

15 If the interaction were simply of the form $J S_{\text{RE}} \cdot S_{\text{Fe}}$, the component of G and g would be related through a single scalar factor. In general, however, J depends on the orbital state of the rare earth ion, and the two g -tensors are not simply related. Even so, the principal axes are in general still the same, and we might guess that corresponding principal values will be in the same sequence.

(See also refs. 8 and 14).

16 A. Herpin, W. C. Koehler and P. Mériel: C. R. Acad. Sci. **251** (1960) 1359.

17 This result is somewhat lower than the value recently calculated by Henderson and White (Phys. Rev. **123** (1961) 1627), who used a simplified expression for M , ignoring the canting of the Yb moments.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN

VOL. 17, SUPPLEMENT B-I, 1962

PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. I

Theoretical Study of the Magnetic Properties of Rare Earth Ions in the Structure of Garnet*

Y. AYANT AND J. THOMAS

*Laboratoire d'Electrostatique et de Physique du Métal
Grenoble, France*

An attempt has been made to interpret for various rare earths in the structure of garnet the magnetic susceptibility curves (Cohen) as well as other data: magnetization curves (Pauthenet), paramagnetic resonance (Wolf, Oxford).

a) In the first approximation, the Hamiltonian is written by the assumption that the ions surrounding the magnetic ion form a perfect cube, and the magnetic properties are deduced by means of Van Vleck's calculation.

b) In the second approximation, the exact arrangement of the neighbours is taken into account. The Hamiltonian is written for one f electron by assuming that the crystalline field is purely electrostatic and that there are punctual charges $-2e$ on the sites occupied by the ions O^{2-} . It is expanded in a series of spherical harmonics, but a multiplicative constant σ_l is introduced for each Y_m^l to take into account the departure from the reality of the hypothesis of punctual charges, the screening effect of the outer shell, and other interactions as covalence. The coefficient a_m^l of Y_m^l for the purely electrostatic field due to punctual charges is

calculated from crystallographic data. Many a_m^l vanish because the arrangement of the neighbours has orthorhombic symmetry, and many others are without interest owing to selection rules. Among what remains, the ones which are not zero when the arrangement of the neighbours have the cubic symmetry are well determined from crystallographic data, but the others are found in the calculation to be the difference of nearly equal terms (these terms are exactly equal in cubic symmetry), so we must consider them as undetermined, the precision on the crystallographic data being too small. Among them $a_2^4 = a_{-2}^4$ is negligible with respect to a_0^4 and a_4^4 , and a_6^6 and a_2^6 with respect to a_0^6 and a_4^6 , and only a_0^2 and $a_2^2 = a_{-2}^2$ are to be taken into account because they are multiplied by $\langle r^2 \rangle$ which is large with respect to $\langle r^4 \rangle$. We can therefore write the Hamiltonian as a linear combination of

$$Y_0^2, Y_2^2 + Y_{-2}^2, Y_0^4, Y_4^4 + Y_{-4}^4, Y_0^6, Y_4^6 + Y_{-4}^6.$$

For n electrons f it is considered that J is a "good quantum number", and the result of compounding the spherical harmonics for the n electrons is a new spherical tensor written in the space of J by the method of polynomials (Y. Ayant and J. Rosset, Ann. Inst. Four. **10**, 1960, pp. 345-358). The Ham-

* Comment to the paper by W.P. Wolf, *et al.*, read by Professor P. Brissonneau.

Hamiltonian is finally written as a linear combination of the spherical harmonics given above as

$$\begin{aligned} \mathcal{H} = & \mathcal{H}_0 + A\{tY_0^2 + t'(Y_2^2 + Y_{-2}^2) + Y_4^0 \\ & + k\sqrt{\frac{5}{14}}(Y_4^4 + Y_{-4}^4) \\ & + s[Y_0^6 + k'\sqrt{\frac{7}{2}}(Y_4^6 + Y_{-4}^6)]\}. \end{aligned}$$

A is an undetermined constant which characterizes the crystalline field energy. t , t' , and s are undetermined parameters of small perturbations. We tried to adjust A , t , t' , and s in order to have a good agreement between the experimental data and the theoretical values of magnetization calculated by Van Vleck's theory from this Hamiltonian.

The results obtained are as follows:

1) The measured Curie constants deviate little (less than 15%) from those expected in the simplifying assumption of cubic neighbours, but only for temperatures higher than about 100°K. For Ytterbium, the agreement is exceptionally good, even at very low temperatures owing to the fact that the splitting of the ground level $^2F_{7/2}$ by the cubic group gives a Kramers doublet as ground sublevel.

2) With the hypothesis a) the constant paramagnetism measured for $T > 100^\circ\text{K}$ when compared with their theoretical values allows us to calculate a crystalline field energy of about 1000°K or more which is a much larger one than that expected in the calculation made from the hydrogenic wave functions. This fact was confirmed by direct spectro-

scopic measurements (Pappalardo, Dreyfus). One has nevertheless continued to considered J to be a "good quantum number", the corrections to be made to this hypothesis being rather small.

3) For temperature below 100°K, it is absolutely necessary to take into account all those terms of the Hamiltonian resulting from the deviation from cubic symmetry of the neighbours. Qualitative interpretation of numerous experimental facts can be made and in favourable cases (Ytterbium, Neodymium, and even Erbium) the calculation has been carried far enough without being found inconsistent with the experiment.

We thus can interpret:

—The values of the factors g_x , g_y , g_z for Ytterbium (paramagnetic resonance).

—The magnetization curve of Erbium gallate, and the fact that the coefficients g_x , g_y , g_z can vary considerably from one garnet to another.

—The susceptibility curve of Neodymium gallate at very low temperatures.

To carry out the calculations it is necessary to know in each particular case precise and numerous experimental data, those correction terms due to the deviation of the neighbours from cubic symmetry having an important effect which varies from one garnet to another. In all cases the terms with $\langle r^6 \rangle$ of the Hamiltonian give but a slight correction.

In the case of Praseodymium the influence of the hyperfine coupling of the ion has also studied (Belorizky).