Electronic Raman Spectra: Crystal Field in Terbium Aluminum Garnet and Europium Gallium Garnet

D. Boal,* P. Grunberg,†‡ and J. A. Koningstein

Department of Chemistry, Carleton University, Ottawa, KiS-5B6, Canada
(Received 25 October 1972)

The crystal-field splittings of the ^7F multiplet of Eu^{3+} and Tb^{3+} have been determined in europium gallium garnet (EuGaG) and terbium aluminum garnet (TbAlG) from light scattering, fluorescence, and absorption spectra. The data were used to derive a set of crystal-field parameters for the two garnet systems. In these calculations the Hamiltonian appropriate for the D_2 symmetry of the rare-earth sites and also the mixing of different J states by the crystal field were taken into account. From the eigenfunctions derived in this way the magnetic-susceptibility-versus-temperature curve was calculated for TbAlG.

INTRODUCTION

The usefulness of electronic Raman spectroscopy (ERS) in determining low-lying electronic levels of rare-earth (RE) ions in crystals has been demonstrated now in a number of cases and a considerable amount of experimental data have been collected.[1] Much of the work has been focussed on RE garnets which are of interest from different aspects. RE aluminum and gallium garnets can serve as models where the RE ions experience a comparatively large crystal field (CF) of low symmetry, namely, D_2. RE iron garnets are interesting mainly because of their large magnetic anisotropy. Although the latter ones are opaque in the visible

region of the spectrum, ERS has been tried, but up to now only the photon spectrum has been observed by light-scattering techniques.[2] CF analysis for the aluminum and gallium systems is not only an interesting task by itself but also an essential prerequisite for the understanding of the magnetic behavior of the iron garnets.

CF calculations mostly yield better results for low-lying levels, and a good experimental method to explore these therefore is desirable. Although one has to admit that ERS mostly yields strong spectra in the same range in which good fluorescence spectra can also be obtained, the fact remains that in crystals with over-all cubic symmetry, such as garnets, absorption and fluorescence from

the RE are completely unpolarized and no informa-
tion can be obtained by these methods about the sym-
metry labelling of the states. This is not the case
with ERS, where this information, although with a
certain degree of ambiguity, is contained in the
polarization features.

CF analysis, including information from ERS,
has been performed for the first time on dysprosium
garnets.[3] Since the Dy^{3+} ion has an uneven num-
ber of electrons, the states are all labelled by the
same quantum numbers and double-valued repre-
sentations of the extended group D_2; the consider-
ation from above is meaningless. Further infor-
mation can only be obtained by the application of
a magnetic field and measurement of the three main
values of the g tensor. This is an advantage over
the even-number-of-electrons case, since a state
can be identified experimentally by three additional
quantities, however, there is a disadvantage in that
the method is restricted to reasonably narrow lines.
For the determination of polarization features, the
linewidth is of minor importance.

The main difficulty with a CF analysis for the RE
garnets is the large number (i.e., nine) of param-
eters which have to be adapted. This requires as
much experimental information as possible, and all
experimental methods should be exhausted before
calculations begin. Fluorescence, absorption, and
Raman spectra therefore were obtained from the
two garnets EuGaG and TbAlG, and the energy-
level schemes were determined. For EuGaG we
were able to obtain electronic Raman spectra with
shifts up to ≈ 5000 cm^{-1}, which to our knowledge
are the largest shifts ever observed in ERS. Thus
the entire manifold ^7F could be explored by this
method. [Lower-lying levels of this manifold (in-
cluding preliminary CF calculations) have been
determined earlier.[4] EuGaG results from infrared
(IR) and fluorescence measurements have also been
reported by Van der Ziel et al.[5] Most results of
ERS on TbAlG have already been published.[6]] A
CF analysis was then performed which allowed for
J mixing of the states of the complete ^7F manifold.
Based upon the eigenfunctions for the CF states
obtained from this analysis, the susceptibility
curve versus temperature finally was calculated
for TbAlG and compared with the experiment. For
EuGaG, this calculation was omitted because of its
low accuracy, caused by the ground level that is a
$^7F_0$ state.

EXPERIMENTAL

Part of the electronic level scheme of the free
Eu^{3+} and Tb^{3+} ions is shown in Fig. 1. In a crys-
tal field of D_2 symmetry these levels split into
two $J+1$ crystal-field levels, but the splitting hard-
ly exceeds 500 cm^{-1}. Since both Eu^{3+} and Tb^{3+} have
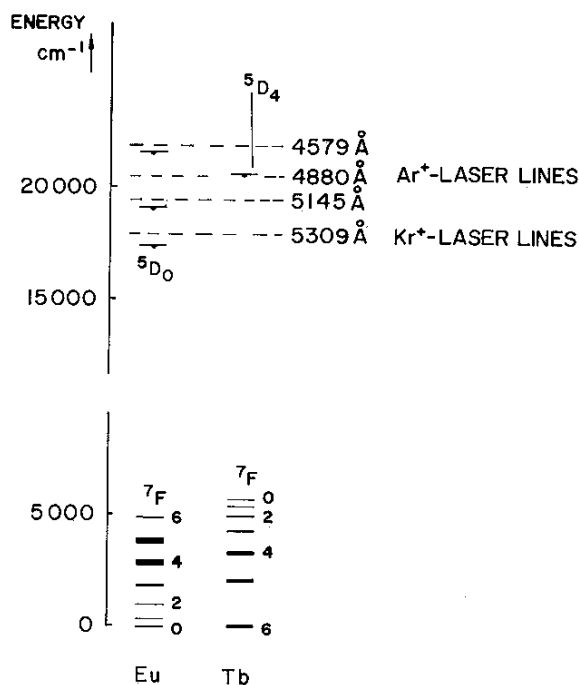an even number of $4f$ electrons, each of the CF

FIG. 1. Energy-level scheme for Eu^{3+} and Tb^{3+} to-
gether with different laser lines used for excitation of
the spectra.

levels belongs to one of the species A, B_1, B_2, B_3
of the single group D_2, and the number by which
each of these representations occurs in a given J
state is obtained in the normal way. A $J=1$ state
is split into three components of symmetry: B_1
$+B_2+B_3$, and a $J=2$ state is split into five levels
of symmetry: $2A+B_1+B_2+B_3$, etc. Here only the
states of the ^7F multiplet shall be investigated, but
the higher lying levels $^5D_4$ for Tb^{3+} and levels $^5D_0$,
$^5D_1$, $^5D_2$ for Eu^{3+} will serve to excite fluorescence
spectra.

Direct transitions from the ground state have to
be explored by IR techniques. A Cary 14 instru-
ment was used for the range 1-3 μ and a Beckman
IR-7 instrument was used to obtain spectra up to
10 μ. For the whole crystal these transitions ap-
pear depolarized because of the over-all cubic
symmetry but are governed by selection rules.
There are neither electric nor magnetic dipole
transitions between states belonging to the same
representation. For EuGaG the ground state $^7F_0$
is of A character and the number of possible transi-
tions to a split ^7F_J state can be read from Tables
I and II. For TbAlG the situation is not as simple
because the symmetry of the ground state cannot
be judged as easily. The fact that, for example,
the absorption spectrum of the split $^7F_5$ state shows
nine lines could serve as an indication that the

TABLE I. Electronic levels (in cm^{-1}) for TbAlG obtained by different methods.

	Absorption	Fluorescence	Light scattering
$^7F_6$	0	0	0
		2	2
	72[a]	74	75
	84[a]	83	84
		...	...
		264	262
			322
			373
	415[b]		
		460	
		470	469
$^7F_5$	2133	2134	2135
	2145	2148	2148
	2175	2179	2178
	2208	2212	2210
	2348	2350	2349
	2373	2376	2377
	2400		2403
	2478		
	2618		
$^7F_4$	3391	3385	
	3400	3398	
	3408	3477	3414
	3449	3445	3450
	3517	3514	3521
	3623	3618	3622
	3702		3704
	3733	3730	
		4004	
$^7F_3$	4371	4372	
		4519	
	4560	4558	
	4628	4627	
	4669	4669	
	4695	4697	
$^7F_2$	5062		
	5548	5551	
	5594	5591	
	5624	5625	
$^7F_1$	5737	5738	
		5868	
	5872	5876	

[a] As high-temperature satellite.
[b] Uncertain.

vacuum—this level becomes sufficiently populated to contribute to the absorption spectrum. It was not possible to resolve this level as a satellite in the absorption spectra. This information could be obtained from absorption and fluorescence measurements in a magnetic field, while Zeeman—Raman data are also available. The best estimate

TABLE II. Electronic levels (in cm^{-1}) for EuGaG obtained by different methods.

	Absorption[a]	Fluorescence	Light scattering
$^7F_0$		0	0
$^7F_1$		305	308
		328	329
		407	411
$^7F_2$			819
		830	834
		859	855
		1323	1324
		1343	1341
$^7F_3$	1830	1829	1832
	1851	1853	1853
	1894	1899	1896
	1925	1920	1929
	1977	1974	1970
		1983	1982
	2068		
		2146	
$^7F_4$			2448
	2831	2829	2831
	2923	2928	2924
		3066	3074
	3090	3088	3086
		3096	3098
	3142		
	3199		3200
	3262		
$^7F_5$	3765	3768	3766
		3823	3822
	3955	3956	3958
	4012		4012
	4017	4017	4020
	4155		
		4165	
	4183		
		4215	
		4232	
$^7F_6$		4939	
		4964	4952
	4990	4990	4990
	5011	5006	5010
	5089		
		5101	5101
	5204		
	5240		5242
	5282		

[a] From Ref. 5.

ground state is of A type (Fig. 2). This is the number of lines which one would expect in this case. This argumentation however leads to a contradiction for the spectrum of $^7F_4$. Here eight lines are found, which, in any case, are too many. However, it has already been determined by ERS[6] that the next level is less than 5 cm^{-1} above the ground state. Since the sample temperature was estimated to be 10 °K when liquid He was in the Dewar— the sample was mounted on a cold-finger tip in
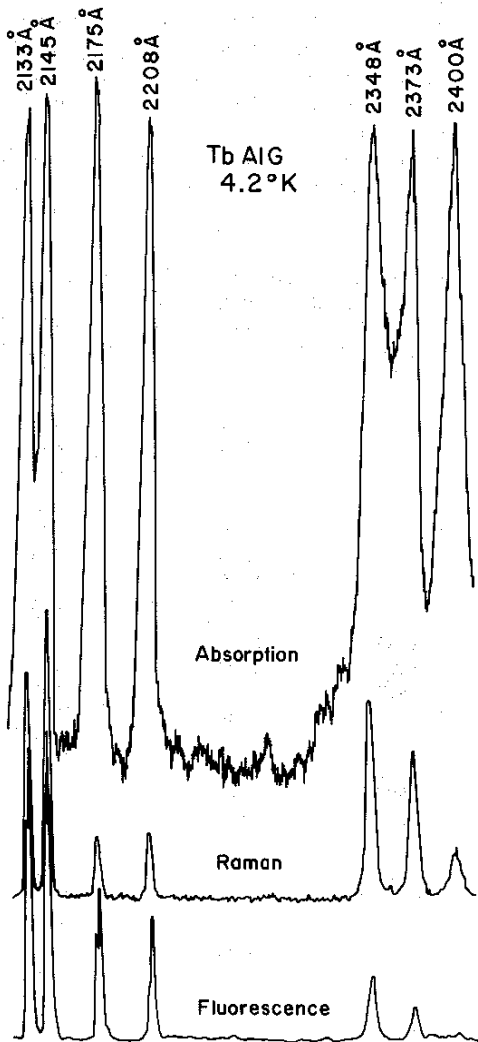
FIG. 2. Splitting of the $^7F_5$ level in TbAlG, as it appears in the light-scattering, fluorescence, and absorption spectra.

of the position of the first excited state at zero magnetic field yielded the result $\Delta E = (2 \pm 0.5 \text{ cm}^{-1})$ above the ground state.

Fluorescence was excited with an Ar^+ laser and a Kr^+ laser source. For TbAlG, it always originated in the lowest CF levels of $^5D_4$. Similarly as in the ground state, the lowest levels of $^5D_4$ consists of a closely spaced doublet, which, in some cases, was useful in the evaluation of the spectra. EuGaG fluorescence originates in different excited states, depending on the laser line used for excitation. As can be seen from Fig. 1, the Kr^+ laser line at 5309 Å will excite only fluorescence from level $^5D_0$. Although the Ar^+ laser lines can be used to excite fluorescence also from higher levels,

fluorescence from $^5D_0$ was found to be by far the strongest. All fluorescence appeared only at very low temperatures (concentrated crystal!); at 80 °K it is quenched almost entirely. For TbAlG at 10 °K only the laser lines greater than 4880 Å can be used for excitation. The 4880-Å laser line falls short in energy by ~ 80 cm^{-1}. This gap can be bridged at higher temperatures when electronic levels at ~ 80 cm^{-1} become populated. With 4880-Å excitation, strong fluorescence therefore occurs at ~ 80 °K, which can be frozen out at lower temperatures.

For the reason just mentioned (at 80 °K) only the 5145-Å Ar^+ laser line can be used to excite the Raman spectrum of TbAlG. With 4880-Å excitation fluorescence is too strong at this temperature. For EuGaG, Raman experiments at low temperatures (> 10 °K) can be disturbed by strong fluorescence. At 80 °K, fluorescence disappears but the quality of the Raman spectrum is nearly unaffected by the temperature increase. Even ERS at temperatures slightly below room temperature have been reported in this case.[4] For further details, in particular the evaluation of Raman spectra via the determination of the scattering tensor, the reader is referred to Refs. 4 and 6.

CRYSTAL-FIELD CALCULATIONS

For the present case the CF Hamiltonian can be written in the form

$$\mathcal{H}_{CF} = A_2^0 \langle r^2 \rangle V_2^0 + A_2^2 \langle r^2 \rangle V_2^2 + A_4^0 \langle r^4 \rangle V_4^0$$

$$+ A_4^2 \langle r^4 \rangle V_4^2 + A_4^4 \langle r^4 \rangle V_4^4 + A_6^0 \langle r^6 \rangle V_6^0$$

$$+ A_6^2 \langle r^6 \rangle V_6^2 + A_6^4 \langle r^6 \rangle V_6^4 + A_6^6 \langle r^6 \rangle V_6^6 .$$

The matrix elements for the V_n^m can be related to the tensor operators U_n^m by simple numerical coefficients.[3,7] Matrix elements of the U_m^n can be calculated from the Wigner–Eckart theorem[8] and using the tables of Nielson and Koster.[9] The $A_n^m \langle r^n \rangle$ are used as free parameters and have to be adapted to describe the experimental results.

A computer program was written calculating the matrix elements of H_{CF} between all states belonging to the ^7F multiplet.

The zeroth-order approximation corresponds to the free-ion limiting case. LS-type eigenfunctions were assumed for the states of the ^7F_J ($J = 0, \ldots, 6$) multiplet. This is a very good approximation in the present case as becomes obvious by inspection of Ofelt's results[10] and consideration of the fact that $\mathcal{H}$ is diagonal in S. Since each ^7F_J state is $(2J+1)$-fold degenerate, one ends up with a 49×49 matrix if full J mixing is included. This matrix can be broken up into four submatrices, each one belonging to one of the four representations of the single group D_2. As a preliminary set of parameters,

those found for the Dy garnets[3,11] were used. The energy-level scheme found from these parameters already showed some resemblance to the experimental one for TbAlG as well as for EuGaG. For the comparison of experimental and calculated energy levels one has to consider what has been said in[4] about the coordinate systems. If the coordinate system is chosen correctly the comparison of theory and experiment becomes unique for EuGaG. This is so because the ground state $^7F_0$ always belongs to the totally symmetric representation. Apart from the coordinate system for TbAlG the experimental symmetry labelling depends on which species is assumed for the ground state. It is always the species of a transition only which can be measured and thus the species of one of the final states has to be known to determine the other one. Only the assumption of a A ground state brought full agreement of calculation and experiment for TbAlG.

After the correlation of theoretical and experimental results had been established a least-square-fit program was used to minimize the remaining deviations. The good agreement between theory and experiment obtained by this procedure is demonstrated in Figs. 3 and 4. The results are also given in Tables III and IV.

SUSCEPTIBILITY

In many cases measurements of the temperature dependence of the susceptibility χ have been used
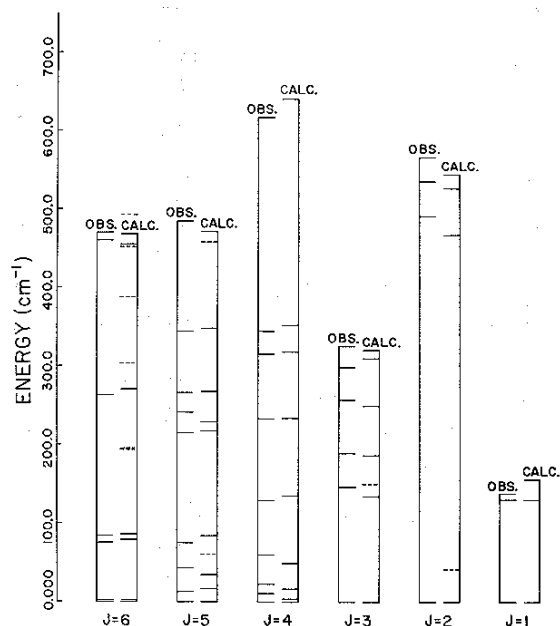

FIG. 3. Experimental (left) and calculated (right) splitting patterns for TbAlG. For parameters see Table II.

TABLE III. Comparison of experimental and calculated energy levels for TbAlG together with experimental and calculated representations. Calculated values (in cm^{-1}) refer to the following parameter set: $A_2^0 \langle r^2 \rangle = -160$, $A_4^0 \langle r^4 \rangle = -291$, $A_6^0 \langle r^6 \rangle = 44$, $A_2^2 \langle r^2 \rangle = 391$, $A_4^2 \langle r^4 \rangle = 220$, $A_6^2 \langle r^6 \rangle = -162$, $A_4^4 \langle r^4 \rangle = 936$, $A_6^4 \langle r^6 \rangle = 753$, $A_6^6 \langle r^6 \rangle = -153$. The error in the value of the parameter is $\pm 3\%$.

$E_{expt.}$	$\Gamma_{expt.}$	$E_{calc.}$	$\Gamma_{calc.}$
0	A	0	A
2	B_3	2	B_3
74	B_1 or B_2	79	B_2
84	B_1 or B_2	86	B_1
...		196	B_1
...		196	A
263	A	271	A
...		303	B_3
...		388	B_2
...		452	B_1
460		455	B_3
470		468	B_2
...		493	A
2134	B_1 or B_2	2133	B_1
2147	B_1 or B_2	2150	B_2
2177	A	2167	A
...		2195	B_3
2209	B_1 or B_2	2217	B_1
2349	B_1 or B_2	2350	B_1
2375	B_1 or B_2	2362	B_2
2402	B_3	2400	B_3
2478	A	2481	A
...		2591	B_2
2618		2604	B_3
3388		3384	B_2
3399		3388	B_1
3411		3400	B_3
3448		3433	A
3517		3519	A
3621		3618	B_2
3703		3702	B_3
3732		3735	B_1
4004		4023	A
4372		4368	B
4519	A	4501	A
...		4519	B_3
4559	B_3	4554	B_2
4628		4617	B_2
4669	B_1 or B_2	4677	B_1
4696		4688	B_3
5062		5074	A
...		5116	B_1
5550		5541	A
5593		5599	B_2
5625		5617	B_3
5738		5731	B_3
5868		5860	B_1
5874		5887	B_2
...		5965	A

to estimate the strength of the CF interaction in RE compounds. These attempts were, in general, only modestly successful because the effect of the CF splitting on the susceptibility is not very pro-
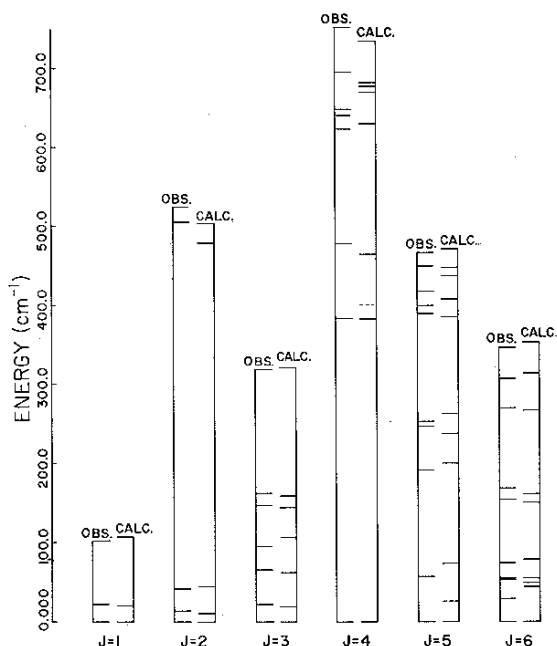
FIG. 4. Experimental (left) and calculated (right) splitting patterns for EuGaG. For parameters see Table IV.

nounced. Alternatively, the eigenfunctions obtained from a CF calculation as presented above can be used to predict the susceptibility. The formula used was derived by Van Vleck and can be written

$$\chi_m = \tfrac{1}{3} N \left(\sum_J e^{-E_J/kT} \right)^{-1} \sum_J \sum_\sigma e^{-E_J/kT}$$
$$\times \left(\frac{\langle J | \mu_\sigma | J \rangle^2}{kT} + \sum_{J'} \frac{2 | \langle J | \mu_\sigma | J' \rangle |^2}{E_{J'} - E_J} \right).$$

χ_m denotes the molar susceptibility and N_0 is Avogadro's number. The symbol J stands for the actual composition of a "J" state in the crystal field, e.g., in terms of a summation of $a_{JM}|J,M\rangle$, where $|J,M\rangle$ are free-ion basis functions. The nondegenerate levels of Eu^{3+} and Tb^{3+} in first approximation carry no magnetic moment because of the symmetric contribution of $|J \pm m\rangle$, and the first part in the bracket on the right-hand side vanishes. This can also be expressed group theoretically. For the direct product of any of the representations A, B_1, B_2, or B_3 with itself, one gets A but the components of the axial vector μ belong to B_1, B_2 or B_3. For the second term one can eliminate, for example, μ_x and μ_y between B_2- and B_3-type states because $B_2 \times B_3 = B_1$ and only μ_y trans forms under B_1. This simplifies the evaluation of the formula given above considerably. Calculations were only performed for TbAlG and in Fig. 5 the

theoretical and experimental χ curves are compared.[12] For EuGaG the effort did not seem to be worthwhile. The first excited state is ~ 300 cm^{-1} above the ground state, and no typical features in

TABLE IV. Comparison of experimental and calculated energy levels for EuGaG together with experimental and calculated representations. Calculated values (in cm^{-1}) refer to the following parameter set: $A_2^0 \langle r^2 \rangle = -80$, $A_4^0 \langle r^4 \rangle = -263$, $A_6^0 \langle r^6 \rangle = 53$, $A_2^2 \langle r^2 \rangle = 237$, $A_4^2 \langle r^4 \rangle = 200$, $A_6^2 \langle r^6 \rangle = -92$, $A_4^4 \langle r^4 \rangle = 993$, $A_6^4 \langle r^6 \rangle = 839$, $A_6^6 \langle r^6 \rangle = -176$. The error in the A_n^m's is 3%.

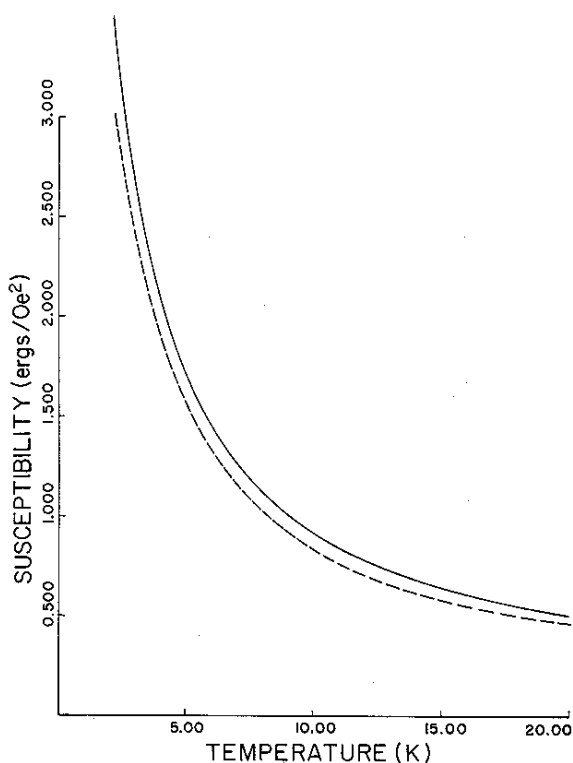| $E_{expt.}$	$\Gamma_{expt.}$	$E_{calc.}$	$\Gamma_{calc.}$
0	A	0	A
306	B_2	306	B_2
328	B_1	327	B_1
409	B_3	414	B_3
819	B_2 or B_1	827	B_3
832	B_3	838	B_2
857	A	872	A
1323	B_1 or B_2	1306	B_1
1342	A	1331	A
1830		1828	B_3
1853	B_1 or B_2	1847	B_1
1896	B_1 or B_2	1890	B_2
1924	B_1 or B_2	1935	B_2
1974	B_3	1972	B_3
1983		1987	A
2146		2146	B_1
2448		2449	A
2830	B_1 or B_2	2831	B_1
...		2849	B_3
2925	B_1 or B_2	2912	B_2
3070		3077	A
3088		3117	B_3
3097	B_3	3125	A
3142		3129	B_2
3199		3182	B_2
3766		3759	B_3
...		3785	B_2
3823		3832	A
3956		3959	B_3
4012		3997	B_2
4018		4021	B_1
4155		4144	B_1
4165		4167	B_3
4183		4196	B_2
4215		4207	A
4232		4230	B_1
4939		4935	A
4958		4979	B_1
4990		4984	B_2
...		4990	B_3
5009		5013	B_2
5089		5085	B_3
5101		5096	A
5204		5201	B_1
...		5201	A
5240		5247	B_2
...		5248	B_1
5282		5288	A
...		5289	B_3

FIG. 5. Experimental (dashed line) and calculated (solid line) susceptibility curve for TbAlG.

the temperature dependence of χ are to be expected. The absolute values on the other hand, are uncertain (as in TbAlG) because of demagnetizing corrections.

CONCLUSIONS

The position of crystal-field components of the ^7F_J levels of TbAlG and EuGaG are reported and a crystal-field analysis has been performed. For the first time in such an analysis for cubic rare-earth garnet crystals, extensive use has been made of the symmetry labelling of some of these crystal-field states. Thus, not only a good fit was obtained between experimental and observed splitting patterns, but there was also agreement of calculated and experimentally determined labelling of the levels. For the latter, the results of an electronic Raman study were paramount. Finally, the temperature-dependent magnetic susceptibility was computed and compared with experiment.

*Present address: Department of Physics, University of Toronto.

†National Research Council of Canada, postdoctoral Fellow.

‡Present address: Institut für Festkorperforschung der KFA, 517 Julich, Postfach 365, West Germany.

[1]J. A. Koningstein and P. Grunberg, Can. J. Chem. 49, 2336 (1971).

[2]P. Grunberg, J. A. Koningstein, and L. G. Van Uitert, J. Opt. Soc. Am. 61, 1613 (1971).

[3]R. L. Wadsack, J. L. Lewis, B. E. Argyle, avd R. K. Change, Phys. Rev. B 3, 4342 (1971).

[4]I. Dabrowski, P. Grunberg, and J. A. Koningstein, J. Chem. Phys. 56, 1264 (1972).

[5]J. P. Van der Ziel and L. G. Van Uitert, Phys. Rev. 186, 332 (1969).

[6]J. A. Koningstein and G. Schaack, Phys. Rev. B 2, 1242 (1970).

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

[8]A. R. Edmonds, Angular Momentum in Quantum Mechanics (Princeton U. P., Princeton, N.J., 1968).

[9]C. W. Nielson and G. F. Koster, Spectroscopic Coefficients for the p^n, d^n, f^n Configurations (MIT, Cambridge, Mass., 1963).

[10]G. S. Ofelt, J. Chem. Phys. 38, 2171 (1963).

[11]P. Grunberg, S. Hüfner, and J. Schmitt, Phys. Rev. 184, 785 (1969).

[12]W. P. Wolf, M. Ball, M. T. Hutchings, M. J. M. Leask, and A. F. G. Wyatt, J. Phys. Soc. Jap. Suppl. 17, 443 (1962).