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cations such as Ca^{2+}, Li^+, Na^+, and K^+ are not accommodated as easily as in the garnet lattice. Infrared snooperscope examination also showed that the scattering from particulate matter was considerably lower than in YIG.

Figure 2 shows a hydrothermally grown $YbFeO_3$ crystal. The perfection of the grown $YbFeO_3$ as indicated by Schulz pictures[12] was quite good. Low-angle grain boundaries were few in number and were less than 2′ which is a considerable reduction over those ordinarily found in the flux-grown material which we have examined. This is perhaps principally due to the fact that flux inclusions which often initiate low-angle grain boundaries are not present in hydrothermal material. Hydrothermal growth is thus capable of producing both orthoferrite and garnet crystals which are substantially superior in some respects to flux-grown material. Hydrothermal growth may also be capable of preparing rare earth orthoferrite crystals of large R^{+3} radii which have proven very difficult to produce from molten salts.

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[12] L. G. Schulz, Trans. AIME 200, 1082 (1954).

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Magnetic Ordering of Terbium in Some Perovskite Compounds

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Four perovskite compounds $ATbO_3$ (A = Fe, Cr, Al, Co) are studied by means of neutron diffraction. Three Nèel temperatures are distinguished. When A is magnetic and $T<T_{N_1}$, the A sublattice orders in a G mode; when $T<T_{N_2}$, the Tb sublattice orders and is coupled with A in the same irreducible representation of the space group *Pbnm*; finally when $T<T_{N_3}$, Tb orders in another mode which is decoupled from A, i.e., Tb orders in a different irreducible representation. The order in the latter case is the only one observed one if A is diamagnetic, and its origin is mainly dipolar. The Nèel temperatures are given; the metamagnetism of Tb is studied for $T<T_{N_3}$.

The perovskite compounds ABO_3, where A is a transition ion or Al, B a rare earth ion, crystallize in the space group *Pbnm*. The A sublattice is generally antiferromagnetic at liquid nitrogen temperature; the B sublattice may order in turn at liquid helium temperature. The magnetic modes F, G, C, A which may form on each sublattice are classified according to the irreducible representations of the group *Pbnm*. If we restrict ourselves to an effective hamiltonian of order two only modes belonging to the same representation are coupled.[1]

$TbFeO_3$[2]

For $T<T_{N_1}=681$°K, the iron spins order in a G_x mode (representation Γ_4). When $T<T_{N_2}=8.4$°K terbium spins order according to the modes F_x and $C_y(\Gamma_2)$, and the iron spins rotate to G_z coupled in the same Γ_2 representation. Finally when $T<T_{N_3}=3.1$°K one observes the modes A_x and $G_y(\Gamma_8)$ for the terbium spins and a G_x mode (Γ_4) decoupled from terbium, for the iron spins. The modes F_x and C_y(Tb) are coupled with G_z(Fe) by anisotropic exchange forces; Tb–Tb exchange is negligible, dipolar forces create the modes A_x and G_y but are unable to couple the two sublattices in *Pbnm*. Dipolar energy has been calculated for different modes and angles ϕ of Tb spins with $0x$. In fact the configuration observed for $T=1.5$°K with $\phi=40°$ has the lower dipolar energy (Fig. 1).

$TbCrO_3$[3]

Here: $T_{N_1}=158$°K; $T_{N_2}=4$°K; $T_{N_3}=3.05$°K. When $T_{N_3}<T<T_{N_2}$, terbium is probably ordered in a combination of F_x and C_y modes. When $T<T_{N_3}$, a dipolar order decoupled from chromium is formed in an enlarged magnetic cell (a, $2b$, c). The propagation vector is $\mathbf{k}=[0\frac{1}{2}0]$. Two two-dimensional representations Γ_{1k} and Γ_{2k} of group *Pbnm* are associated with this

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[1] E. F. Bertaut, Treatise of Magnetism (1963) H. Suhl and G. Rado, Eds. (Academic Press Inc., New York) **III**, 149.

[2] E. F. Bertaut, J. Chappert, J. Mareschal, J. P. Rebouillat, and J. Sivardière, Solid State Commun. **5**, 293 (1967).

[3] E. F. Bertaut, J. Mareschal, and G. F. De Vries, J. Phys. Chem. Solids, **28**, 2143, 1967.

TABLE I. Observed modes of terbium.

$TbAO_3$	$TbFeO_3$	$TbCrO_3$	$TbAlO_3$	$TbCoO_3$	$TbVO_3$
T_{N_1}	681°K	158°K			
T_{N_2}	8.4°K	4°K			
T_{N_3}	3.1°K	3.05°K	4°K	3.31°K	
A 77°K	$G_x=4.8$	G_z			C_x
4.2°K	$G_z=4.8$	$G_z=2.85$			$C_x=1.3$
1.5°K	$G_x=4.8$	G_z			C_x
Tb 4.2°K	$F_x=2.4$ $C_y=1.9$ $M=3.1$	$C=1.4$			$C_x=5.9$ $F_y=4.8$ $M=7.6$
1.5°K	$A_x=6.61$ $G_y=5.6$	$C_{xy}=1.4$ $A_xG_y=8.5$	$G_x=6.9$ $A_y=4.6$	$A_x=6.44$ $G_y=4.58$	C_x F_y
M(Tb) at 1.5°K	8.6	8.6	8.25	8	7.6
Angle (M, x) at 1.5°K	40°		34°	35.4°	39.1°
E dipolar Tb at 1.5°K	-9×10^7 ergs	-12×10^7 ergs	-6.7×10^7 ergs	-10.2×10^7 ergs	

vector. Again all spins may be characterized by 4 vectors **F**, **G**, **C**, **A**, all z components belong to Γ_{2k} and all x, y-components to Γ_{1k}. The noncollinear observed mode is $G_xA_y(\Gamma_{1k})$, which, here, is equivalent to A_xG_y. The type of order may be described by piling up two kinds of antiferromagnetic sheets parallel to $0yz$. Dipolar coupling between two neighbouring sheets is strictly zero. This fact explains the occurrence of "stacking faults". The average distance between two stacking faults is estimated from line broadening to be of the order of 80 Å. A magnetic field of 6250 Oe at 1.5°K is sufficient to remove the stacking faults.

$TbAlO_3$[4]

When $T<T_N=4$°K, the terbium spins order in a G_xA_y mode (Γ_5). It is quite remarkable that $TbAlO_3$ and $DyAlO_3$ [5] are already ordered whereas no ordering is observed in $HoAlO_3$ and $ErAlO_3$ even down to 1,5°K. This fact may be related to the moment values. Indeed we find about the same moment values for Tb^{3+}, Dy^{3+}, Ho^{3+} and Er^{3+} as in the corresponding garnets (Fig. 2). The dipolar origin of AG structures is supported by the fact that the dipolar energy levels of FC modes are much higher than the AG levels plotted in Fig. 1.

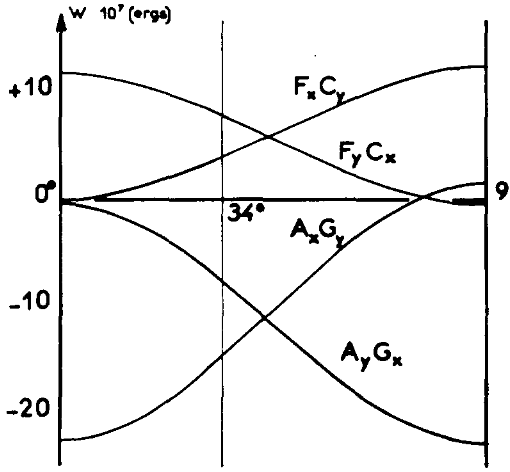

FIG. 1. Angular variation of dipolar energy for the configuration AG and FC in $TbAlO_3$.

$TbCoO_3$[6]

In this compound Co is diamagnetic in the low spin state $(t_{2g})^5$ and the terbium behaves exactly as in the aluminate. $T_N=3.31$°K, the A_xG_y arrangement is

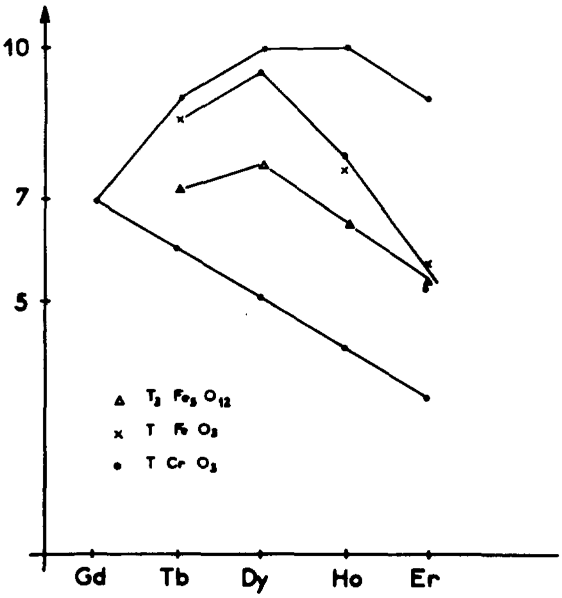

FIG. 2. Rare earth moments in perovskite and garnet structures.

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[4] H. J. Bielen, J. Mareschal, and J. Sivardière Z. Angew. Phys., **23**, 4243, 1967.

[5] P. Mériel (private communication).

[6] J. Mareschal (to be published).

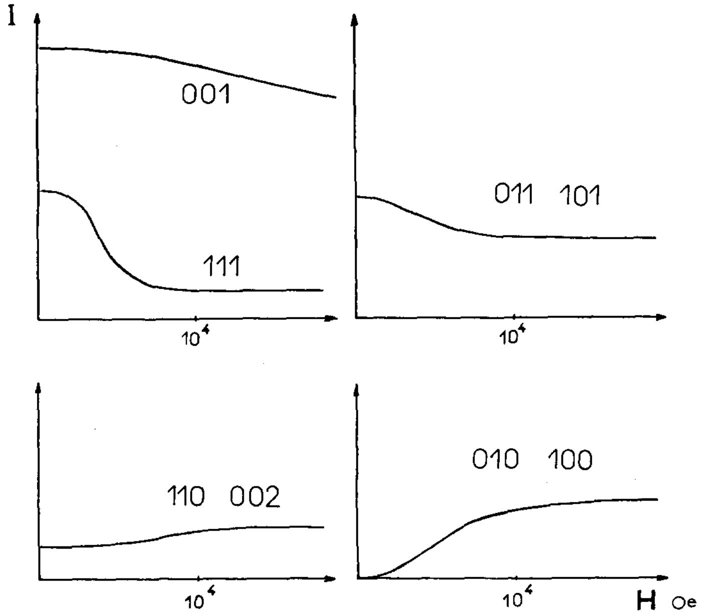

FIG. 3. Magnetic intensities of TbFeO$_3$ vs magnetic field (applied along the diffusion vector).

observed. Our results are summarized in Table I. We added also TbVO$_3$[5] in which no dipolar order was observed.

METAMAGNETISM OF Tb^{3+}

In the four compounds ATBO$_3$ the terbium spins are ordered at 1.5°K, mainly under the influence of dipolar forces. A metamagnetic behavior with a threshold field of the order of magnitude of dipolar fields (10^4 Oe) may be expected and is observed indeed by neutron diffraction on powder samples with a magnetic field along the diffusion vector. As an example we choose here TbFeO$_3$. The applied field is always too small to disturb the G mode of the iron spins. Two cases may be distinguished. In the perpendicular case, when H is perpendicular to the $0xy$ plane only a small F_z component appears, but the A_xG_y configuration is essentially conserved (see Fig. 3). The effect is much stronger in the "parallel" case, when H has at least one component in the $0xy$ plane. A large decrease of the (111) line is observed. In the same way the (101) and (011) peaks of the G-type decrease, the former more than the latter: H_{xz} is more effective than H_{yz}. This means that x is an easier direction than y and in fact in the four compounds the x-component of the Tb spins is larger than the y-component. Of course the application of a field H in the $0xy$ plane favors also the modes C_y or C_x which are coupled with F_x or F_y(Γ_2 and Γ_3).

In no case do we observe the disappearance of the A_xG_y configuration, and a saturation effect is observed when the critical field is about 4000 Oe. The anisotropy field in the xy plane is about 10 000 Oe; indeed, if H is greater than 10 000 Oe, the peaks (010) and (100) are of equal intensity which means that the components H_x and H_y have equivalent effects. Under these conditions (anisotropy field greater than ordering field) an applied field gives rise to spin flip effects without any orientation of the spins in a perpendicular direction (passing from AG to FC-configurations corresponds to the flipping of two terbium moments per unit cell).

Similar results have been observed on TbCoO$_3$. The critical field is more important, about 10 000 Oe. There is no indication of any change of the Co^{3+} low spin state for the fields we have used.

CONCLUSION

In the compounds TbAO$_3$ at a very low temperature, terbium orders in the modes A and G favored by dipolar forces. But it is the crystalline field anisotropy which fixes the direction of the moments.