Anisotropic magnetization studies of R_2 CoGa₈ single crystals (R=Gd, Tb, Dy, Ho, Er, Tm, Y, and Lu)

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Single crystals of R_2 CoGa₈ series of compounds were grown by high temperature solution growth (flux) method. These compounds crystallize in a tetragonal crystal structure with the space group P4/mmm. It has been found that R_2 CoGa₈ phase only forms with the heavier rare earths, starting from Gd with a relatively large c/a ratio of ≈ 2.6 . The resultant anisotropic magnetic properties of the compounds were investigated along the two principal crystallographic directions of the crystal, viz., along the [100] and [001] directions. The compounds Y_2 CoGa₈ and Lu₂CoGa₈ show diamagnetic behavior down to 5 K, pointing out the nonmagnetic nature of Co in these compounds and a relatively low density of electronic states at the Fermi level. Compounds with the magnetic rare earths antiferromagnetically order at temperatures lower than 30 K. The Néel temperature of Tb₂CoGa₈ exceeds that of the Gd analog. The easy axis of magnetization for R_2 CoGa₈ and Tm₂CoGa₈, whereas the magnetization of Gd₂CoGa₈ was found to be almost isotropic. The magnetization behavior is analyzed on the basis of crystalline electric field model. The estimated crystal field parameters explain the magnetocrystalline anisotropy in this series of compounds.

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I. INTRODUCTION

 $R_n T X_{3n+2}$ (R=rare earths, T=Co, Rh, and Ir, and X=In and Ga) form a family of compounds, mainly consisting of two groups with n=1 and n=2. Both groups of compounds are structurally similar and exhibit a variety of interesting physical phenomena, which include heavy fermions, superconductivity and their coexistence, pressure induced superconductivity, magnetic ordering, etc. Compounds of n=1group have been extensively investigated compared to n=2. The latter group of compounds (R_2TX_8) were first reported by Kalychak *et al.*,¹ who reported the crystallographic details of these compounds. Later on, the interest in these compounds grew further due to the interesting behavior shown by the Ce compounds. Ce₂RhIn₈ antiferromagnetically orders with a Néel temperature of 2.8 K and it undergoes pressure induced superconductivity at 2 K under a pressure of 2.3 $GPa.^2 Ce_2CoIn_8$ is a Kondo lattice, exhibiting heavy fermion superconductivity with a $T_c = 0.4$ K (Refs. 3 and 4) at ambient pressure, while Ce_2IrIn_8 is a heavy fermion paramagnet.⁵

The magnetic properties of polycrystalline R_2 CoIn₈ compounds were reported by Devang *et al.*⁴ These compounds crystallize in the tetragonal structure with the space group P4/mmm. Some of their interesting features are a crystal field split nonmagnetic doublet ground state of Pr^{3+} ions in Pr_2 CoIn₈, field induced ferromagnetic behavior at low temperatures in Dy₂CoIn₈ and Ho₂CoIn₈, and an anomalously high magnetoresistance (~2700%) at 2 K in Tb₂CoIn₈. By considering these interesting behaviors in the indium analogs (to the best of our knowledge, there are no reports on the corresponding gallium compounds), we decided to study the R_2 CoGa₈ for various rare earths. Here, we report on our detailed structural and magnetization studies in this series of single crystals.

II. EXPERIMENT

Single crystals of R_2 CoGa₈ (where R=Gd, Tb, Dy, Ho, Er, Tm, Lu, and Y) compounds were grown by the flux method. The starting materials used for the preparation of R_2 CoGa₈ single crystals were high purity metals of rare earths (99.95%), Co (99.9%), and Ga (99.999%). Owing to the low melting point of Ga, the single crystals were grown in Ga flux. From the previous studies,³ it was observed that the R_2 CoIn₈ crystals were grown in the temperature range between 750 and 450 °C. We have also employed the same temperature range for the growth of R_2 CoGa₈ compounds. A button of R_2 Co with excess of Ga (R:Co:Ga=2:1:27) was taken in an alumina crucible and then sealed in an evacuated quartz ampoule. The ampoule was then heated up to 1050 °C over a period of 24 h and held at this temperature for 24 h for proper homogenization. The furnace was then cooled very rapidly down to 750 °C to avoid the formation of any unwanted phase. From 750 to 400 °C, the furnace

TABLE I. Lattice parameters, unit cell volume, and c/a ratio for the R_2 CoGa₈ series of compounds.

	Lattice 1	parameter	Volume	
Rare earth	a (Å)	<i>b</i> (Å)	(Å ³)	c/a
Gd	4.265(3)	11.099(6)	201.89	2.602
Tb	4.243(1)	11.043(8)	198.80	2.602
Dy	4.231(4)	11.027(7)	197.39	2.606
Но	4.219(7)	10.994(2)	195.69	2.605
Er	4.210(2)	10.964(1)	194.32	2.604
Tm	4.199(3)	10.938(4)	192.85	2.604
Lu	4.181(7)	10.903(1)	190.93	2.607
Y	4.249(8)	11.053(2)	199.55	2.601



FIG. 1. (Color online) Powder x-ray diffraction pattern recorded for crushed single crystals of Ho_2CoGa_8 at room temperature. The solid line through the experimental data points is the Rietveld refinement profile calculated for the tetragonal Ho_2CoGa_8 .

was cooled down at a rate of 1 °C/h, followed by a fast cooling to room temperature. The crystals were separated by centrifuging and as well treating them in hot water. The obtained crystals were platelets with sizes of roughly 5×5 $\times 1$ mm³. In some of the cases, the small platelets stick together to form a big crystal (roughly $7 \times 5 \times 4$ mm³). An energy dispersive x-ray analysis (EDAX) was performed on all of the obtained single crystals to identify their phase. The EDAX results confirmed the crystals to be of the composition 2:1:8. To check for the phase purity, powder x-ray diffraction pattern of all of the compounds were recorded by powdering a few small pieces of single crystal. Our attempts to make the compound with lighter rare earths failed. We did not attempt to make Yb and Eu compounds. It was found that in all of the cases, the crystallographic (001) plane was perpendicular to the flat plates of the crystal. The crystals were oriented along the [100] and [001] crystallographic axes by using Laue x-ray diffractometer and cut along the principal directions for the purpose of magnetization measurements by spark erosion cutting machine. The magnetic measurements were performed by using a superconducting quantum interference device (Quantum Design) and vibrating sample magnetometer (Oxford Instruments).

III. RESULTS

Crystal structure

The R_2 CoGa₈ series of compounds form in a tetragonal structure with a space group P4/mmm (No. 123). One of the



FIG. 2. (Color online) Unit cell volume of R_2 CoGa₈ compounds plotted against the corresponding rare earths.

compounds of the series Ho2CoGa8 is well cited for this particular structure. In order to confirm the phase homogeneity of the compound with proper lattice and crystallographic parameters, a Rietveld analysis of the observed x-ray pattern of all of the compounds was done by using the FULLPROF program.⁶ The lattice parameters thus obtained are listed in Table I and a representative Rietveld refined plot of Ho₂CoGa₈ is shown in Fig. 1. We obtained a χ^2 value of 2.6, a goodness of fit of 1.7, and a Bragg R factor of 0.081. The crystallographic parameters for each of the constituent atoms (at various crystallographic sites) in Ho₂CoGa₈ are presented in Table II. It may be noted that there is only one site for the rare-earth atom in the unit cell, which makes the compound amenable for CEF analysis. Both the lattice parameters *a* and *c* are smaller than the corresponding In compounds.⁴ One of the possible reasons is the smaller metallic radii of Ga $(\approx 1.3 \text{ Å})$ compared to that of In $(\approx 1.6 \text{ Å})$. The unit cell volumes of the R_2 CoGa₈ compounds are plotted against their corresponding rare earths in Fig. 2. The unit cell volume and both the lattice parameters decrease as we move from Gd to Lu. This is attributed to the well known lanthanide contraction. The (c/a) ratio remains constant (≈ 2.6) for all the compounds but it is slightly less than that of the corresponding In compounds (≈ 2.63). The large (c/a) ratio indicates the significant structural anisotropy in these compounds. The crystal structure of R_2 CoGa₈ is shown in Fig. 3.

The central portion of the unit cell between the rare-earth planes (along the *c* axis) and including them is similar to the unit cell of RGa_3 phase. In fact, the lattice constant *a* of R_2CoGa_8 phase is approximately equal to that of the RGa_3 (cubic) phase⁷ and the remaining structure above and below it forms the CoGa₂ layers. The unit cell of R_2CoGa_8 may be viewed as formed by the stacking of RGa_3 units and CoGa₂ layer alternately along the *c* axis. It is imperative to mention here one similarity between RGa_3 and R_2CoGa_8 compounds;

TABLE II. Refined crystallographic parameters for Ho₂CoGa₈.

Atom	Site symmetry	x	у	Z.	U_{eq} (Å ²)	Occ.
Но	2g	0	0	0.306(4)	0.588(2)	2
Co	1a	0	0	0	1.186(4)	1
Gal	2e	0	0.5	0.5	1.771(1)	2
Ga2	2h	0.5	0.5	0.295(2)	0.40(1)	2
Ga3	4i	0	0.5	0.114(1)	0.074(4)	4



FIG. 3. (Color online) Tetragonal unit cell of R_2 CoGa₈ compounds.

viz., in both cases, the compounds form only with heavy rare earths. Gd is on the borderline of stability, which forms the R_2 CoGa₈ phase but not the RGa₃ phase.⁷ A similar comparison is also possible for indides [R_2 CoIn₈ (Ref. 8) and RIn₃ (Ref. 9)], where only Lu and La are on the borderline of stability and do not form R_2 CoIn₈ phase, whereas RIn₃ forms for the entire rare-earth series. Hence, the nonformation of RGa₃ phase with lighter rare earths is one of the possible reasons for the nonformation of the corresponding R_2 CoGa₈ compounds. Therefore, RX_3 (X=In and Ga) can plausibly be considered as one of the basic building blocks for the formation of R_2 CoX₈ (X=In and Ga) compounds.

IV. MAGNETIC PROPERTIES

A. Y₂CoGa₈ and Lu₂CoGa₈

These two compounds with the nonmagnetic Y and Lu, respectively, show diamagnetic behavior. The susceptibility of both the compounds is shown in Fig. 4. It is negative and nearly temperature independent at high temperatures and exhibits a weak upturn at low temperatures crossing into the positive region below 10 K. Assuming a magnetic moment of 1 μ_B /impurity, a good fit of the modified Curie–Weiss expression,

$$\chi = \chi_0 + \frac{C}{T - \theta_p},\tag{1}$$

to the data lead to paramagnetic impurity ion concentration of a few ppm and θ_p is nearly zero. The value of χ_0 is found to be -2.08×10^{-4} emu/mol and -3.13×10^{-4} emu/mol for Y₂CoGa₈ and Lu₂CoGa₈, respectively. These data conclu-



FIG. 4. (Color online) Temperature dependence of the magnetic susceptibility in Y_2CoGa_8 and Lu_2CoGa_8 . The solid line through the data points implies the modified Curie–Weiss fitting. The inset shows the C/T versus T^2 plot of Y_2CoGa_8 at low temperature.

sively show the nature of nonmagnetic Co atoms in this series of compounds.

The diamagnetic behavior of Y₂CoGa₈ and Lu₂CoGa₈ is in contrast to the Pauli-paramagnetic behavior shown by the nonmagnetic indide Y₂CoIn₈ and indicates a low density of electronic density of states at the Fermi level in the gallides, such that the diamagnetic contribution due to the filled electronic shells exceeds the Pauli paramagnetic contribution from the conduction electrons. Indeed, the coefficient of the electronic heat capacity (γ) , which is proportional to the density of states at the Fermi level, of Y_2CoGa_8 (2 mJ/K² mol, as shown in the inset of Fig. 4) is comparably less than that of Y_2CoIn_8 (Ref. 4) (13 mJ/K² mol). If the density of states at the Fermi level decreases on replacing In by Ga in these R_2 Co X_8 (where X=In and Ga) series of compounds, it should result in a weaker conduction electron mediated RKKY magnetic interactions between the rare-earth ions in R_2 CoGa₈ compounds. This may be one of the reasons that the Néel temperatures of R₂CoGa₈ series of compounds are lower than those of the corresponding indides R_2 CoIn₈.

B. Gd₂CoGa₈

We next describe the magnetization of Gd₂CoGa₈, as Gd is an S state ion in which the crystal electric field induced anisotropy is zero in the first order. The susceptibility of Gd₂CoGa₈ along the [100] and [001] directions in an applied magnetic field of 5 kOe is shown in Fig. 5(a). The low temperature part is shown as an inset of Fig. 5(a). The susceptibility shows a peak due to antiferromagnetic transition at $T_N=20$ K, which is followed by an upturn below ≈ 15 K. Quantitatively similar behavior is seen with the field applied in the [100] and [001] directions, respectively. The minor difference in the susceptibility along the two axes may be due to the second order anisotropy arising from the dipoledipole interaction. The linear behavior of the magnetic isotherms at 2 K (Fig. 6) for both the axes further corroborates the antiferromagnetic nature of the magnetically ordered state. In the paramagnetic state the susceptibility was fitted to the modified Curie–Weiss law, as shown in Fig. 5(b). The



FIG. 5. (Color online) (a) Magnetic susceptibility of Gd₂CoGa₈; the inset shows the magnified view of low temperature susceptibility. (b) Inverse magnetic susceptibility with a modified Curie–Weiss fit.

obtained effective magnetic moments presented in Table III are close to that of the theoretically expected one. The paramagnetic Curie temperatures θ_p are -69 and -67 K, respectively, for the [100] and [001] directions. The relatively high value along both the directions indicates strong antiferromagnetic interaction among the Gd³⁺ moments. The upturn in the susceptibility at low temperatures is often attributed to a canting of antiferromagnetically aligned moments. A similar behavior has earlier been seen in GdCo₂Si₂,¹⁰ which was later shown to be due to a noncollinear amplitude modulated structure.¹¹ So, we assume that a similar or some complicated stable magnetic structure is present in Gd₂CoGa₈.



FIG. 6. (Color online) Magnetic isotherm of Gd_2CoGa_8 at 2 K with the field along the [100] and [001] directions.

C. R_2 CoGa₈ (R=Tb, Dy, and Ho)

In these three compounds, the easy axis of magnetization lies along the [001] direction. The data clearly show the anisotropic behavior of the magnetization in both the paramagnetic and antiferromagnetically ordered states arising due to the influence of crystal electric fields (CEFs) on Hund's rule derived ground states of the free R^{3+} ions. Figure 7(a) shows the susceptibility of Tb₂CoGa₈ from 1.8 to 300 K in a magnetic field of 5 kOe along the two crystallographic directions ([100] and [001]). The data show an antiferromagnetic transition at $T_N=28$ K. It is to be mentioned here that the ordering temperature is higher compared to that of Gd₂CoGa₈, which is attributed to CEF effects, as described in Sec. V. The anisotropic behavior of the susceptibility below the Néel temperature shows the [001] direction as the easy axis of magnetization. In contrast, the susceptibility along [100] remains below that of the [001] direction in the entire temperature range followed by a knee at the ordering temperature. The Curie-Weiss fits of the inverse susceptibility in the paramagnetic state gives $\mu_{\rm eff}$ and θ_p as 9.55 $\mu_B/{\rm Tb}$ and 9.66 μ_B /Tb and -58 and -16 K for field parallel to the [100] and [001] directions, respectively. The obtained effective moment for both the axes is close to that of the theoretical

TABLE III. Comparison of Néel temperatures of R_2 CoIn₈ with R_2 CoGa₈ compounds. Paramagnetic Curie temperature (θ_p), effective magnetic moment (μ_{eff}), and χ_0 for R_2 CoGa₈ compounds. NA: data not available, PP: Pauli paramagnetic, and Dia: diamagnetic.

	R_2 CoIn ₈		R_2 CoGa ₈					
			$\mu_{ m eff} \ (\mu_B/R)$		$egin{array}{c} heta_p \ ({ m K}) \end{array}$		χ_0 (emu/mol)	
R	T_N (K)	T_N (K)	[100]	[001]	[100]	[001]	[100]	[001]
Gd	33.5	20	7.94	7.9	-69	-67	7.2×10^{-4}	3.4×10^{-4}
Tb	30	28	9.55	9.66	-58	-16	0	0
Dy	17.4	18	10.53	10.47	-45	-6	9.0×10^{-4}	1.2×10^{-3}
Но	7.6	6	10.5	10.6	-18.6	-1.5	8.0×10^{-4}	3.0×10^{-4}
Er	N.A	3	9.5	9.59	-5.2	-11.2	0	0
Tm	N.A	2	7.57	7.35	-1.7	-12.6	1.7×10^{-3}	2.5×10^{-4}
Lu	N.A	Dia						
Y	P.P	Dia						



FIG. 7. (Color online) (a) Magnetic susceptibility of Tb_2CoGa_8 and (b) inverse magnetic susceptibility; the solid lines through the data point indicate the CEF fit.

value (9.72 μ_B /Tb). The polycrystalline average of θ_p is -45.3 K, which indicates the presence of strong antiferromagnetic interactions in the compound.

The anisotropic magnetic behavior is further corroborated by the magnetic isotherms at T=2 K for field along the two principal directions, viz., [100] and [001], as shown in Fig. 8(a). The magnetization at T=2 K for $H\parallel$ [001] undergoes multiple metamagnetic transitions at 3.5, 4.8, 6.6, 9, and 10 T. The magnetic transition at 6.6 T is a predominant one, whereas the others represent minor reorientation of the moments with field. The saturation magnetization obtained at 12



FIG. 8. (Color online) (a) Magnetic isotherms of Tb_2CoGa_8 at 2 K for the field along [100] and [001]. (b) Magnetic isotherms along the [001] direction at various temperatures.



FIG. 9. (Color online) (a) Magnetic susceptibility of Dy_2CoGa_8 and (b) inverse magnetic susceptibility; the solid lines through the data point indicate the CEF fit.

T at 2 K is about $4.2\mu_B/\text{Tb}$, which is less than half of the saturation moment of Tb³⁺ ions $(9\mu_B/\text{Tb})$. Furthermore, high magnetic field is required to obtain the full saturation value of the Tb moments. As the temperature is increased, the sharpness of the metamagnetic transition decreases and it shifts toward lower fields [as shown in Fig. 8(b)] due to the extra thermal energy available for the reorientation of the moments. At 30 K, the magnetization is linear, which indicates the paramagnetic state of the compound. The magnetic isotherm at 2 K with the field along [100] [represented by the triangles in Fig. 8(a)] is a straight line with a magnetization value of $2.6\mu_B/\text{Tb}$ at 12 T, which indicates the hard axis of magnetization.

The thermal variation of the magnetic susceptibility of Dy₂CoGa₈ is similar to that of Tb₂CoGa₈. An antiferromagnetic transition occurs at $T_N = 18$ K, as shown in Fig. 9(a). In the paramagnetic state, the inverse susceptibility was fitted to the Curie–Weiss law with $\mu_{eff}=10.4\mu_B/Dy$ and $10.5\mu_B/Dy$ and $\theta_p = -45$ and -6 K along the [100] and [001] axes, respectively. The effective moments are close to the theoretical value (10.63 μ_B) and the polycrystalline average of θ_p is -32 K, indicating an antiferromagnetic interaction. The magnetic isotherms with field along the two crystallographic directions are shown in Fig. 10(a). The temperature variation of magnetic isotherms was measured only along the [001] easy axis. The magnetization along [001] at 2 K undergoes two metamagnetic transitions at $H_{c1}=3.4$ T and H_{c2} =8.6 T. After the second metamagnetic transition, the magnetization reaches about $7.1\mu_B/\text{Dy}$ at 12 T. This value is less than the ideal saturation value of $10\mu_B/\text{Dy}$ for Dy^{3+} ion. A hysteresis was observed [not shown in Fig. 10(a)] between the two metamagnetic transitions, which may be due to the anisotropic behavior of the reoriented moments. The temperature variation of the magnetic isotherm is similar to that of Tb₂CoGa₈, namely, the decrease in the sharpness and shift toward lower magnetic fields of the metamagnetic transition



FIG. 10. (Color online) Magnetic isotherms of Tb_2CoGa_8 at 2 K for the field along [100] and at various temperatures for [001] direction and (b) the magnetic phase diagram of Tb_2CoGa_8 . The solid line in (b) is a guide to the eye.

with temperature. In Tb₂CoGa₈, the magnetization at 12 T was found to initially increase with temperature and then decreases near the Néel temperature of the compound, whereas in Dy₂CoGa₈, it continuously decreases with temperature. This effect is attributed to the strong antiferromagnetic coupling of the Tb³⁺ moments compared to that of Dy³⁺ moments. This is also evident from the polycrystalline average θ_p of both the compounds. Because of the strong coupling, the thermal energy acts as a helping hand for the reorientation of the moments, whereas in Dy₂CoGa₈, the field energy is sufficient to break the antiferromagnetic coupling. From the differential plots of the isothermal magnetization curves (not shown here), we have constructed the magnetic phase diagram, as depicted in Fig. 10(b). H_{c1} at first increases with the increase in temperature and then decreases above 10 K and finally vanishes for temperature above 15 K, while the H_{c2} decreases continuously with the increase in the temperature. At low temperatures and for fields less than 3.4 T, the systems is in a purely antiferromagnetic state, as indicated by (AF-I) in Fig. 10(b), and then undergoes a complex magnetic structure (AF-II) for fields between H_{c1} and H_{c2} and finally enters into the field induced ferromagnetic state.

The magnetic susceptibility of Ho₂CoGa₈ in an applied magnetic field of 5 kOe along the [100] and [001] axes is shown in Fig. 11(a). The compound orders antiferromagnetically at T_N =6 K. Overall, the susceptibility along the [001] and [100] directions shows a similar behavior, unlike that in Tb₂CoGa₈ and Dy₂CoGa₈ analogs. The data indicate a less anisotropic behavior of Ho₂CoGa₈ compared to the former two compounds. The Curie–Weiss fit of the inverse susceptibility in the paramagnetic state of the compound gives μ_{eff} =10.48 μ_B /Ho and 10.6 μ_B /Ho and θ_p =-18.6 and



FIG. 11. (Color online) (a) Magnetic susceptibility of Ho_2CoGa_8 and (b) inverse magnetic susceptibility; the solid lines through the data point indicate the CEF fit.

-1.5 K along the [100] and [001] directions, respectively. The effective moments are close to the theoretically expected value (10.6 μ_B /Ho) and the polycrystalline average of θ_P is -12.9 K, which is in accordance with the antiferromagnetic transition in the compound. A lower absolute value of θ_p compared to those of compounds with R=Gd, Tb and Dy, indicates weaker interaction among the Ho³⁺ moments. This is evident in the magnetic isotherm of the compound along the easy axis of magnetization (as shown in Fig. 12). The metamagnetic transition occurs at lower fields compared to the former compounds. The magnetic isotherm at 2 K (Fig. 12) along the [001] axis undergoes two metamagnetic transitions at $H_{c1}=1.55$ T and at $H_{c2}=4.0$ T. Both of them induce large changes in the magnetization. The magnetization at 12 T and 2 K is $8.2\mu_B/$ Ho. This is close to the saturation moment of $10\mu_B$ for Ho³⁺ moments. Thus, the second metamagnetic transition drives the compound to a field induced ferromagnetic state. With the increase in the temperature, the metamagnetic transitions broaden and shift toward lower fields and their sharpness decreases. Above the ordering tem-



FIG. 12. (Color online) Magnetic isotherms of Ho_2CoGa_8 at 2 K for the field along [100] and at various temperatures for the [001] direction.



FIG. 13. (Color online) (a) Magnetic isotherm of Ho_2CoGa_8 at 2 K for the field along [100] and [001] directions and (b) the magnetic phase diagram of Ho_2CoGa_8 . The solid line in (b) is a guide to the eye.

perature of the compound (6 K), the magnetic isotherms at 10 and 15 K tend toward saturation at high fields and the moment at 10 K and 12 T is above $8.2\mu_B/\text{Ho}$. At 25 K, the magnetic isotherm is a straight line as expected for a paramagnetic state. The magnetization with field along the hard [100] direction is not a straight line as observed for other compounds, but the moment tends toward saturation with a value of $\approx 7\mu_B$ /Ho at 12 T. At high fields (above 8 T), the behavior of the compound is similar in both the directions (except that the moment is little less along the hard direction). This is because the field energy is sufficient to overcome the anisotropic energy barrier existing within the compound. This also supports the initial explanation of less anisotropy of Ho₂CoGa₈ compared to that of Tb₂CoGa₈ and Dy₂CoGa₈. From the differential plots of the isothermal magnetization along [001] direction, we have constructed the magnetic phase diagram, as shown in Fig. 13(b). It is obvious from Fig. 13(b) that both the metamagnetic transitions shift toward lower fields with the increase in temperature and finally merge with each other at the ordering temperature.

D. R₂CoGa₈ (R=Er and Tm)

Although these compounds also antiferromagnetically order, the easy axis of magnetization is now along the [100] direction. Er₂CoGa₈ and Tm₂CoGa₈ antiferromagnetically order at 2 and 3 K, respectively. The obtained value of μ_{eff} and θ_p are presented in Table III. The effective moment for both the compounds along both the crystallographic directions is close to their theoretically expected value (9.59 μ_B /Er and 7.57 μ_B /Tm). The polycrystalline average of the paramagnetic Curie temperature for Er₂CoGa₈ and



FIG. 14. (Color online) (a) Magnetic susceptibility of Er_2CoGa_8 for the temperature range of 1.8 to 25 K. (b) Inverse magnetic susceptibility; the solid lines through the data point indicate the CEF fit.

 Tm_2CoGa_8 are -7.13 and -4.2 K, respectively. Both of them are negative and are lower compared to the other R_2 CoGa₈ compounds, indicating a gradual weakening of the antiferromagnetic interactions among the rare-earth moments in this series. The susceptibility of Er₂CoGa₈ along both directions is shown in Fig. 14(a). The susceptibility along the [100] direction shows a peak at the antiferromagnetic transition temperature, whereas that along the [001] direction does not show any ordering down to 1.8 K. The inverse susceptibility is plotted in Fig. 14(b). Both the plots are close to each other indicating a weak anisotropy of the compound. In addition, there is a crossover of the susceptibility at about 164 K, indicating a change in easy axis of magnetization with temperature. Similar behavior has been observed in Er₂PdSi₃.¹² Such a behavior may possibly arise due to the magnetic behavior of the compound lying on the border of the anisotropic crossover along the crystallographic axis. This is also supported by the crystal field calculation on the compound discussed in Sec. V. The magnetic isotherm along both the direction is shown in Fig. 15. The magnetization along the [100] direction undergoes a metamagnetic transition at 0.25 T and tends to saturate at higher fields. The moment at 1.8 K and 12 T is $9\mu_B/\text{Er}$. With the increase in the temperature (at 4 and 10 K, not shown in Fig. 15), the metamagnetic transition vanishes but the behavior of the magnetization remains the same with the moment little less than that at 2 K. The magnetization behavior along the [001] direction is almost similar to that of the [100] direction. For field parallel to [100], the magnetization reaches a moment of $5.6\mu_B/\text{Er}$ at 1.8 K and 12 T. In the case of Tm_2CoGa_8 , the susceptibility along both crystallographic directions show antiferromagnetic behavior at 50 Oe [inset of Fig. 16(a)]. When the field



FIG. 15. (Color online) Magnetic isotherm of Er_2CoGa_8 at 2 K for the field along the [100] and [001] directions.

is increased to 5 kOe, antiferromagnetic transition along both axes vanishes. This indicates a weak interaction among the moments such that the antiferromagnetic peak shifts with small applied fields and vanishes even at 5 kOe. The magnetic isotherm at 1.8 K for both crystallographic axes is shown in Fig. 17. The behavior of magnetization along both axes is qualitatively similar. However, the magnetization along the [100] direction is higher than that of the [001] direction. At approximately 11.2 T, there is a cross over with the magnetization along the [100] axis, exceeding the magnetization along the [100] axis. High field magnetization measurements are necessary to probe this behavior.

V. DISCUSSION

An interesting magnetic behavior is exhibited by the R_2 CoGa₈ series of compounds. The nonmagnetic compounds Y_2 CoGa₈ and Lu₂CoGa₈ show diamagnetic behavior. Compounds with magnetic rare earths (R=Gd, Tb, Dy, Ho, Er,



FIG. 16. (Color online) (a) Magnetic susceptibility of Tm_2CoGa_8 ; the inset shows the magnified view of low temperature susceptibility. (b) Inverse magnetic susceptibility; the solid lines through the data point indicate the CEF fit.



FIG. 17. (Color online) Magnetic isotherm of Tm_2CoGa_8 at 2 K for the field along the [100] and [001] directions.

and Tm) antiferromagnetically order at low temperatures. The Néel temperatures are listed in Table III. For comparison, the Néel temperatures of the corresponding indides are also listed. The transition temperature is less compared to that of the corresponding polycrystalline indium analogs R_2 CoIn₈. According to the de Gennes scaling, in the mean field approximation, the magnetic ordering temperatures T_M of the isostructural members of a rare-earth series of compounds are proportional to $(g_J-1)^2 J(J+1)$, where g_J is the Landé g factor and J is the total angular momentum. The Néel temperature of the R_2 CoGa₈ series of compounds is plotted in Fig. 18 along with their de Gennes expected values, which is normalized to T_N of Gd₂CoGa₈. A fairly large deviation of T_N of the Tb and Dy compounds from the de Gennes expected scaled value is noticeable. The ordering temperature of Tb₂CoGa₈ is even higher than that of the corresponding Gd compound. A similar behavior was also observed for RRh_4B_4 (Ref. 13) compounds and Noakes et al.¹⁴ showed it to be due to the CEF effects. The magnetic susceptibility data presented above therefore provide a good opportunity to attempt a crystal electric field analysis on this series of compounds. From the estimated crystal field parameters, we found that the enhancement in the ordering temperature of Tb and Dy can be attributed to CEF effects, as described later in this section.

The rare-earth atom in R_2 CoGa₈ occupies the 2g Wyckoff's position with a tetragonal C_{4v} point symmetry. The CEF Hamiltonian for a tetragonal symmetry is given by



FIG. 18. (Color online) Néel temperature of the R_2 CoGa₈ compounds compared to that expected from de Gennes scaling. The lines joining the data points are guides to the eye.

TABLE IV. CEF parameters for R₂CoGa₈ compounds obtained from the inverse susceptibility fit.

R	$\begin{array}{c} B_2^0 \\ (\mathrm{K}) \end{array}$	B_4^0 (K)	B_4^4 (K)	$\begin{array}{c} B_6^0 \\ (\mathrm{K}) \end{array}$	B_6^4 (K)	$\lambda^{[100]}$ (mol/emu)	$\lambda^{[001]}$ (mol/emu)	$ \mathcal{J}_{\text{ex}}^{[100]}/k_B $ (K)	$ \begin{array}{c} \mathcal{J}_{\mathrm{ex}}^{[001]}/k_B \\ (\mathrm{K}) \end{array} $
Tb	-1.61	0.0049	-0.0515	-7.0×10^{-5}	1.63×10^{-3}	-2.95	-4.7	-2.24	-4.94
Dy	-0.7	0.005	0.001	9.0×10^{-8}	1.0×10^{-4}	-2.5	-2.0	-1.28	-1.94
Но	-0.22	-1.45×10^{-3}	-0.0314	-2.0×10^{-5}	-2.0×10^{-5}	-1.2	-1.2	-0.51	-0.59
Er	0.089	1.3×10^{-4}	0	4.3×10^{-6}	2.5×10^{-4}	-0.782	-0.274	-0.35	-0.32
Tm	0.35	1.72×10^{-6}	0.0248	-8.46×10^{-6}	9.1×10^{-4}	0.723	0	-0.53	-0.075

$$\mathcal{H}_{\rm CEF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4, \qquad (2)$$

where B_{ℓ}^{m} and O_{ℓ}^{m} are the CEF parameters and the Stevens operators, respectively.^{15,16} The CEF susceptibility is defined as

$$\chi_{\text{CEF}i} = N(g_J \mu_B)^2 \frac{1}{Z} \left(\sum_{m \neq n} |\langle m | J_i | n \rangle|^2 \frac{1 - e^{-\beta \Delta_{m,n}}}{\Delta_{m,n}} e^{-\beta E_n} + \sum_n |\langle n | J_i | n \rangle|^2 \beta e^{-\beta E_n} \right),$$
(3)

where g_J is the Landé g factor, and E_n and $|n\rangle$ are the *n*th eigenvalue and eigenfunction, respectively. J_i (where i=x, y, and z) is a component of the angular momentum, and $\Delta_{m,n} = E_n - E_m$, $Z = \sum_n e^{-\beta E_n}$, and $\beta = 1/k_B T$. The magnetic susceptibility including the molecular field contribution λ_i is given by

$$\chi_i^{-1} = \chi_{\text{CEF}i}^{-1} - \lambda_i. \tag{4}$$

The inverse susceptibility of the R_2 CoGa₈ (R=Tb, Dy, Ho, Er, and Tm), as shown in Figs. 7(b), 9(b), 11(b), 14(b), and 16(b), respectively, was fitted to the above discussed CEF model Eqs. (2)–(4). The values of the CEF parameters thus obtained are presented in Table IV and the corresponding energy levels are shown in Fig. 19. The dominant crystal field parameter B_2^0 is negative for Tb, Dy, and Ho compounds. This is consistent with the uniaxial ([001] as an easy axis) magnetic anisotropy present in these compounds. The sign of the B_2^0 changes for Er and Tm compounds, which is consistent with the change in the easy axis of magnetization. The change in the direction of the easy axis of magnetization follows the general trend observed in a number of tetragonal rare-earth series of compounds RRh_4B_4 ,¹³ $RAgSb_2$,¹⁷ and



FIG. 19. (Color online) CEF energy level splitting of the ground state of the R^{3+} ions in R_2 CoGa₈ compounds.

 $RRhIn_5$.¹⁸ For Er₂CoGa₈, the estimated B_2^0 is 0.089 K, which is close to zero, indicating that the compound is on the border line of the magnetic anisotropy crossover. The current set of CEF parameters could even explain the crossover in the magnetic susceptibility of Er₂CoGa₈. According to mean field theory, the CEF parameter B_2^0 can be related to the exchange constant and paramagnetic Curie temperature by the relation¹⁹

$$\mathcal{A}_{p}^{[001]} = \frac{J(J+1)}{3k_{B}} \mathcal{J}_{ex}^{[001]} - \frac{(2J-1)(2J+3)}{5k_{B}} B_{2}^{0}, \qquad (5)$$

$$\theta_p^{[100]} = \frac{J(J+1)}{3k_B} \mathcal{J}_{\text{ex}}^{[100]} + \frac{(2J-1)(2J+3)}{10k_B} B_2^0.$$
(6)

The obtained value for \mathcal{J}_{ex} along both the crystallographic directions is presented in Table IV. The negative value along both the principal directions implies that the anitferromagnetic interaction is dominant in this series of compounds. In the case of R_2 CoGa₈ (R=Tb, Dy, and Ho), the exchange constant \mathcal{J}_{ex} has a higher value along [001] compared to that of the [100] direction. This implies that the antiferromagnetic exchange interaction is stronger along the [001] direction, thus supporting our experimental observation of magnetic easy axis for these compounds. For R_2 CoGa₈ (R=Er and Tm), \mathcal{J}_{ex} is dominant along the [100] direction, which is again consistent with our magnetic susceptibility data.

The magnetic transition temperature (T_M) of a compound in the presence of crystalline electric field is given by Noakes *et al.*¹⁴ as

$$T_M = 2\mathcal{J}_{\text{ex}}(g_J - 1)^2 \langle J_z^2(T_M) \rangle_{\text{CEF}},\tag{7}$$

where $\langle J_z^2(T_M) \rangle_{\text{CEF}}$ is the expectation value of J_z^2 at T_M under the influence of crystalline electric field alone. \mathcal{J}_{ex} is the exchange constant for the RKKY exchange interaction between the rare-earth atoms. Now, for the compounds with tetragonal structure, the dominating crystal field term is B_2^0 , so neglecting the higher order term and when the ordering is along the [001] direction, the above equation can be rewritten as¹⁴

$$T_M = 2\mathcal{J}_{\text{ex}}(g_J - 1)^2 \sum_{J_z} \frac{J_z^2 \exp\left(-3J_z^2 B_2^0/T_M\right)}{\exp\left(-3J_z^2 B_2^0/T_M\right)}.$$
 (8)

The transition temperature T_M was calculated by using the values of the exchange constant \mathcal{J}_{ex} obtained from Eq. (5) for the easy axis of magnetization and with the correspond-

ing B_2^0 crystal field parameter. The magnetic transition temperature for Tb₂CoGa₈ and Dy₂CoGa₈ thus estimated was found to be \approx 82 and (\approx 22), respectively. This shows the enhancement in the transition temperature in presence of CEF compared to that expected from de Gennes scaling. Although the estimated T_N in Tb₂CoGa₈ is unexpectedly high, the preceding analysis shows that the enhancement of T_N of Tb₂CoGa₈ can be due to CEF effects.

VI. CONCLUSION

To conclude, we have successfully grown the single crystals of R_2 CoGa₈ (R=Gd, Tb, Dy, Ho, Er, Tm, Lu, and Y) by

using Ga as flux. This series of compounds forms only with the higher rare earths. The phase purity of the crystals was confirmed by means of powder x-ray diffraction. Y_2CoGa_8 and Lu₂CoGa₈ show diamagnetic behavior, indicating a low density of states at the Fermi level and a filled 3*d* of Co band. Compounds with magnetic rare earths antiferromagnetically order at low temperatures. The Néel temperature of Tb₂CoGa₈ and Dy₂CoGa₈ appreciably deviates from expected value of de Gennes scaling. The reason is attributed to crystal field effects. The easy axis of magnetization for R_2CoGa_8 (*R*=Tb, Dy, and Ho) is along the crystallographic [001] direction. It changes to the (100) plane for Er₂CoGa₈ and Tm₂CoGa₈.

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