JOURNAL OF SOLID STATE CHEMISTRY 13, 315–318 (1975)

Magnetic Properties of $Ln_{2-x}Ln_xCo_{17}$ Compounds* ($Ln = Gd$, Dy, Ho, or Er, $Ln' = Th$ or Ce)

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Received June 7, 1974

Magnetic and structural characteristics of the ternary systems $Ln_{2-x}Th_xCo_{17}$ ($Ln = Gd$, Dy, Ho, and Er) and $Ln_{2-x}Ce_xCo_{17}$ ($Ln = Gd$, Dy, and Ho) are presented. Incorporation of Th in the lattice stabilizes the Th_2Zn_{17} structure, whereas incorporation of Ce does not; if the binary system has the Th_2Ni_{17} structure the incorporation of Ce leaves the structure unchanged. The antiferromagnetic Ln–Co coupling observed in the Ln_2Co_{17} systems persists in the ternary alloys. The moment of the cobalt sublattice is decreased when more than half of the Ln is replaced by Th, suggesting that the extra electron contributed by Th enters the Co *d*-band or *d*-shell. The direction of easy magnetization is in the basal plane for all composition in the Gd, Dy, and Ho systems. In $Er_{2-x}Th_xCo_{17}$ the easy direction is along the *c*-axis for $x = 0$ and 0.2, but is in the basal plane for higher thorium contents.

I. Introduction

As noted in the preceding paper (*1*) rare earth compounds with transition metals have received very considerable attention in recent years because of their usefulness for permanent magnet application (*2*, *3*). Research has been primarily concentrated on the $LnCo_5$ compounds ($Ln = La$–Sm) which possess high magnetocrystalline anisotropies, large magnetic moments and high Curie temperatures. Although the Ln_2Co_{17} compounds have much higher moments and Curie temperatures compared to the $LnCo_5$ compounds, their unfavorable anisotropies have made them useless for practical applications. In this laboratory it has been found that it is possible to change the easy direction of magnetization in the R_2Co_{17} compounds from the basal plane to the *c*-axis by substituting for cobalt either iron or manganese (*4*). This opened up consideration of a new series of compounds of potential use for permanent magnet application.

The magnetic moments of the rare earth and cobalt in the light Ln_2Co_{17} compounds ($Ln = Ce$, Pr, Nd) are coupled parallel to each other, whereas in the Ln_2Co_{17} compounds with $Ln = Sm$–Yb the moments are coupled antiparallel (*3*). If the moments in the heavy rare earth–cobalt compounds were aligned parallel, these compounds would be of a great practical value. The present work represents an attempt to change the magnetic coupling by increasing the electron concentration; this is expected to produce a reversal of coupling of the Ln and Co sublattices if they interact via the RKKY mechanism (*5*). In the present study Ln^{3+} in the Ln_2Co_{17} compounds is replaced by Th, which is quadripositive, and Ce, which behaves as if it has a valence between 3+ and 4+.

II. Experimental Details

The rare earths used had a reported purity of 99.9% and were obtained from Research Chemicals. The cobalt was spectroscopic standard grade, obtained from Johnson–Matthey. It had a stated purity of 99.999%. The thorium used had a purity of 99.9%; it was melted before use to rid it of some volatile impurities.

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* This work was assisted by a contract with the U.S. Atomic Energy Commission.

TABLE I

MAGNETIC AND STRUCTURAL PROPERTIES OF $Ln_{2-x}Th_xCo_{17}$ COMPOUNDS

	$\mu_{sat}(\mu_B/f.u.)$			
x	Ln = Gd	Dy	Ho	Er
0	13.70	8.30[b]	8.60[a]	10.50[a,c]
0.2	14.05	14.77[b]	11.95[a]	12.62[a,c]
0.6	16.97	17.42	14.41	15.02[a]
0.8	18.47	—	—	—
1.0	19.16	19.61	17.21	17.91
1.4	21.18	21.33	19.36	—
1.6	—	—	—	22.17
1.8	—	—	22.86	—
2.0	24.05	24.05	24.05	24.05

[a] Alloy has the Th_2Ni_{17} structure.

[b] Alloy consists of two phases, the Th_2Ni_{17} and Th_2Zn_{17} structures.

[c] Alloy has the easy axis of magnetization along the c-axis.

The rest of the alloys exist in the Th_2Zn_{17} structure and have their easy axes of magnetization in the basal plane.

TABLE II

MAGNETIC AND STRUCTURAL PROPERTIES OF $Ln_{2-x}Ce_xCo_{17}$ COMPOUNDS

	$\mu_{sat}(\mu_B/f.u.)$		
x	Ln = Gd	Dy	Ho
0	13.70	8.3[b]	8.60[a]
0.2	15.30	10.3[a]	—
0.4	—	12.3[a]	12.20[a]
0.6	17.10	—	—
0.8	—	—	15.00[a]
1.0	19.30	—	16.40[a]
1.2	—	18.0[a]	—
1.6	22.80	—	22.20[a]
1.8	24.00	23.3[a]	23.70[a]
2.0	25.70	25.70	25.70[a]

[a] Alloy has the Th_2Ni_{17} structure.

[b] Alloy consists of two phases, the Th_2Ni_{17} and Th_2Zn_{17} structures.

The unmarked alloys have the Th_2Zn_{17} structure. All alloys have their easy axes of magnetization in the basal plane.

The elements in their proper proportions were induction melted in a water cooled copper boat under a flowing atmosphere of purified argon gas. The cast ingots were subsequently annealed at 1000°C for a week in vacuum. The alloys were analyzed by powder X-ray diffraction using a G.E. XRD-5 diffractometer equipped with molybdenum and cobalt radiation. All the lines in the X-ray diffraction data could be indexed according to either a Th_2Ni_{17} or Th_2Zn_{17} type of structure (*6*). (See Tables I and II.)

Magnetic data were obtained using a Faraday balance, the details of which have been described previously (*7*). Loosely packed powders were used for the measurements. All the compounds investigated saturated easily at 4.2 K at an applied field of 20 kOe, and hence no extrapolation technique was applied to obtain the saturation magnetization.

The determination of easy axis of magnetization was accomplished by examining the X-ray diffraction peaks of powders oriented with an applied field of 6 kOe.

III. Results and Discussion

The magnetic data are shown in Tables I and II. The saturation moments obtained in this study for the binary alloys agree very well with those reported by other investigators (*8–10*). Structures of the alloys are also listed in Tables I and II. Ln_2Co_{17} compounds crystallize in both the rhombohedral Th_2Zn_{17} and hexagonal Th_2Ni_{17} structures (*11*). Both these structures can be regarded as being derived from the $LnCo_5$ structure ($CaCu_5$-type). Pairs of Co atoms replace Ln in an ordered fashion to generate the Th_2Ni_{17} and Th_2Zn_{17} structures, which are closely related, differing only in stacking sequence (*12*).

In the present investigation it is observed that replacement of Dy, Ho, or Er by thorium stabilized the Th_2Zn_{17} structure, whereas cerium substitution tends to leave the structure unaltered. The differing behavior of Th and Ce in these ternaries indicates that Ce has an effective valence less than 4.

Thorium substituted compounds for Ln = Dy and Ho show an initial large increase in the total moment and as x is further increased a

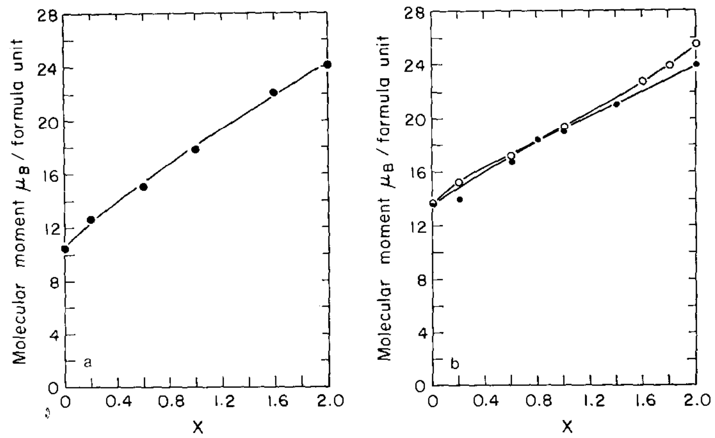

FIG. 1. Variation of magnetic moment as a function of x for the Gd and Er ternaries. a: $Er_{2-x}Th_xCo_{17}$. b: ●$Gd_{2-x}Th_xCo_{17}$; ○$Gd_{2-x}Ce_xCo_{17}$.

linear increase in the moment is observed; for the Gd and Er systems the moment rises almost linearly with increasing Th content. The increase in the moment observed in all these ternaries as x is increased is due to the replacement of magnetic rare earth, which is coupled antiparallel to cobalt, by nonmagnetic thorium and less strongly magnetic cerium. Cerium in these compounds behaves, as noted above, as if it has a valence between 3 and 4. If it were tetravalent, the moment of Th_2Co_{17} and Ce_2Co_{17} would be the same.

The moments listed in Tables I and II make it clear that the antiferromagnetic Ln–Co coupling is not altered by including Th or Ce in the Ln sub-lattice. For example, in $Ho_{1.4}Th_{0.6}Co_{17}$ the expected moment for ferromagnetic Ho–Co coupling is 41.7 μ_B/f.u. (formula unit), whereas experiment shows 11.95 μ_B/f.u. (The expected moment is computed using 27.7 μ_B as the Co sublattice contribution—deduced from the moment observed for Gd_2Co_{17}—and 10 μ_B as the atomic moment of Ho.)

Assuming antiferromagnetic coupling and the moment for the lanthanide to be that of the free ion, the cobalt moment can be computed from the total observed moment. In the case

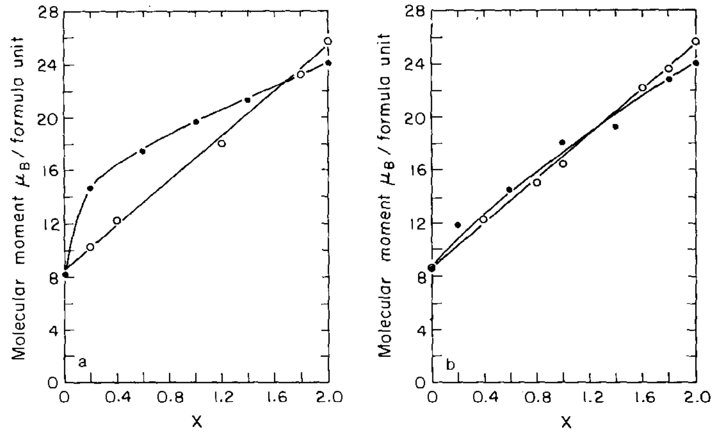

FIG. 2. Variation of magnetic moment as a function of x for the Dy and Ho ternaries. a: ●$Dy_{2-x}Th_xCo_{17}$; ○$Dy_{2-x}Ce_xCo_{17}$. b: ●$Ho_{2-x}Th_xCo_{17}$; ○$Ho_{2-x}Ce_xCo_{17}$.

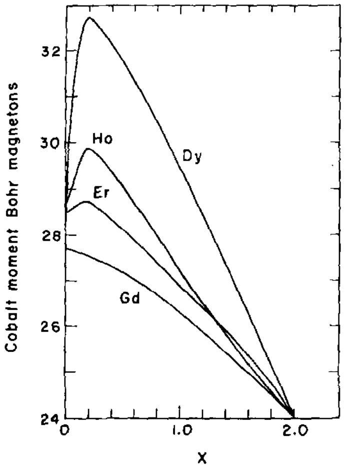

FIG. 3. Variation of cobalt sublattice moment in the $Ln_{2-x}Th_xCo_{17}$ systems.

of Ho_2Co_{17} neutron diffraction data have shown (*13*) the moment of holmium to be 10 μ_B, and hence the use of free ion values for the rare earth magnetic moment appears to be justified. Figure 3 shows the cobalt moment as a function of x. It is seen that the cobalt moment increases initially and then decreases. This increase is pronounced in the case of dysprosium and holmium. In the $LnCo_5$ and Ln_2Co_{17} compounds the moment of cobalt reaches a maximum at dysprosium and terbium, respectively. In the case of $LnCo_3$ compounds (*14*) the moment of cobalt reaches almost 2 μ_B at terbium, holmium, and erbium. The increase of cobalt moment with varying Ln has been attributed to the polarization of the 3*d* band by the spin of the rare earth (*15*). Substitution of thorium for the rare earth tends to increase the electron concentration. As the electron concentration is increased, this polarization effect should increase and produce an increase in the cobalt moment. At the same time the extra electrons are filling the 3*d* band and causing a decrease in the moment. For small values of x we see an increase in the moment of cobalt, but as x is further increased the moment decreases suggesting that the polarization effect is small compared to band filling.

In the case of cerium substituted compounds the cobalt moment is difficult to compute because of the uncertain moment on the cerium.

The easy direction of magnetization in all the Gd, Dy, and Ho compounds remains unchanged by thorium and cerium substitution; it remains in the basal plane. In the case of $Er_{2-x}Th_xCo_{17}$ compounds the *c*-axis remains as the easy direction of magnetization for $x = 0$ and 0.2 but changes over to the basal plane beyond $x = 0.2$.

The failure to achieve ferromagnetic Ln–Co coupling when the Th and Ce ternaries are formed is ascribed to electron absorption into the Co *d*-band or shell referred to above. The absorption probably takes place at a rate to maintain a fixed electron concentration. The Ln_2Co_{17} systems thus behave in a fashion similar to the $LnCo_5$ and $LnFe_2$ based ternaries studied earlier.

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