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Paramagnetic torque in cubic rare-earth compounds

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Paramagnetic torque appears in cubic rare-earth intermetallics as an interesting experimental probe for studying the magnetic response to different couplings such as bilinear exchange, crystalline electric field, and quadrupolar interactions. Starting from the high-order magnetic susceptibility tensor for 432, $\bar{4}3m$, $m3m$ high-symmetry classes, its expression is given within the mean-field approximation and allows one to determine the anisotropy of the initial curvature of the isothermal magnetization in the presence of an applied magnetic field. It is shown that at the magnetic transition, the twofold axis is never the easy magnetization direction. Torque measurements in the paramagnetic phase of CsCl-type structure compounds, TmZn and TmCd, are then presented. They are in full agreement with the third-order magnetic susceptibility previously studied and allow a more precise determination of the quadrupolar interactions in these systems.

I. INTRODUCTION

The analysis of the magnetic response to an external magnetic field has been extensively developed in magnetic systems with regard to very different motivations.[1,2] In the case of $4f$ magnetism, studying the paramagnetic regime using the susceptibility formalism is known to be very fruitful for determining the strength of different coexisting interactions, in particular the Heisenberg-type bilinear exchange and the crystalline-electric-field (CEF) term. In *cubic* systems, the linear term of the field expansion of the magnetization is isotropic, but beyond it, the H^3 term is anisotropic due to the mixing of the $4f$ wave functions by the CEF. This third-order magnetic susceptibility describes the initial curvature of the magnetization curve and is usually negative. In addition to information on the CEF-level scheme itself, it may also provide one with indications on the existence of additional couplings such as $4f$ quadrupolar interactions.[3] In particular, it may become positive in the presence of the magnetoelastic coupling and/or of positive quadrupolar pair interactions.[4-6] Thus, analyzing the third-order magnetic susceptibility constitutes an additional experimental probe with regard to quadrupolar interactions in full coherency with the elastic constants and parastriction measurements.[5]

An interesting alternate experimental method was proposed a few years ago by measuring the H^4 term of the magnetic torque in the paramagnetic regime.[7] Unfortunately, the expressions of the torque were established using a wrong magnetic-susceptibility tensor. We present here the relevant formalism for the paramagnetic torque, then determinations by this method of the quadrupolar coupling in TmZn and TmCd CsCl-type intermetallics.

II. FORMALISM

A. The susceptibility tensor

Magnetization, as with most properties of crystals, cannot be described without reference to directions, and requires polar tensors of even rank to be related to the external magnetic field.[8] In cubic symmetry, using the notations of Birss, polar tensors of rank m, S_m, and T_m, are relevant for 23, $m3$ symmetry classes and 432, $\bar{4}3m$, $m3m$ symmetry classes, respectively. The second-rank tensors, S_2 and T_2, exhibit a unique diagonal matrix element xx, and the first-order magnetic susceptibility is isotropic. The fourth-rank tensor S_4 includes $xxxx$, $xxyy$, $yyxx$ elements. The T_4 tensor includes only two elements $xxxx$, $xxyy$ (Table 4f, pp. 62–66 of Ref. 8).

Since in CsCl-type lattices the 4f-site symmetry is $m3m$, only the second case, with T_4, will be considered in the following. The results are valid for a great number of other rare-earth compounds such as pnictides (NaCl-type) and Laves phases ($MgCu_2$-type) including dialuminides of Ref. 7. Describing the magnetization induced by a magnetic field in the fourfold axis system leads to

$$\begin{aligned} M_x &= \chi H_x + \chi_a H_x^3 + 3\chi_b H_x (H_y^2 + H_z^2) + \cdots , \\ M_y &= \chi H_y + \chi_a H_y^3 + 3\chi_b H_y (H_z^2 + H_x^2) + \cdots , \\ M_z &= \chi H_z + \chi_a H_z^3 + 3\chi_b H_z (H_x^2 + H_y^2) + \cdots , \end{aligned} \tag{1}$$

with $\chi_a = \chi_{xxxx}$ and $\chi_b = \chi_{xxyy}$.

Along the main crystallographic directions, one gets

$$\begin{aligned} M^{[001]} &= \chi H^{[001]} + \chi_a (H^{[001]})^3 + \cdots , \\ M^{[111]} &= \chi H^{[111]} + \frac{\chi_a + 6\chi_b}{3} (H^{[111]})^3 + \cdots , \\ M^{[110]} &= \chi H^{[110]} + \frac{\chi_a + 3\chi_b}{2} (H^{[110]})^3 + \cdots . \end{aligned} \tag{2}$$

For $\chi_a > 3\chi_b$, the magnetization is maximum, therefore the energy is minimum, for a magnetic field applied along a fourfold axis, which becomes the direction of easy magnetization at the magnetic-ordering temperature at least in the case of a second-order magnetic transition. For $\chi_a < 3\chi_b$, the threefold axis is favored. For $\chi_a = 3\chi_b$, the crystal is magnetically isotropic up to the third order. The twofold axis is never the easy magnetization direction *close to the magnetic transition* in cubic compounds. Effectively, such a situation has, to our knowledge, never been reported in the literature: a twofold axis as an easy magnetization direction is observed *only at low temperature* in some Nd, Tb, and Ho compounds such as Nd-, Tb-, HoZn (Ref. 9), $HoAl_2$ (Ref. 10), Nd-, $HoCo_2$ (Ref. 11), and Nd-, TbCd.[12]

For any other crystallographic direction, the magnetization is no longer collinear to the field. The resulting magnetic torque may be calculated either directly from Eqs. (1) or from deriving the thermodynamical potential with respect to the θ, φ angular coordinates of the magnetic field in spherical symmetry, [001] being the z axis.[13] Keeping φ constant leads to

$$C=(\chi_a-3\chi_b)\frac{\sin 2\theta}{2}[\sin^2\theta(\cos^4\varphi+\sin^4\varphi)-\cos^2\theta]H^4+\cdots . \tag{3}$$

For H in the (010) plane and (110) plane, respectively, one gets

$$\begin{aligned} C^{[010]}&=\frac{\chi_a-3\chi_b}{4}\sin 4\theta H^4+\cdots , \\ C^{[110]}&=\frac{\chi_a-3\chi_b}{8}[\sin 2\theta+\tfrac{3}{2}\sin 4\theta]H^4+\cdots . \end{aligned} \tag{4}$$

Note that a magnetic field within the (111) plane leads to a zero component of the torque along [111].

Thus the χ_a and χ_b susceptibilities can be achieved by measuring in the paramagnetic phase either the isothermal magnetization for a magnetic field applied along the [001] and [111] axes[3] or the isothermal magnetic torque when rotating the magnetic field in a given crystallographic plane [Eq. (4)]. In this latter case, *only a combination* of χ_a and χ_b may be achieved.

B. Origin of the third-order magnetic susceptibility

The following step describes χ_a and χ_b in terms of magnetic couplings. Since in rare-earth intermetallics with nonmagnetic alloyed metals the bilinear interaction energy is usually smaller than the CEF one, a quantum treatment is required using both the Stevens-operator formalism and the mean-field approximation. The Hamiltonian also includes quadrupolar (magnetoelastic and pair interactions) couplings. Perturbation theory up to the fourth order for the magnetization, and up to the second order for the quadrupolar components leads to the free energy associated with the tetragonal (γ) and trigonal (ε) symmetry-lowering modes.[5] Equilibrium expressions are then deduced, in particular, for the H^3 term of the magnetization:

$$\begin{aligned} \chi_{M\gamma}^{(3)}&=[1-n\chi_0]^{-4}\left[\chi_\gamma^{(3)}+2G^\gamma\frac{(\chi_\gamma^{(2)})^2}{1-G^\gamma\chi_\gamma}\right] , \\ \chi_{M\varepsilon}^{(3)}&=[1-n\chi_0]^{-4}\left[\chi_\varepsilon^{(3)}+6G^\varepsilon\frac{(\chi_\varepsilon^{(2)})^2}{1-3G^\varepsilon\chi_\varepsilon}\right] , \end{aligned} \tag{5}$$

where the χ's are one-ion susceptibilities only determined by the CEF. n is the bilinear exchange coefficient, which is obtained from the fit of the first-order susceptibility. G^μ ($\mu=\gamma,\varepsilon$) is the total quadrupolar coefficient that receives both magnetoelastic and pair-interaction contributions. $\chi_{M\mu}^{(3)}$ is then related to χ_a and χ_b as follows:

$$\chi_a=\chi_{M\gamma}^{(3)} ,$$

$$\chi_b=\frac{3\chi_{M\varepsilon}^{(3)}-\chi_{M\gamma}^{(3)}}{6} ,$$

and Eqs. (4) transform into

$$\begin{aligned} C^{[010]}&=\tfrac{3}{8}(\chi_{M\gamma}^{(3)}-\chi_{M\varepsilon}^{(3)})\sin 4\theta H^4+\cdots , \\ C^{[110]}&=\tfrac{3}{16}(\chi_{M\gamma}^{(3)}-\chi_{M\varepsilon}^{(3)})(\sin 2\theta+\tfrac{3}{2}\sin 4\theta)H^4+\cdots . \end{aligned} \tag{4$'$}$$

III. APPLICATIONS TO TmZn AND TmCd

These systems are dominated by quadrupolar interactions, the best signature of which is the occurrence in the paramagnetic phase of a quadrupolar ordering at $T_Q=4.2$ and 8.55 K, respectively. A large cubic-tetragonal symmetry lowering is then induced at T_Q with $(c/a)-1=-0.3\%$ in TmCd and -0.8% in TmZn. Whereas TmCd remains paramagnetic, TmZn is an overcritical system with $T_c=8.12$ K, very close to T_Q. The above susceptibility formalism has been shown to be fully relevant for describing all the magnetic and elastic properties.[5]

In both compounds, $\chi_{M\varepsilon}^{(3)}$ was well described by the susceptibility formalism at any temperature, whereas some discrepancy occurred for $\chi_{M\gamma}^{(3)}$ close to T_Q: in TmZn, G^γ ranges from 27 to 30 mK according to the temperature.[3] This feature, observed for the symmetry-lowering mode corresponding to the quadrupolar order parameter, was due to residual strain effects induced by the large magnetoelastic coupling. Additional data are presented here for $\chi_{M\gamma}^{(3)}$, each of them being collected in virgin condition after warming up the sample at about 100 K, then cooling it down to the desired temperature without entering the ordered phase (Fig. 1). $\chi_{M\gamma}^{(3)}$ is now described in a temperature range larger than previously with a $G^\gamma=27$ mK parameter.

Paramagnetic torques have been measured for a magnetic field of constant modulus in rotation in fourfold and twofold planes. The magnetic field ranges from 0 to 2 T and the temperature from 4.2 to 20 K. In these conditions, the amplitude of the torque exhibits a H^4 variation at any temperature. Torque curves (Fig. 2) were also analyzed by means of a Fourier-series expansion:

$$\Gamma(\theta)-\Gamma_{\mathrm{app}}\sin\theta=\Gamma_2\sin 2\theta+\Gamma_4\sin 4\theta+\Gamma_6\sin 6\theta+\cdots . \tag{6}$$

Γ_{app} is a systematic error with the apparatus. For instance, at 12 K and for H in the (001) plane, the following values are obtained: $\Gamma_2=684$, $\Gamma_4=20\,460$, and $\Gamma_6=1090$ dyn cm ($\Gamma_{\mathrm{app}}\sim 0$). The 6θ contribution is about 5% of the 4θ one. The 2θ term is still smaller (3.3%). It may

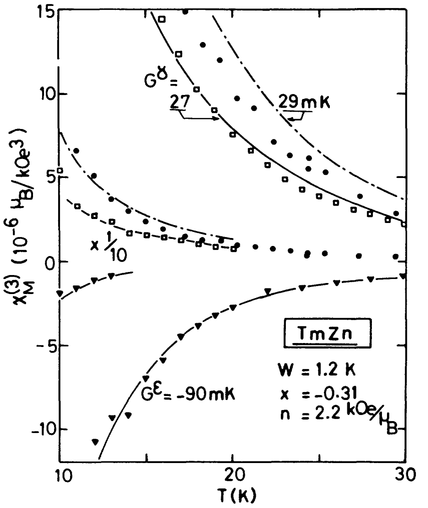

FIG. 1. Third-order magnetic susceptibility in TmZn for a magnetic field applied along [001] (●, data from Ref. 3; open squares, present work) and [111] (triangles). Full lines are calculated according to Eqs. (5) with the parameters indicated; *W* and *x* are the usual CEF parameters.

originate from a misorientation of the crystal with regard to the field plane as well as from the presence of residual magnetostrictive strains as previously observed on the isothermal [001] magnetization curves. For *H* in the twofold plane, Eqs. (4′) reveal that Γ_4 and Γ_2 are in a ratio of $\frac{3}{2}$: at 15 K, the Fourier analysis leads to $\Gamma_4/\Gamma_2=7896/5541=1.42$. The small difference to $\frac{3}{2}$ corresponds to the 2θ contribution from either the misorientation of the sample or the residual strains. The Γ_6 contribution is small (182 dyn cm) as the $\Gamma_{\text{app}}=160$ dyn cm correction. This justifies restricting the formalism to second- and fourth-rank terms.

The deduced temperature of $\chi^{(3)}_{M\gamma}-\chi^{(3)}_{M\varepsilon}$ are compared in Figs. 3 and 4 with calculated ones, and also with varia-

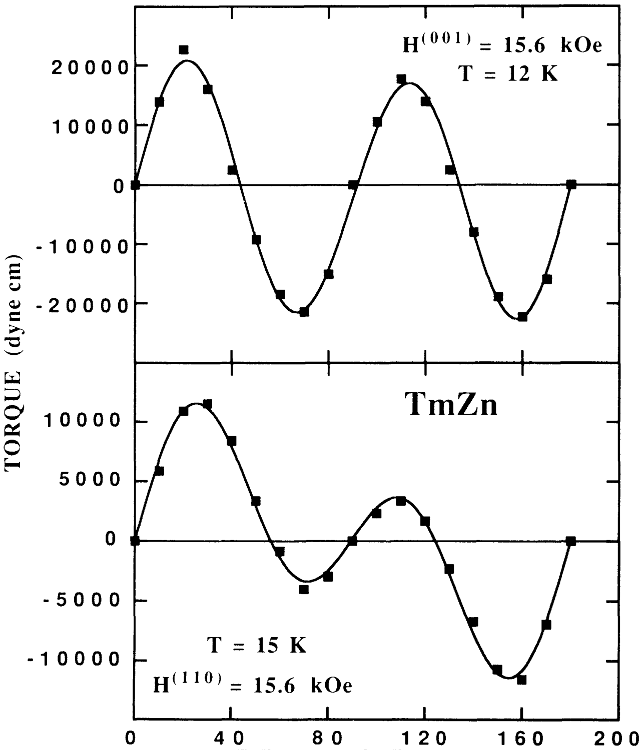

FIG. 2. Paramagnetic torque as a function of the rotation angle θ of the applied field in a fourfold plane (upper part) and a twofold one (lower part) in the paramagnetic range of TmZn [■, data; the full line is calculated according to Eq. (6). The θ origin is along a fourfold axis].

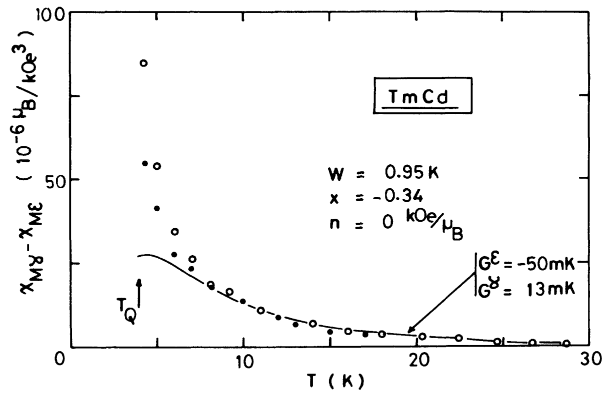

FIG. 3. Temperature variation of the anisotropy of the third-order susceptibility in TmCd (open dots, from [001] and [111] magnetization curves; full dots, from paramagnetic torque). The full line is calculated according to Eqs. (5) with the parameters indicated.

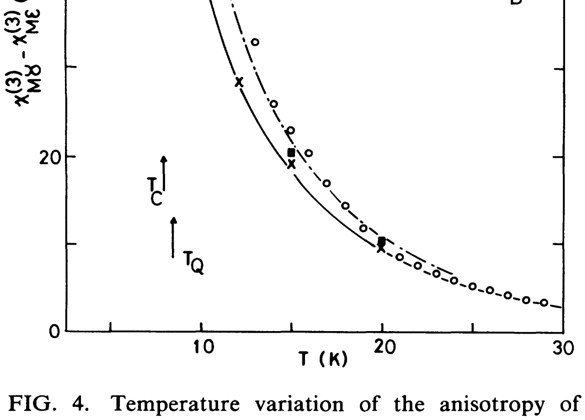

FIG. 4. Temperature variation of the anisotropy of the third-order susceptibility in TmZn (○, from [001] and [111] magnetization curves; ■, from paramagnetic torque within a fourfold plane; x, from paramagnetic torque within a twofold plane). Full lines are calculated according to Eqs. (5) with the parameters indicated.

tions deduced from isothermal magnetization curves. In TmCd, the two sets of experimental data are in good agreement. They exhibit a shift from the calculations only close to T_Q, with a smaller overestimation of $\chi_{M\gamma}^{(3)}-\chi_{M\epsilon}^{(3)}$ in the torque process. In TmZn also, the torque data are slightly smaller than the magnetization ones. This may indicate that, due to the in-plane field rotation, torque data are less affected by residual magnetoelastic strains. In TmZn, the deduced G^{γ} value, 26 mK, is in close agreement with the one obtained from the $C_{11}-C_{12}$ elastic constant softening ($G^{\gamma}=25$ mK).

Magnetic torque measurements in the paramagnetic phase of cubic compounds appear to be an interesting experimental probe with regard to quadrupolar interactions. This technique is complementary to the analysis of magnetization curves, in spite of the fact that it does not lead to the two third-order susceptibilities, but only to their difference.

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