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Magnetostructural transition in Ho_5Ge_4

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First-principles calculations predict that, in the antiferromagnetic state, Ho_5Ge_4 should adopt a unique monoclinic structure with an unusual distortion in the *ac* plane, making it a unique member of a broadly researched R_5T_4 family of compounds that are best known for their giant magnetocaloric, magnetoresistive, and magnetostrictive effects. Experiments prove that, in Ho_5Ge_4, the magnetic transition from the paramagnetic to the antiferromagnetic state is indeed accompanied by a structural transformation from the Sm_5Ge_4-type orthorhombic to the predicted monoclinic structure. Surprisingly, a magnetic field can partially reconstruct the high-temperature paramagnetic Sm_5Ge_4-type structure of Ho_5Ge_4 when applied to the magnetically ordered compound.

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I. INTRODUCTION

Physics is continuously enriched by experiments and theory, yet combining the two is most beneficial because first-principles calculations, for example, require ground-state structural data, without which prediction of properties becomes questionable. If reliable crystallographic data are available, theoretical predictions may guide experiments to possible discoveries, minimizing unnecessary waste of time and resources. By taking Ho_5Ge_4 as an example, we show how the existing pool of knowledge paves the path to the discovery of a unique structural polymorph in the broadly studied R_5T_4 (R=rare earth metal and T=group 14 element) compounds.

The crystallography,[1] basic magnetic properties,[2] and magnetic structure[3] of several R_5T_4 compounds were reported a few decades ago. However, these materials did not draw much attention until the discovery of the giant magnetocaloric effect (GMCE), resulting from the concomitant magnetic and structural transitions in $Gd_5Si_2Ge_2$.[4,5] Similar magnetostructural transitions (MST) are exhibited by several other members of the R_5T_4 family.[6–8] The quest to understand correlations between magnetism and structure resulted in a broad research of the R_5T_4 series of intermetallics.[9–20]

The R_5T_4 compounds adopt layered structures made up of pseudo-two-dimensional nanoslabs, each formed by five monolayers of R and T atoms. Rearrangements of these slabs give rise to three different crystal structures, namely, the Gd_5Si_4-type orthorhombic structure [referred as *O*-I type; space-group (SG) *Pnma*], $Gd_5Si_2Ge_2$-type structure (M type; SG $P112_1/a$), and Sm_5Ge_4-type (*O*-II type; SG *Pnma*).[19] In all R_5T_4 compounds known to date, the MST involves a change from the paramagnetic (PM) M-type structure or antiferromagnetic (AFM) *O*-II type structure to the ferromagnetic (FM) *O*-I type structure.[14,19,21,22] These transformations involve shear displacements of the slabs, and breaking and reforming of the interslab *T*-*T* bonds. In every case reported to date, the intraslab bonds remain intact during these transformations.[14,19,22]

Recent investigation by Pereira *et al.*[23] shows that Ho_5Ge_4, which in the past was known to exhibit a second-order transition at its AFM ordering temperature [T_N=21 K,[2] or 23 K (Ref. 24)], undergoes an incomplete MST at T_N =25 K. We note that all of the existing experimental and theoretical data indicate that neither the *O*-I nor M-type structures support antiferromagnetism,[7,10,19,25] and therefore, the occurrence of a structural transition coupled with the AFM ordering in Ho_5Ge_4 appears extremely unusual and intriguing. Moreover, this looks like an interesting case to test whether first-principles theory can achieve predictive power. In this paper we show that a unique monoclinic distortion of the parent *O*-II structure of Ho_5Ge_4 predicted by theory underpins the observed MST.

II. THEORETICAL CALCULATIONS

Remembering that the M-type R_5T_4 structure does not support AFM order, the total-energy calculations for the PM, FM, and AFM states were carried out as a function of the monoclinic angle for all possible monoclinic maximal non-isomorphic subgroups of *Pnma*, namely, $P112_1/a$, $P12_1/m1$, and $P2_1/n11$, and the results are shown in Fig. 1. The groups $P112_1/a$, $P12_1/m1$, and $P2_1/n11$ correspond to the monoclinic distortions in the *ab*, *ac*, and *bc* planes, respectively.

Even though the electronic structure calculations may be performed using either the tight-binding linear muffin-tin orbital (TB LMTO) method within atomic sphere approximation (ASA), or the full potential based methods, we note that for closed structures both methods yield results with nearly identical precision.[26] Thus, in this work the total-energy calculations have been performed by employing the TB LMTO-ASA within the local spin-density approximation (LSDA) by treating 4*f* electrons as core electrons.[27,28] For these calculations, a total of 170 irreducible **k** points have been used from the 8×8×8 Brillouin-zone mesh for **k** space integration in all three types of the monoclinic distortions of the original *O*-II structure. The low-temperature (~20 K) lattice constants of Ho_5Ge_4 were extrapolated from the room-temperature values, using the reported coefficient of linear thermal expansion,[23] and the atomic positions were generated using symmetry relationships between *Pnma* and each of the three monoclinic subgroups. The PM state was mod-

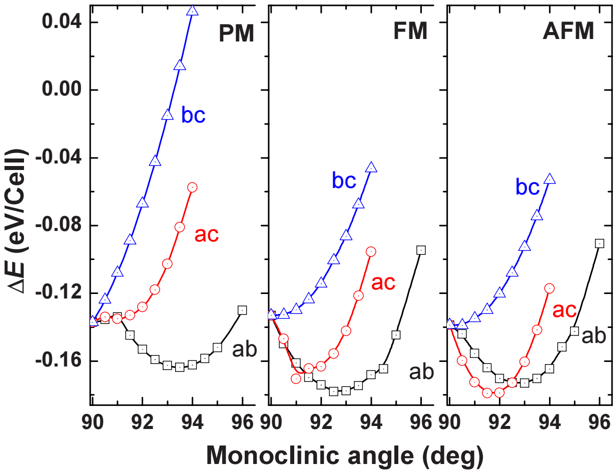

FIG. 1. (Color online) Variations in the PM, FM, and AFM total energies (ΔE) of Ho_5Ge_4 as functions of the monoclinic angle for the monoclinic distortions in the *ab* (SG $P112_1/a$), *ac* (SG $P12_1/m1$), and *bc* (SG $P2_1/n11$) planes.

eled by assigning equal up and down spins in the $4f$ shell of the Ho ion, whereas the AFM and FM structures were constructed by assuming, respectively, the antiparallel and parallel couplings between the ferromagnetic slabs.[29]

The total-energy calculations show that in both the PM and FM states, the "standard" monoclinic (M-type) structure with a distortion in the *ab* plane has the lowest energy, whereas in the AFM state, a different monoclinic structure with a distortion in the *ac* plane has the lowest energy.[30] Therefore, the total-energy considerations indicate that, if the FM state would be the ground state, the Ho_5Ge_4 would adopt a monoclinic structure with the "conventional" distortion in the *ab* plane; however, in the AFM state it should adopt a different monoclinic structure with a small distortion in the *ac* plane.

It is well known that, owing to the inclusion of the entropy term in the free energy, the high-symmetry structures are preferred at high temperature (HT) whereas the low-symmetry structures are favored at low temperatures (LT).[31] In the AFM state the monoclinic structure with a distortion in the *ac* plane is favored by both the total-energy and entropy considerations thereby indicating that the PM to AFM transition in Ho_5Ge_4 should be accompanied by a structural transformation from the orthorhombic *O*-II type structure to a new monoclinic structure distorted in the ac plane (henceforth called the Mβ structure).

III. EXPERIMENTAL DETAILS

To verify the theoretical predictions described above, we have carried out the magnetization, heat capacity, and temperature- and field-dependent crystallographic studies. The polycrystalline sample of Ho_5Ge_4 was prepared by arc melting of the stoichiometric quantities of Ho and Ge under argon atmosphere. The Ho was prepared by the Materials Preparation Center[32] of the Ames Laboratory and was 99.98 wt. % pure with respect to all other elements in the periodic table. The Ge was obtained from Cerac Inc., USA and was 99.999 wt. % pure. The phase analysis using the x-ray powder diffraction shows that the Ho_5Ge_4 is a single phase alloy crystallizing in the Sm_5Ge_4-type *O*-II structure. The magnetization (M) measurements under zero-field cooled (ZFC), field cooled cooling (FCC), and field cooled warming (FCW) conditions were carried out in a superconducting quantum interference device (SQUID) magnetometer. The heat-capacity measurements were carried out in an adiabatic heat-pulse calorimeter.[33] The temperature and field-dependent x-ray powder-diffraction (XRD) data were collected on a Rigaku TTRAX powder diffractometer using Mo K_α radiation in the 2θ range of $9°-52°$.[34]

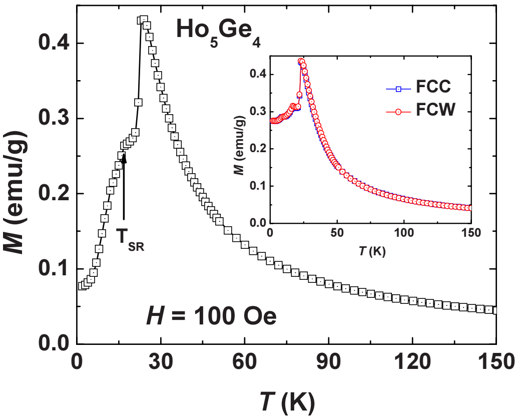

FIG. 2. (Color online) Temperature (T) dependence of the magnetization (M) data of Ho_5Ge_4 obtained under ZFC condition in an applied field (H) of 100 Oe. The arrow in the figure indicates an additional magnetic transition in the magnetically ordered phase. The inset shows the M-T data collected in the same field under FCC and FCW conditions.

IV. EXPERIMENTAL RESULTS AND DISCUSSIONS

Figure 2 shows $M(T)$ data for Ho_5Ge_4, collected under ZFC mode in an applied field of 100 Oe. We note that the $M(T)$ of Ho_5Ge_4 shows an AFM-like peak at $T_N=23$ K and the transition from AFM to PM state is quite sharp, signaling a possibility of first-order transformation. Apart from bulk magnetic ordering at T_N, the $M(T)$ data show a weak anomaly around $T_{SR}=16$ K, presumably due to a spin reorientation transition arising from the change in the magnetic structure.[3] The temperatures associated with AFM to PM transition and the spin reorientation transitions agree well with previous reports.[2,3,23,24] The $M(T)$ under FCC and FCW conditions is shown as inset of Fig. 2. We note that, unlike many of the R_5T_4 compounds exhibiting first-order MST,[8,17,35] the FCC and FCW $M(T)$ data do not exhibit any irreversibility.

In order to understand the character of the AFM-PM transition, the temperature dependencies of heat capacity (C) of Ho_5Ge_4 were measured in 0, 10, 20, and 50 kOe magnetic fields (Fig. 3). In accordance with the $M(T)$, the zero-field $C(T)$ data also show two anomalies at 17 and 23 K, which are close to T_{SR} and T_N, respectively. At T_N, the zero-field $C(T)$ peak is sharp and weakly asymmetric, thus confirming the first-order character of the transition at T_N. With increas-

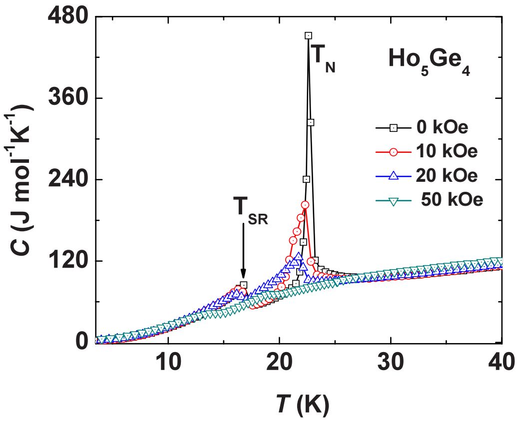

FIG. 3. (Color online) Temperature (T) dependence of the heat capacity (C) of Ho_5Ge_4 under various applied magnetic fields (H).

ing field, the height of the $C(T)$ peak at T_N decreases, and its position shifts toward lower temperatures, which corroborates the AFM nature of the magnetic ordering. We note that, as the magnetic field increases to 20 and 50 kOe, the sharp peak becomes rounded off, indicating a changeover of the transition at T_N to second order. The first-order transition at T_N in Ho_5Ge_4 is in contrast with the previous report[24] and the discrepancy can be attributed to interstitial impurities[8] associated with a lower purity of Ho used in Ref. 24.

The $M(T)$ and $C(T)$ clearly establish that the Ho_5Ge_4 undergoes a first-order transition at T_N. Therefore, in view of the theoretical predictions, and strong coupling between the magnetic and structural degrees of freedom exhibited by many of the R_5T_4 compounds,[7,8,12,14,16,17,21,22] the temperature dependence of the crystal structure has been studied in detail (Table I). At 293 K, the Ho_5Ge_4 compound crystallizes in the O-II type structure, which is preserved down to 24 K. However, in accord with the first-principles calculations, in the AFM state, the compound adopts the monoclinic Mβ structure (SG $P12_1/m1$). Furthermore, the theoretical calculations repeated using the real crystallographic data (Table I) rather than those extrapolated from room temperature show that in Ho_5Ge_4 the AFM Mβ state is indeed the ground state. The O-II to Mβ transformation is complete, and the Mβ structure is retained down to 5 K.

Thus, the XRD, $M(T)$, and $C(T)$ data establish that, at T_N, Ho_5Ge_4 exhibits a coupled and complete MST from PM O-II to the low-temperature AFM Mβ structure. It is worth mentioning that to date all known R_5T_4 compounds with nonzero single R^{3+} ion anisotropy exhibit incomplete structural transitions, and varying range of decoupling of the magnetic and structural transitions. The degree of incompleteness and range of decoupling increase as one moves from Gd to the heavier lanthanides.[6–8,16,17,35] Therefore, the presence of a complete and coupled MST in Ho_5Ge_4 is quite intriguing. At T_N, the change from the O-II to Mβ structure is accompanied by positive discontinuities of 0.04%, 0.04%, and 0.03% along the a, b, and c axes, respectively, whereas the unit-cell volume exhibits a discontinuity of ~0.1%.

We note that, contrary to all known MSTs in R_5T_4,[10,19,21,22] the O-II to Mβ transformation in Ho_5Ge_4 is accompanied by a positive unit-cell volume discontinuity and it does not involve the shear displacements of the slabs and, therefore, both the interslab and intraslab bonds remain practically unaltered (average bond-length changes are less than 2%) during this transformation. Due to the absence of shear displacements, the unit-cell volume discontinuity in Ho_5Ge_4 is much smaller compared to those seen in many of the R_5T_4 compounds (0.1% in Ho_5Ge_4 vs 0.5%–1.2% in other R_5T_4 compounds),[8,14,16,17,21,22] which is in accord with the linear thermal-expansion measurements of Pereira *et al.*[23] During the MST, the extent of conversion between two phases is determined by a balance between the magnetic and strain energies.[36] Since the volume discontinuity involved in the O-II to Mβ conversion in Ho_5Ge_4 is roughly ten times smaller compared to other R_5T_4 compounds, the strain en-

TABLE I. Crystallographic data of Ho_5Ge_4 at 293 and 15 K.

T=293 K; SG $Pnma$; a=7.5789(2), b=14.5876(4), c=7.6478(2) Å, β=90°				T=15 K, SG $P12_1/m1$; a=7.5661(2), b=14.5589(3), c=7.6226(2) Å, β=90.572(2)°			
Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
				Ho1A	−0.0328(4)	0.6021(2)	0.1793(4)
Ho1	−0.0295(2)	0.6001(1)	0.1787(2)	Ho1B	0.4691(4)	0.5998(2)	0.3212(4)
				Ho2A	0.3827 (4)	0.1167(2)	0.1640(4)
Ho2	0.3787(2)	0.1173(1)	0.1625(2)	Ho2B	0.8771(4)	0.1173(2)	0.3370(4)
				Ho3A	0.2122 (5)	1/4	0.4982(7)
Ho3	0.2100(3)	1/4	0.4998(3)	Ho3B	0.7120(6)	1/4	−0.0030(7)
				Ge1A	0.2210(8)	0.0445(4)	0.4695(9)
Ge1	0.2175(5)	0.0454(2)	0.4671(5)	Ge1B	0.7223(8)	0.0471(4)	0.026(1)
				Ge2A	0.085(1)	1/4	0.111(2)
Ge2	0.0801(7)	1/4	0.1149(7)	Ge2B	0.583(1)	1/4	0.386(1)
				Ge3A	0.338(1)	1/4	0.858(1)
Ge3	0.3347(6)	1/4	0.8647(7)	Ge3B	0.832(1)	1/4	−0.364(1)

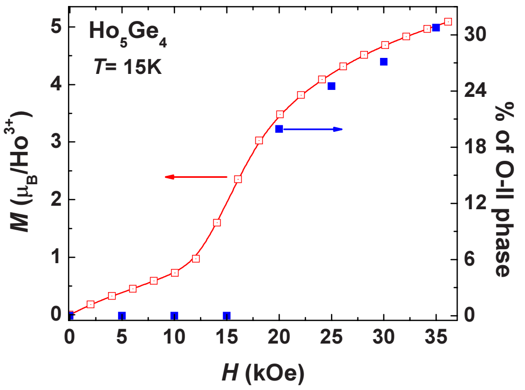

FIG. 4. (Color online) Field (H) dependence of magnetization (M) and molar concentration of the O-II phase at 15 K. The open symbols represent the magnetization data whereas the closed ones represent the concentration of O-II phase.

ergy involved in the MST in Ho_5Ge_4 is expected to be low. Thus, the completeness of the MST in Ho_5Ge_4 may be attributed to a small contribution from strain energy.

In order to further understand the correlations between the magnetic and structural properties of Ho_5Ge_4, the field dependence of the magnetization and crystal structure below T_N was also studied. The data at 15 K are shown in Fig. 4. The $M(H)$ isotherms collected below T_N show metamagnetism; the critical field (H_C, determined as the field corresponding to the maximum in dM/dH plot) for the metamagnetic transition decreases with increasing temperature (18 kOe at 2 K vs 12 kOe at 20 K). The x-ray diffraction results reveal that, in association with the metamagnetic transition, Ho_5Ge_4 exhibits an incomplete structural transition from a low-field LT Mβ to a high-field HT O-II structure. Above the critical field both the Mβ and O-II structures coexist, which is similar to that observed in many other R_5T_4 (Refs. 6, 16, and 17) and other compounds, including manganites.[37,38] At 15 K and H=35 kOe, the molar concentration of the O-II phase is ~31%, and the molar concentration of O-II follows the variations seen in the M-H data.

A similar correspondence between the M-H data and the field-induced structural changes has been observed in other R_5T_4 compounds as well; however, in all these compounds, the high magnetic field always promoted the formation of the LT phase.[10,14,16,17] At 15 K the field driven Mβ to O-II transformation is accompanied by the unit-cell volume discontinuity of 0.67%, which is quite large compared to the discontinuity of 0.1% seen at T_N in the temperature-dependent data. This difference can be attributed to the magnetostriction effect brought about by rotation of the anisotropic orbital charge densities of Ho^{3+} ion during the field driven reconstruction of the O-II phase from the Mβ phase.[39] The incompleteness of the field-induced transformation to the O-II phase, therefore, can be in part ascribed to the enhancement in the strain energies associated with the large volume change. Furthermore, only those grains that have their easy magnetization axes parallel or nearly parallel to the magnetic field vector are expected to easily undergo the field-induced magnetostructural transition.[16] Hence, the incompleteness of the magnetic field-induced crystallographic transformation in Ho_5Ge_4 is a result of both the magnetocrystalline anisotropy and increased strain energy.

V. CONCLUSIONS

In summary, the first-principles calculations show that, in the AFM state, the Ho_5Ge_4 should adopt a unique monoclinic Mβ structure. The experimental investigations of the magnetization and heat capacity, together with temperature-dependent and magnetic field-dependent XRD, indicate that the Ho_5Ge_4, which was previously reported to possess a second-order transition at T_N,[2,24] indeed exhibits a first-order magnetostructural transition from the high-temperature paramagnetic O-II to the low-temperature AFM Mβ structure. The Mβ structure is a unique crystal structure which was not known for R_5T_4 compounds. The analysis of the temperature- and field-dependent XRD data reveals that both the strain energies associated with the MST and magnetocrystalline anisotropy play important roles in determining the degree of completeness of the structural transformation in the R_5T_4 family of intermetallic compounds.

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