the crossover of two resonance frequencies,[3,4] and the "solid effect," either in the laboratory frame[5] or in the rotating frame.[6] We shall see that all these experiments can be interpreted as thermal mixings, i.e., as the equalization of the temperatures of two systems.

In this description, the dynamic polarization by "solid effect" then appears as the cooling of a spin system. As this spin system experiences a magnetic field, such a cooling results in an enhancement of its polarization.

In the present work, we describe experiments of cooling of a spin system in low or even zero field through thermal mixing with a second spin system.[7] When performed in zero field, this cooling does not produce any polarization. However, the resulting increase of order is conserved if an adiabatic magnetization is performed afterwards, giving rise to a polarization. In contrast with the solid effect, cooling and production of polarization thus take place in two consecutive steps.

These experiments are performed under "low-field" conditions, i.e., when the effective energies of individual spins are comparable with the spin-spin interactions. In contradistinction, "high-field" conditions are realized

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