TmCd quadrupolar ordering and magnetic interactions

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The paramagnetic compound TmCd crystallizes with the CsCl-type structure. Its Jahn-Teller behavior was first observed by Lüthi and coworkers. We analyze here various physical properties with a pure-harmonic-elasticity model. The structural transition between cubic and tetragonal phases is now fully described (first-order character and temperature of occurrence) as well as the magnetic susceptibility, magnetization process, specific-heat, elastic-constant, and strain data. The relevant Hamiltonian takes into account the second-order magnetoelastic coupling and the quadrupolar exchange in addition to the cubic crystal field and the Heisenberg bilinear interactions. TmCd appears to be closely related to isomorphous TmZn and completes the illustration of the competition between bilinear and quadrupolar interactions occurring in some rare-earth intermetallics. In these two compounds, the quadrupolar exchange is many times stronger than the magnetoelastic coupling and the quadrupolar ordering then drives the structural transition. This situation is opposite to that occurring in (actual) Jahn-Teller compounds.

I. INTRODUCTION

Magnetoelastic effects have been extensively studied for the last few years in cubic-rare-earth (R) intermetallics. They have in particular required developing a quantum treatment for the same reason as for analyzing the magnetization processes: for a given J manifold, the cubic crystalline electric field (CEF) strongly mixes the pure $|J_z\rangle$ wave functions, this gives rise to an anisotropic reduction of the moment modulus beside the energy anisotropy. In addition the $4f$ electric quadrupole interacts with both the lattice (magnetoelastic coupling) and other $4f$ quadrupoles (quadrupolar exchange interactions). These two quadrupolar effects are usually driven by the ferromagnetic ordering according to a magnetostrictive process. A pure structural transition, however, is observed for two isomorphous compounds with a CsCl-type structure, namely[1] TmCd and[2] TmZn. Whereas this transition is well known to occur through a Jahn-Teller process for transition-metal-ion compounds and rare-earth insulators,[3] there are only two instances known up to now in cubic-rare-earth intermetallics.

In TmCd, the extensive work of Lüthi and coworkers[1] has shown a first-order transition at $T_Q = 3.16$ K, between cubic and tetragonal phases, the compound remaining paramagnetic down to 30 mK. For understanding the observed properties, the authors used a CEF level scheme with the nonmagnetic doublet Γ_3 as the ground state, but the structural transition was then calculated to be of second order and anharmonic lattice terms were invoked for inducing the observed first-order character.

Moreover TmZn (Ref. 2) revealed a first-order structural transition at $T_Q = 8.55$ K above the ferromagnetic ordering at $T_c = 8.12$ K. As in TmCd ($c/a - 1 = -6 \times 10^{-4}$),[4] the low-temperature structure is tetragonal ($c/a - 1 = -9 \times 10^{-3}$). All the physical properties were found to depend strongly on the precise mixing of the $4f$ wave functions. They were fully understood with the magnetic triplet $\Gamma_5^{(1)}$ as ground state, the Γ_3 doublet lying 37 K above; this level scheme was obtained without ambiguity from neutron spectroscopy in the cubic range.

The comparison of the physical properties of the RCd and RZn series raised some doubts on the validity of the level scheme previously proposed for TmCd.[1] This motivated us to perform new experiments. We want then to compare first TmCd to the other RCd and RZn compounds. Last we propose a cubic level scheme fully describing our data on magnetic susceptibility and magnetization in high-magnetic fields, as well as the results of Ref. 1 on the specific heat and elastic constants.

II. DISCUSSION OF THE VARIOUS PARAMETERS

A. Basic Hamiltonian

The Hamiltonian may be written using the operator-equivalent theorem[5] and the molecular-field approximation. It was fully discussed in Refs. 2 and 6. In order to define the various parameters, we give here only its expression:

$$\mathcal{H} = \mathcal{H}_{\mathrm{CEF}} - \{[3k_B\Theta^*/J(J+1)]\langle\vec{J}\rangle + g_J\mu_B\vec{H}\}\vec{J} + \mathcal{H}_Q + \mathcal{H}_{\mathrm{me}} + E_e \,. \quad (1)$$

$$\mathcal{H}_{\mathrm{CEF}} = A_4\langle r^4\rangle\beta_J O_4 + A_6\langle r^6\rangle\gamma_J O_6 = (Wx/F_4)O_4 + [W(1-|x|)/F_6]O_6 \quad (2)$$

is the usual cubic CEF Hamiltonian with $O_4 = O_4^0$

$+5O_4^4$ and $O_6 = O_6^0 - 21O_6^4$.[7] Θ^* measures the strength of the Heisenberg bilinear interactions, H is the internal magnetic field.

$$\mathcal{H}_Q = -K_1(\langle O_2^0\rangle O_2^0 + 3\langle O_2^2\rangle O_2^2) - 4K_2(\langle P_{xy}\rangle P_{xy} + \cdots) \quad (3)$$

is the quadrupolar exchange term.

$$\mathcal{H}_{me} = -B_1(\epsilon_3 O_2^0 + \sqrt{3}\epsilon_2 O_2^2) - B_2(\epsilon_{xy}P_{xy} + \epsilon_{yz}P_{yz} + \epsilon_{zx}P_{zx}) \quad (4)$$

is the one-ion magnetoelastic Hamiltonian, linear in strain and limited to the second order as usually accepted.[8-10] Note that the substitution of the ϵ's equilibrium values in (1) leads to

$$\mathcal{H}_Q + \mathcal{H}_{me} = -G_1(\langle O_2^0\rangle O_2^0 + 3\langle O_2^2\rangle O_2^2) - G_2(\langle P_{xy}\rangle P_{xy} + \cdots) \quad (5)$$

with $G_1 = K_1 + B_1^2/(C_{11} - C_{12})_0$ and $G_2 = 4K_2 + B_2^2/4C_{44_0}$. $(C_{11} - C_{12})_0$ and C_{44_0} are the elastic constants without magnetic interactions.

B. Application to TmCd

Among the parameters $(W, x, \Theta^*, G_1, G_2)$ of Eq. (1), Θ^* is the simplest one to be understood in TmCd. The magnetic properties are very similar in the RCd (Ref. 11) and RZn (Ref. 12) series. GdCd ($\Theta^* = 256$ K) and GdZn ($\Theta^* = 270$ K), TbCd ($\Theta^* = 166$ K) and TbZn ($\Theta^* = 200$ K) exhibit a pronounced ferromagnetic behavior which, however, decreases strongly at the end of the RCd series ($\Theta^* = 4$ K in ErCd instead of 26 K in ErZn). Thus bilinear interactions may be extrapolated to a minute value in TmCd as confirmed in Sec. III.

About the quadrupolar terms, we will limit ourselves to the case where only the G_1 term exists, according to the observed tetragonal-symmetry lowering. G_1 must describe the first-order structural transition experimentally observed at $T_Q = 3.16$ K: we have drawn in Fig. 1 the diagram giving the G_1 values for negative $A_4\langle r^4\rangle$, $A_6\langle r^6\rangle$ ($W > 0, x < 0$) with the $\Gamma_5^{(1)}$ ground state. We are then involved with only two parameters W and x.

For many of the equiatomic compounds (the RCd excepted) the cubic CEF parameters are known with accuracy from neutron spectroscopy.[2,13] In Rh, Pd, Ag, Cu, and Zn intermetallics $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$ are always negative. Cd is located below Zn in the IIB class with the same electronegativity. RCd and RZn have close lattice parameters [3.665 Å for TmCd (Ref. 1) and 3.525 Å for TmZn (Ref. 2)]. Indeed from the magnetic properties studied in RZn and RCd single crystals, the same easy and hard magnetization directions are observed for a given $4f$ ion. Starting from the same level scheme leads to a first rough description of the magnetization processes in each Cd or Zn compound. In TmCd, with negative $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$ parameters ($W > 0, x < 0$), either the nonmagnetic Γ_3 doublet or the magnetic $\Gamma_5^{(1)}$ triplet may be found as ground state. In the first case $W = 1.4$ K, $x = -0.8$ can define the level scheme chosen in Ref. 1; they lead to $A_4\langle r^4\rangle = -170$ K, a value appearing erratic in comparison with observations in all isomorphous intermetallics. In the latter case, the TmZn situation provides a good starting point: $W = 1.2$ K, $x = -0.31$ correspond to $A_4\langle r^4\rangle = -38$ K, $A_6\langle r^6\rangle = -19.6$ K.[2]

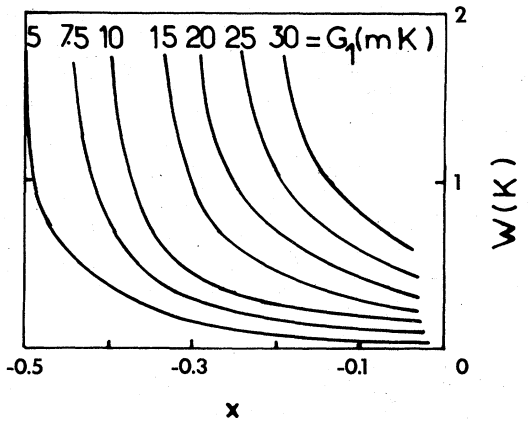

FIG. 1. G_1 value as a function of the cubic crystal field through the occurrence of the structural transition at $T_Q = 3.16$ K in TmCd.

III. DISCUSSION OF EXPERIMENTAL RESULTS

A. Paramagnetic susceptibility

Two single crystals of TmCd and $Tm_{0.30}Y_{0.70}Cd$ were studied with a translation balance in a magnetic field of 1 kOe.

1. Cubic range

The temperature variation of the reciprocal susceptibility is found to be linear from 100 to 350 K. Extrapolation downwards leads to a paramagnetic Curie temperature $\Theta_p = 0 \pm 1$ K. Below 100 K, χ^{-1} deviates from linearity (inset of Fig. 2) and shows a negative curvature (Fig. 2) down to 2 K for the dilute compound. This indicates a magnetic ground state, as proved by the χ^{-1} variation calculated with $W = 0.9$ K and $x = -0.35$; the spacing $\Gamma_5^{(1)} - \Gamma_3 = 23$ K is in agreement with the Schottky anomaly observed in specific-heat data.[1] However, this solution is not unique and a large set of level schemes keeping $\Gamma_5^{(1)} - \Gamma_3$ constant ranging from ($W = 1.1 \pm 0.3$ K, $x = -0.4$) – ($W = 0.7 \pm 0.2$ K, $x = -0.2$) would be satisfactory.

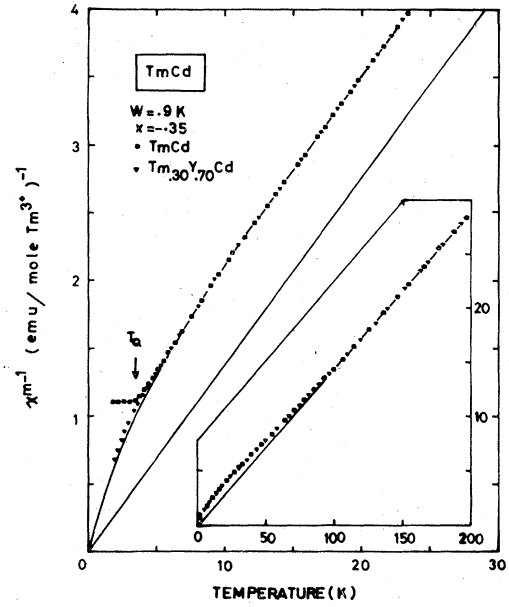

FIG. 2. Low-temperature reciprocal susceptibility for one Tm^{3+} mole in TmCd (□) and $Tm_{0.30}Y_{0.70}Cd$ (▼). The straight line is the extrapolation of the linear high-temperature variation. The full curve is calculated with $W = 0.9$ K, $x = -0.35$. The inset gives the variation up to high temperature. The straight line corresponds to the linear extrapolation.

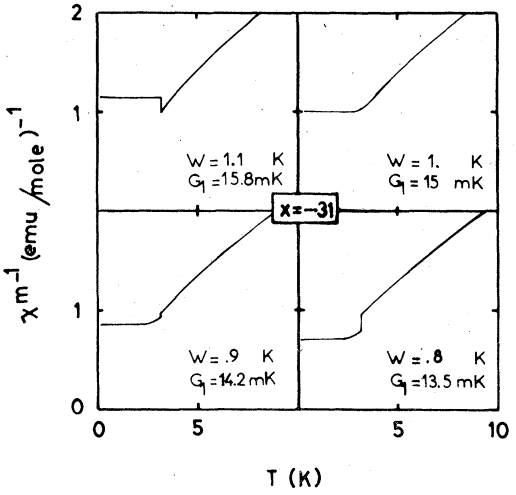

FIG. 3. Calculated χ^{-1} curves according to W for $x = -0.31$.

2. *Tetragonal range*

The occurrence of the structural transition is revealed by an angular point at T_Q (Fig. 2). The Van Vleck behavior below T_Q indicates the nonmagnetic $|1\rangle$ singlet issued from the $\Gamma_5^{(1)}$ triplet to be the ground state in the tetragonal range (see the magnetic characteristics for $\Gamma_5^{(1)}$ and Γ_3 levels in Table I). This nonmagnetic ground state and the weakness of Θ^* prevent any ferromagnetic ordering as observed down to 30 mK.[1]

The absence of discontinuity at T_Q indicates that the main Van Vleck contribution $\langle 1|J_z|4\rangle/(E_1 - E_4)$ is not noticeably modified. With G_1 bound to W, x (Fig. 1), calculations of χ^{-1} taking into account all the levels can determine precisely the level scheme as shown in Fig. 3. The possible (W, x) sets then range from $(W = 1.3 \pm 0.2$ K, $x = -0.4) - (W = 0.85 \pm 0.1$ K, $x = -0.25)$ this range being consistent with the preceding one but smaller.

In addition, calculations indicate that increasing the magnetic field smooths and shifts the structural transition towards high temperatures, in agreement with the temperature variation of the reciprocal magnetization obtained with a 14.24-kOe field (Fig. 5 in Ref. 1).

TABLE I. Matrix elements of the magnetic dipolar and quadrupolar operators for $\Gamma_5^{(1)}$ and Γ_3 in cubic symmetry (Tm^{3+} ion).

	$\Gamma_5^{(1)}$			Γ_3	
	$\|1\rangle$	$\|2\rangle$	$\|3\rangle$	$\|4\rangle$	$\|5\rangle$
$\langle i \|g_J J_z\| i\rangle$	0	3.15	−3.15	0	0
$\langle i \|O_2^0\| i\rangle$	15	−7.5	−7.5	+36	−36

B. Magnetization in high fields

We have performed magnetization measurements on a spherical single crystal in magnetic fields up to 150 kOe and at temperatures from 1.5 to 300 K. The field was applied along a fourfold axis in order to eliminate any G_2 contribution (Fig. 4). Above 50 K the usual paramagnetic behavior is observed, but below an inflexion point appears more and more pronounced when decreasing the temperature. The corresponding critical-field value decreases before vanishing in the tetragonal phase.

For fitting this set of curves we have kept W and x free and G_1 bound to them. Good fits are allowed with only (W, x) values ranging from $(W = 0.9 \pm 0.15$ K, $x = -0.4) - (W = 0.8 \pm 0.1$ K, $x = -0.28)$; this range is included in the previously obtained ones. For instance (Fig. 4) with $W = 0.95$ K, $x = -0.335$, $G_1 = 12.5$ mK, the agreement is quite satisfactory. Such an agreement cannot be obtained with the Γ_3 ground state.

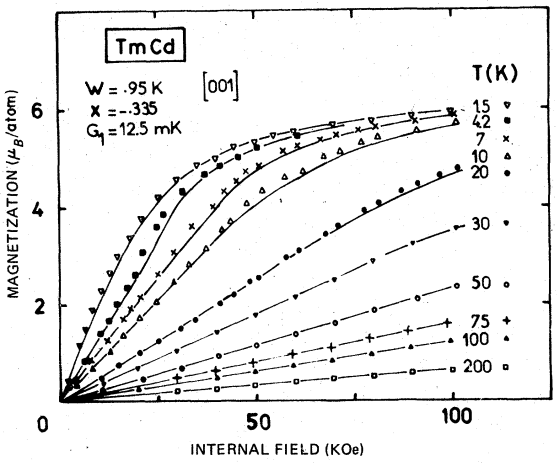

FIG. 4. Experimental and calculated isothermal magnetization curves for a fourfold field direction in TmCd.

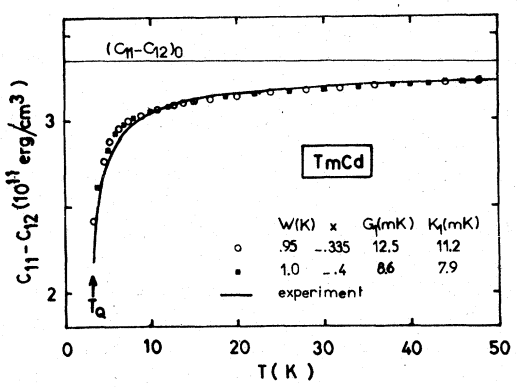

FIG. 5. $C_{11}-C_{12}$ mode calculated with $W=0.95$ K, $x=-0.335$, $G_1=12.5$ mK (○) and $W=1$ K, $x=-0.4$, $G_1=8.6$ mK (■) and compared with the experimental curve from Ref. 1.

C. Elastic constants and magnetostriction

The sound-velocity mode $C_{11}-C_{12}$ is given by the usual expression:

$$(C_{11}-C_{12})/(C_{11}-C_{12})_0=(1-G_1\chi_s)/(1-K_1\chi_s)\,, \qquad (6)$$

where χ_s is the strain susceptibility calculated from the cubic level scheme. Equation (6) vanishes at the quadrupolar-ordering temperature T_Q in the case of a second-order transition. This is the case when the ground state is a doublet[3,10] as proposed for TmCd (Ref. 1), where anharmonic effects were supposed to remove the structural transition at a temperature higher than the calculated one and change the second-order character into a first-order one. In the case of a triplet ground state a first-order transition may be calculated with the pure-harmonic-elasticity model,[2,10] and T_Q is then defined by the coexistence of both cubic and tetragonal phases, the softening remaining unachieved.

The results of Lüthi et al. can be fitted to the $\Gamma_5^{(1)}$ ground state. As an example we have drawn in Fig. 5 in addition to the experimental curve (Fig. 10 of Ref. 1) the values calculated with the two level schemes ($W=0.95$ K, $x=-0.335$, $G_1=12.5$ mK) and ($W=1$ K, $x=-0.4$, $G_1=8.6$ mK). This gives, respectively, $K_1=11.2$ and 7.9 mK. Then $B_1^2/C_0=1.3$ and 0.7 mK leads to $|B_1|=12.7$ and 9.3 K in each case.

The spontaneous strain is found to be about -10^{-3} and -0.6×10^{-3} in Refs. 1 and 4. With $W=0.95$ K, $x=-0.335$ and $G_1=12.5$ mK the $\langle O_2^0\rangle$ mean value is calculated to be 26 at 1.5 K in null field. $C_0=1.25\times10^5$ K and $B_1=-12.7$ K give $\epsilon_3=-2.5\times10^{-3}$. In a parallel way these level schemes and parameters closely agree with parastriction measurements on TmCd from 10 K up to room temperature.[14]

IV. SUMMARY

The physical properties of TmCd appear to be fully described without invoking any anharmonic lattice contribution. The paramagnetic susceptibility is sufficient by itself for determining the cubic level scheme. The Schottky anomaly on the specific heat is found to be induced by a $\Gamma_5^{(1)}-\Gamma_3$ spacing of about 24 K. The magnetization curves under high-magnetic fields are described when including the quadrupolar contributions as well as the tetragonal strain and the sound velocity.

The sensitive dependence of these properties on the precise $4f$-wave-function mixing leads to a narrow range of solutions in the Lea, Leask, and Wolf (W,x) plane for defining the cubic level scheme: $W=0.95\pm0.08$ K and $x=-0.34\pm0.03$. The ground state is then the $\Gamma_5^{(1)}$ magnetic triplet. According to the precise level scheme, we find then: $G_1=12.5\pm2.5$ mK, $K_1=11\pm3$ mK, $B_1=-12\pm1.5$ K.

The comparison with the TmZn situation may be then developed. The CEF parameters $A_4\langle r^4\rangle=-32\pm7$ K and $A_6\langle r^6\rangle=-15\pm3$ K are close to the TmZn ones. About this latter compound we have built the magnetic and structural phases diagram resulting from the competition of both bilinear and quadrupolar interactions. The Fig. 10 of Ref. 2 is drawn for $W=1.2$ K, $x=-0.31$; all the TmZn physical properties, especially the first-order character of the structural transition are correctly described with $\Theta^*=8.1$ K, $G_1=25.5$ mK, $K_1=19$ mK, and $B_1=-27$ K. Note that in this diagram a $G_1=15$ mK value gives a first-order tran-

sition at $T_Q = 3.3$ K for $\Theta^* = 0$ K. TmCd thus gives a complementary illustration of this competition between the two kinds of interactions. The relative contribution of the quadrupolar exchange to G_1 is stronger in TmCd ($K_1/G_1 = 0.9$ instead of 0.75 in TmZn); this is due to the weaker magnetoelastic contribution (1.3 ± 0.4 mK instead of 6.5 mK). There are first observations of such ratio values: the quadrupolar ordering here drives the symmetry lowering. TmZn and TmCd differ from the vanadates[15] or other actual Jahn-Teller compounds[3] where the magnetoelastic coupling is the main second-order contribution and drives the symmetry lowering.

Magnetoelastic and quadrupolar exchange contributions may originate from the d character of the conduction band near the $4f$ ion. In CsCl-type rare-earth intermetallics, the e_g subband has been calculated by the APW method close to the Fermi level,[16] and the $4f$-shell band coupling may select particular band wave functions favoring tetragonal strain, but the propagation process of the local $4f$-band interaction leading to quadrupolar exchange remains a difficult problem.

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