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Magnetic Structure of the TmNi Compound Crystal Field Effect

By

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The TmNi compound crystallizes in the FeB-type structure (space group Pnma) where the Tm^{3+} ions occupy a very low symmetry site (m). Below its Curie temperature (7 K), TmNi shows a ferromagnetic behaviour. From neutron diffraction studies at 1.3 K a non-collinear magnetic structure of this compound is deduced. The exchange energy is small with respect to the total crystal field splitting of the ground multiplet J. With a point charge model the crystal field parameters are calculated and the direction and magnitude of the magnetic moments of the Tm^{3+} ions in each site are determined. The good agreement between experimental results and calculations confirms the predominance of the crystal field in determining the magnetic stucture of this compound.

Le composé TmNi cristallise dans la structure Pnma, isotype de FeB, dans laquelle les ions Tm^{3+} sont dans un site de très basse symétrie (m). Au-dessous de sa température de Curie (7 K) TmNi présente un comportement ferromagnétique. A partir d'un diagramme de diffraction neutronique à 1,3 K nous avons déterminé la structure magnétique non colinéaire du composé. L'énergie d'échange est beaucoup plus faible que la décomposition totale du multiplet fondamental J par le champ cristallin. A l'aide d'un modèle de charges ponctuelles nous calculons les paramètres de champ cristallin et nous déterminons la direction et la valeur des moments magnétiques des ions Tm^{3+} sur chaque site. Le bon accord entre les résultats observés et calculés confirme le rôle prépondérant du champ cristallin dans la stabilité de la structure magnétique.

1. Introduction

In the equiatomic rare earth–nickel compound RNi the exchange interactions are produced through conduction electrons. Furthermore the exchange interaction is of the same order of magnitude as that of the crystal field. In some compounds, the total splitting of the ground state multiplet J by crystal field is preponderant. This happens for the TmNi compound. Using a point charge model, we deduce the direction and magnitude of the Tm^{3+} ion magnetic moment and finally we compare these results to those obtained by neutron diffraction.

In 1964, Abrahams et al. [1] and also Walline and Wallace [2] studied the crystallographic structures and magnetic properties of the RNi compounds. The first authors found all RNi alloys isomorphous to the CrB orthorhombic compound, whereas Walline and Wallace specified that compounds from dysprosium to thulium crystallize in the FeB-type structure. More recently, Paccard [3] and Lemaire and Paccard [4] have re-examined the RNi compounds and made a precise crystal structure determination of TbNi.

The FeB-type crystallographic structure of TmNi belongs to the Pnma (D_{2h}^{16}) space group and can be described by trigonal prisms formed of rare earth atoms at the corners and one nickel atom in the centre. Thulium and nickel atoms are in the same (4c) site with m(Cs) symmetry whose atomic positions are: (1) in $(x, \frac{1}{4}, z)$, (2) in $(-x, \frac{3}{4}, -z)$, (3) in $(\frac{1}{2} - x, \frac{3}{4}, \frac{1}{2} + z)$, and (4) in $(\frac{1}{2} + x, \frac{1}{4}, \frac{1}{2} - z)$.

2. Experimental

The rare-earth elements used were 99.9% pure, the nickel was 99.99% pure. The intermetallic compound was prepared by induction melting of the constituents at 1100 °C in an alumina crucible, under helium atmosphere of 3 bar to reduce the evaporation of Tm. No attack reaction between the crucible and the constituents was observed. The purity of the sample was checked by X-ray analysis. Magnetic measurements were made at the "Laboratoire de Magnétisme du Centre National de la Recherche Scientifique, Grenoble" in fields up to 24 kOe produced by an electromagnet. The magnetic structure was studied at the "Laboratoire de Diffraction Neutronique du Centre d'Etudes Nucléaires de Grenoble". Wavelength of the neutrons was 1.14 Å.

3. Magnetic Measurements

Below its Curie temperature, TmNi exhibits a ferromagnetic behaviour [1, 2]. On a polycrystalline sample, we studied the magnetization versus applied field variation at 1.8 K and the magnetization versus temperature variation in a 100 Oe external field (Fig. 1). At 1.8 K in an applied field of 24 kOe, the magnetization does not attain saturation; it is 4.1 μ_B per thulium atom. The ferromagnetic Curie temperature is 7 K. These results are in rather good agreement with those obtained by the previous authors [1, 2]. In the paramagnetic region, the observed deviation from a Curie-Weiss law confirms the importance of crystal field effects on the magnetic behaviour of TmNi.

4. Neutron Diffraction Results

To resolve the magnetic structure of this compound, neutron diffraction patterns have been made at 1.3 and 77 K (Fig. 2). The nuclear Bragg peaks observed at 77 K can be indexed in the orthorhombic cell with the parameters:

$$a = 6.96\ \text{Å}\,, \quad b = 4.11\ \text{Å}\,, \quad c = 5.40\ \text{Å}\,.$$

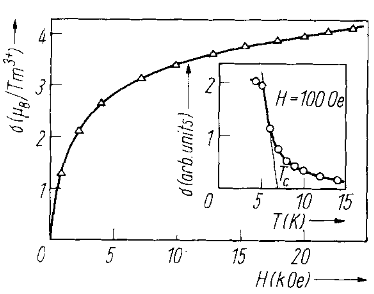

Fig. 1. Variation of magnetization as a function of the applied field at 1.8 K. The insert shows the variation of magnetization as function of temperature under 100 Oe

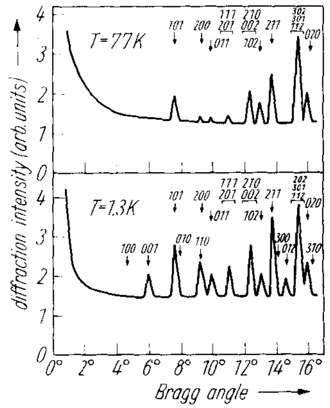

Fig. 2. Neutron diffraction patterns at 77 and 1.3 K; $\lambda = 1.14$ Å

Table 1

Observed and calculated neutron diffraction intensities at 77 K ($R = 4.2\%$)

h k l	θ	I_{cal}		I_{obs}
1 0 1	7.68	17.3		16.5
2 0 0	9.43	10.3		9.1
0 1 1	10.04	7.4		8.7
1 1 1	11.11	3.0	3.1	3.0
2 0 1	11.25	0.1		
0 0 2	12.20	0.5	55.8	53.7
2 1 0	12.39	55.3		
1 0 2	13.10	35.3		42.3
2 1 1	13.84	104.4		102.4
1 1 2	15.40	193.9	242.2	245.6
2 0 2	15.51	48.3		
3 0 1	15.52	0.0		
0 2 0	16.10	78.9		73.4

With these data we have refined the atomic position parameters of thulium and nickel; these are for thulium, $x = 0.177$ and $z = 0.134$ and for nickel, $x = 0.040$ and $z = 0.630$. The calculated nuclear intensities are compared with the observed ones in Table 1, where the discrepancy factor,

$$R = \frac{\sum |I_{\text{obs}} - I_{\text{cal}}|}{\sum I_{\text{obs}}},$$

is 4.2%. At 1.3 K the neutron diffraction pattern (Fig. 2) exhibits an increase in intensity of most of the nuclear reflections and moreover superstructure peaks which can be indexed with the same orthorhombic cell. The extinction conditions limiting the possible reflections of the Pnma space group are no longer valid. The superstructure lines are characteristic of an antiferromagnetic arrangement $\boldsymbol{C}_a$ of the thulium magnetic component parallel to $\boldsymbol{a}$ (Fig. 3). The increase of nuclear peaks is due to a ferromagnetic arrangement $\boldsymbol{F}_c$ of the thulium magnetic component parallel to $\boldsymbol{c}$. This results in a non-collinear structure with the moments lying in the ac plane. We obtain the best agreement with no magnetic moment on nickel and a moment of $(5.9 \pm 0.5)\,\mu_{\text{B}}$ on thulium which makes an angle of $(38 \pm 2)°$ with c-axis. The discrepancy factor is 7.2% (Table 2). On Fig. 3 we represent the projec-

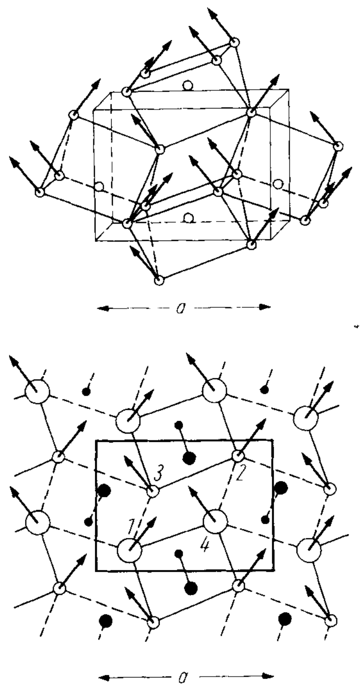

Fig. 3. Magnetic structure of TmNi defined with the basic vectors $\boldsymbol{C}_a = \boldsymbol{M}_{1a} + \boldsymbol{M}_{2a} - \boldsymbol{M}_{3a} - \boldsymbol{M}_{4a}$, $\boldsymbol{F}_c = \boldsymbol{M}_{1c} + \boldsymbol{M}_{2c} + \boldsymbol{M}_{3c} + \boldsymbol{M}_{4c}$

Table 2

Observed and calculated neutron diffraction intensities at 1.3 K ($R = 7.2\%$)

$h\,k\,l$	θ	$I_{M_{\text{cal}}}$		$I_{M_{\text{cal}}} + I_{N_{\text{cal}}}$	I_{obs}
1 0 0	4.70	0.0		0.0	n.o.
0 0 1	6.06	12.4		12.4	11.8
1 0 1	7.68	30.8		48.1	40.3
0 1 0	7.97	0.0		0.0	n.o.
1 1 0	9.27	28.6	43.8	54.1	48.0
2 0 0	9.43	15.2			
0 1 1	10.04	27.2		34.6	26.8
1 1 1	11.11	36.5	44.2	47.3	46.9
2 0 1	11.25	7.7			
0 0 2	12.20	0.0	44.9	100.7	96.5
2 1 0	12.39	44.9			
1 0 2	13.10	6.2		41.5	42.6
2 1 1	13.84	47.2		151.6	155.5
3 0 0	14.23	0.0		0.0	n.o.
0 1 2	14.64	35.9		35.9	45.7
1 1 2	15.40	10.1	50.6	292.8	311.1
2 0 2	15.51	15.1			
3 0 1	15.52	25.4			
0 2 0	16.10	28.6	28.8	107.7	100.7
3 1 0	16.39	0.2			

tion of the magnetic structure on the *ac* plane. This structure is isomorphous to that of ErNi [5] and belongs to the magnetic space group Pn′m′a.

5. Crystal Field Calculation and Interpretation

In the orthorhombic cell the four Tm^{3+} ions are in the same (4c) site with very low symmetry C_s(m). For such a symmetry the crystal field splits totally the multiplet ground state $^3\text{H}_6$ ($J = 6$). For TmNi $T_c = 7$ K, thus the exchange energy between the thulium ions is small with respect to the total splitting of the free ion in the crystal field (a few hundred K). In these conditions only the low-lying states are relevant for the magnetic properties.

If the singlet ground state $|a\rangle$ is well separated from the first excited level (with respect to the exchange energy), there will be no possible magnetic order down to 0 K. Thus, for the compound to be ordered it is necessary that the two low-lying states $|a\rangle$ and $|b\rangle$ are separated by an energy Δ of only a few K. We can obtain a cooperative phenomenon only if the exchange energy in the case when the two singlets have the same energy ($\Delta = 0$), is greater than $\Delta/2$ [6 to 8].

The magnetic moment is proportional to matrix elements of the form $\langle a|\,\boldsymbol{J}\,|b\rangle$. The condition for a non-zero matrix element implies that the representation $\Gamma^{(J)}$, according to which the components of J transform exists in the decomposition of $\Gamma^{(a)} \times \Gamma^{(b)}$ representation. If $\Gamma^{(a)}$ and $\Gamma^{(b)}$ are one-dimensional, $\Gamma^{(J)}$ is also one-dimensional. Thus the magnetic moment is fixed in a direction which may be determined by the product $\Gamma^{(a)} \times \Gamma^{(b)}$. We obtain an Ising-like model.

Table 3

Irreducible representations of $C_s(m)$ and $C_{2v}(mm2)$ point groups. Components of $\boldsymbol{J}$ associated with these representations

$C_s(m)$		$C_{2v}(mm2)$	
${}^{(1)}\Gamma_1$	J_z	${}^{(1)}\Gamma_1$	
${}^{(1)}\Gamma_2$	J_x or J_y	${}^{(1)}\Gamma_2$	J_y
		${}^{(1)}\Gamma_3$	J_z
		${}^{(1)}\Gamma_4$	J_x

In the $C_s(m)$ group there are only two irreducible first-order representations, Γ_1 and Γ_2 (Table 3). If the two singlets belong to the same representation the moments will be in the direction $(0z)$ perpendicular to the mirror plane. If they belong to two different representations they will be fixed in a direction of the mirror plane which cannot be determined because J_x and J_y transform in the same representation Γ_2 ($\Gamma_1 \times \Gamma_2 = \Gamma_2$). On the other hand in the $C_{2v}(mm2)$ group (Table 3), where J_x, J_y, and J_z transform in different representations, the magnetic moments are in the direction of a symmetry axis.

The crystal field Hamiltonian in the C_s symmetry can be written by using the Stevens equivalent operators [9]:

$$H_c = \alpha\,(V_2^0\,O_2^0 + V_2^{-2}\,O_2^{-2} + V_2^2\,O_2^2) + H_4 + H_6\,.$$

The quantization axis $0z$ (b-axis) is chosen perpendicular to the mirror plane; $0x$ and $0y$ are respectively taken to be parallel to the c- and a-axes (Fig. 4a). The $C_s(m)$ group differs from the C_{2v} group by the presence of imaginary terms like $V_2^{-2}\,O_2^{-2}$, $V_4^{-4}\,O_4^{-4}$, etc. in the Hamiltonian H_c with C_s symmetry. With the help of a point charge model we have calculated the V_l^m parameters for the (1) Tm^{3+} ion. We have taken a charge $+3\,e$ for Tm^{3+} ions and we have assumed a zero charge on nickel atoms. This supposition is justified since YNi exhibits only a Pauli paramagnetism [2]. Moreover we have neglected the conduction electron contribution to the crystal field. The calculation shows that the second-order terms play a preponderant part in H_c. Under these conditions Rossat-

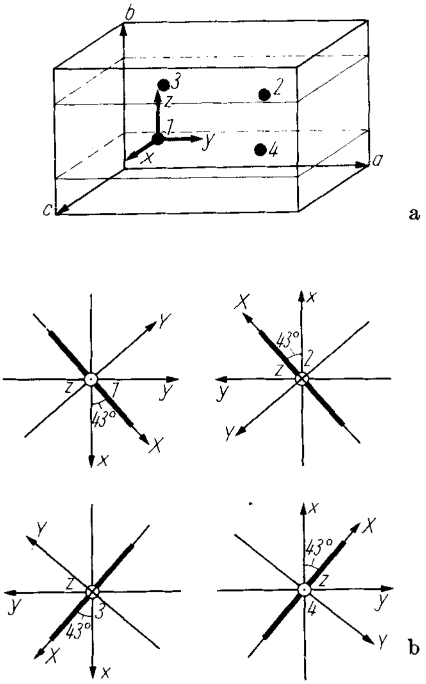

Fig. 4. a) Reference axes and atomic positions in the unit cell chosen for the calculations. b) Reference axes before and after rotation in each site deduced by symmetry operation

Mignod and Tcheou [10] have shown that by a rotation around the 0z-axis with angle φ such that tg $2\varphi = V_2^{-2}/V_2^2$, it is possible to get rid of the second-order term $V_2^{-2} O_2^{-2}$ and thus to obtain a crystal field Hamiltonian having a C_{2v}-like symmetry. This calculation gives $\varphi = +43°$. The diagonalization of H_c written in the $0XYz$-axes deduced from the $0xyz$ ones by the rotation around the 0z-axis ($\varphi = 43°$) shows that the ground state is composed of two closely spaced singlets belonging to the Γ_4 and Γ_1 representations of the C_{2v} group. The first excited state is at about 50 K and the highest state is at about 250 K. Thus the magnetic moments must be fixed in the $0X$-direction making an angle of 43° with the $0x$ direction, i.e. with the c-axis (Fig. 4b). Taking into account the above approximations these results are in good agreement with the angle of $(38 \pm 2)°$ found experimentally by neutron diffraction. The calculated eigen functions give a moment of $6.8\,\mu_B$ for Tm^{3+} assuming the same energy for the two singlets states. This value is very close to that of the free Tm^{3+} ion ($7\,\mu_B$). The discrepancy between the experimental value of the magnetic moment ($5.9\,\mu_B$) and the calculated one arises probably from the fact that the two singlets are separated by an energy gap Δ of a few K.

The direction of magnetic moments of the other ions in the unit cell is deduced from that of the ion (1) by symmetry operations: the inversion $\bar{1}|(1) \to (2), (3) \to (4)|$ and the two-fold rotation $2_x|(1) \to (3), (2) \to (4)|$. Fig. 4b shows the direction of the magnetic moment of these four ions. The result is in very good agreement with the structure determined by neutron diffraction.

6. Conclusion

Although the point charge model is over-simplified, it allows to interpret correctly the observed magnetic structure. The determination of the direction of magnetic moments depends only on the ratio V_2^{-2}/V_2^2 which eliminates the screening effect and the value of $\langle r^2 \rangle$. In the TmNi compound the ferromagnetic structure is essentially determined by the crystal field. The ground state is well described by a two singlet states model with $|M_J = \pm 6\rangle$ (the quantization axis being parallel to the easy magnetization direction) separated by an energy gap Δ of a few K.

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