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## The structure and uniaxial magnetocrystalline anisotropy of novel intermetallic compounds $\text{La}_2\text{Co}_{17-x}\text{V}_x$

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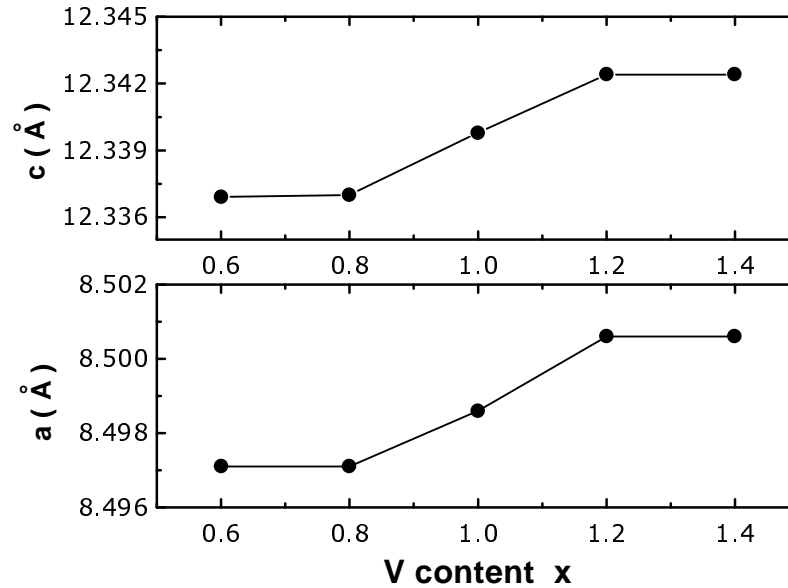
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**Abstract.** The crystal structure and magnetic properties of new intermetallic compounds  $\text{La}_2\text{Co}_{17-x}\text{V}_x$  ( $0.8 \leq x \leq 1.2$ ) have been investigated by x-ray powder diffraction and magnetic measurement. The lattice parameters of  $\text{La}_2\text{Co}_{17-x}\text{V}_x$  with the rhombohedral  $\text{Th}_2\text{Zn}_{17}$ -type structure are  $a = 8.4971$ – $8.5006$  Å,  $c = 12.3370$ – $12.3424$  Å. V atoms show a strong preference for occupying 6c crystallographic positions. The  $\text{La}_2\text{Co}_{17-x}\text{V}_x$  compounds are ferromagnetic. The Curie temperature decreases from 926 to 827 K and the saturation magnetic moment decreases from 22.5 to 19.6  $\mu_B$  fu<sup>-1</sup> with  $x = 0.8$ – $1.2$ . The  $\text{La}_2\text{Co}_{16}\text{V}$  compound exhibits favourable uniaxial anisotropy and the easy magnetization direction is parallel to the  $c$  axis. The anisotropy field is 19 kOe at 1.5 K for the  $\text{La}_2\text{Co}_{16}\text{V}$  compound. The reasons that  $\text{La}_2\text{Co}_{17}$  does not exist and  $\text{La}_2\text{Co}_{16}\text{V}$  has uniaxial anisotropy are discussed.

The high saturation magnetization and Curie temperature of  $\text{R}_2\text{Co}_{17}$  ( $R =$  rare earth elements) compounds make these materials favourable potential candidates for permanent magnet applications. Unfortunately the cobalt sublattice anisotropy in such compounds proved to be easy plane anisotropy [1]. The presence of ‘dumb-bell’ pairs of Co atoms in such compounds has an unfavourable influence on the magnetocrystalline anisotropy [2]. The overall anisotropy of  $\text{R}_2\text{Co}_{17}$  compounds is the result of competition between the anisotropy of the R sublattice and Co sublattice. Consequently, the  $\text{R}_2\text{Co}_{17}$  compounds are either weak uniaxial (e.g.  $\text{Sm}_2\text{Co}_{17}$ ) or planar (e.g.  $\text{Pr}_2\text{Co}_{17}$ ,  $\text{Nd}_2\text{Co}_{17}$ ). Afterwards, it was found that in the  $\text{R}_2\text{Co}_{17}$  compounds the anisotropy can be increased or the planar can be converted to the uniaxial by replacing Co by an appropriate amount of other 3d or 4d transition metals [3, 5]. In our work we guessed that  $\text{La}_2\text{Co}_{17}$  perhaps had uniaxial anisotropy because La with a larger atomic radius could increase the Co–Co distance in dumb-bell sites. However,  $\text{La}_2\text{Co}_{17}$  does not exist. In this paper, new compounds  $\text{La}_2\text{Co}_{17-x}\text{V}_x$  with favourable uniaxial anisotropy are synthesized by substituting a small amount of V for part of the Co, and here we report the crystal structure and magnetic properties of  $\text{La}_2\text{Co}_{17-x}\text{V}_x$  compounds. The reasons that  $\text{La}_2\text{Co}_{17}$  does not exist and  $\text{La}_2\text{Co}_{16}\text{V}$  has uniaxial anisotropy are discussed.

$\text{La}_2\text{Co}_{17-x}\text{V}_x$  ( $x = 0.5, 0.6, 0.8, 1.0, 1.2, 1.4, 1.5$ ) compounds were prepared by argon arc melting of the appropriate amounts of the starting materials. The purity of the starting materials was better than 99.9%. To ensure the homogeneity of the samples the ingots were



**Figure 1.** Dependence of the lattice parameters of  $\text{La}_2\text{Co}_{17-x}\text{V}_x$  on the V content  $x$ .

**Table 1.** The lattice parameters and magnetic data of  $\text{La}_2\text{Co}_{17-x}\text{V}_x$  compounds.  $T_C$  is the Curie temperature (in K),  $\mu_s$  the saturation moment (in  $\mu_B \text{ fu}^{-1}$ ),  $\mu_{Co}$  the magnetic moment per Co atom (in  $\mu_B/\text{Co}$ ).

| $x$ | $a$ (Å) | $c$ (Å) | $T_C$ | $\mu_s$ | $\mu_{Co}$ |
|-----|---------|---------|-------|---------|------------|
| 0.8 | 8.4971  | 12.3370 | 926   | 22.5    | 1.39       |
| 1.0 | 8.4986  | 12.3398 | 880   | 21.6    | 1.35       |
| 1.2 | 8.5006  | 12.3424 | 827   | 19.6    | 1.24       |

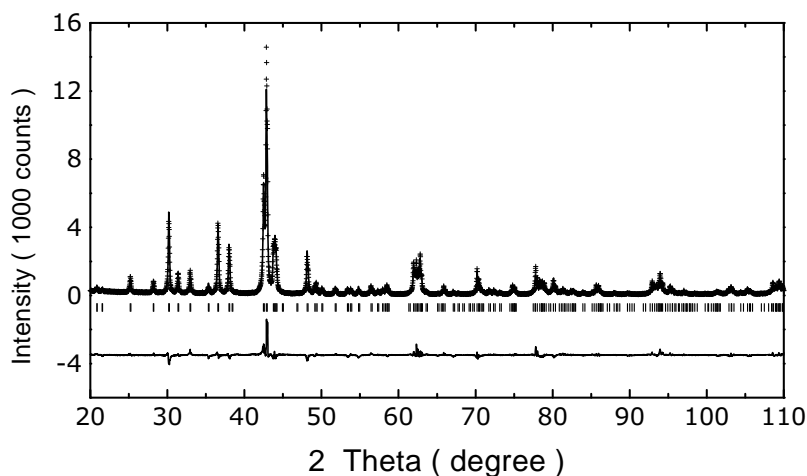
**Table 2.** The values of  $R$  factor from Rietveld refinement for the V occupancy in different crystallographic positions.

|              | 6c   | 9d    | 18h   | 18f   |
|--------------|------|-------|-------|-------|
| $R_p$ (%)    | 10.1 | 10.43 | 10.43 | 10.46 |
| $R_{wp}$ (%) | 13.2 | 13.61 | 13.61 | 13.62 |

turned upside and down and melted several times. The weight loss of the samples during melting was less than 1%. After arc melting, the samples were annealed in vacuum at 1273 K for two weeks. The phase identification of the samples was carried out by x-ray powder diffraction, using a four-layer monochromatic focusing Guinier de Wolff camera and Co  $K\alpha$  radiation. The x-ray diffraction (XRD) data used to determine crystal structure parameters were collected by a Rigaku Rint-2400 diffractometer with Cu  $K\alpha$  radiation and graphite monochromator, operating in step-scan mode with a scanning step of  $2\theta = 0.02^\circ$  and a sampling time of 2 s. The magnetic properties of samples were determined by a magnetic balance and a vibrating and extraction sample magnetometer.

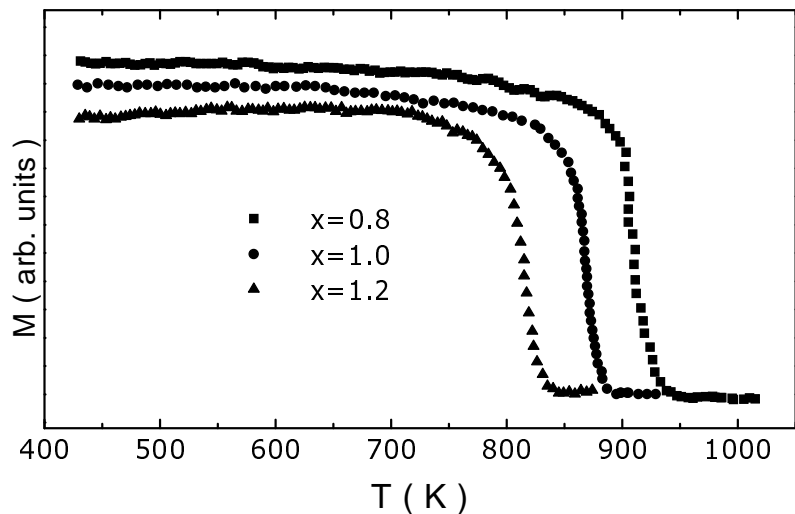
**Table 3.** Rietveld refinement results for the atomic positions in a unit cell of the  $\text{La}_2\text{Co}_{16}\text{V}$  compound.

| Atom     | Position | $x/a$     | $y/b$ | $z/c$     |
|----------|----------|-----------|-------|-----------|
| 6La      | 6c       | 0         | 0     | 0.3469(1) |
| 9Co      | 9d       | 0.5       | 0     | 0.5       |
| 18Co     | 18h      | 0.5       | 0     | 0.1553(2) |
| 18Co     | 18f      | 0.2888(2) | 0     | 0         |
| 3Co + 3V | 6c       | 0         | 0     | 0.0925(3) |

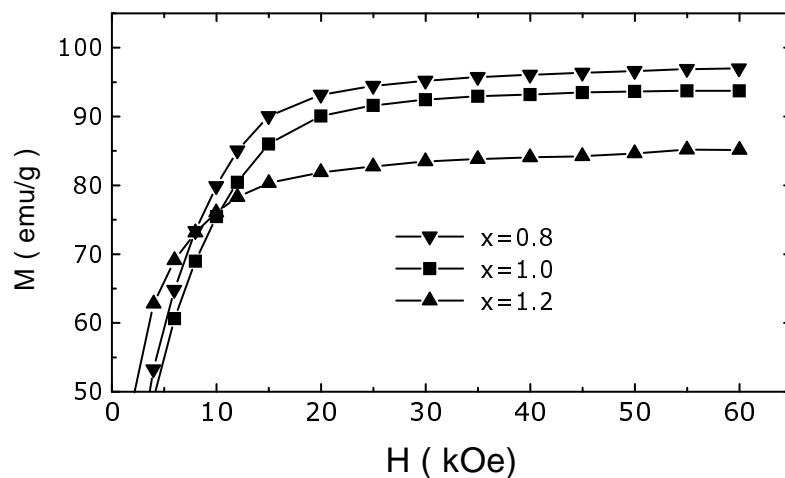
**Figure 2.** Output from Rietveld analysis of the XRD pattern of  $\text{La}_2\text{Co}_{16}\text{V}$ . The observed data are indicated by crosses and the calculated profile by the continuous line overlying them. The lower curve is the difference between the observed and calculated intensity at each step, plotted on the same scale at the bottom. The bars denote the calculated Bragg-reflected positions.

For annealed samples  $\text{La}_2\text{Co}_{17-x}\text{V}_x$  ( $x = 0.5, 0.6, 0.8, 1.0, 1.2, 1.4, 1.5$ ) compounds x-ray diffraction patterns revealed that single-phase samples were obtained in the composition range  $0.8 \leq x \leq 1.2$ . The x-ray diffraction patterns were successfully indexed with a rhombohedral  $\text{Th}_2\text{Zn}_{17}$ -type structure using the program TREOR [6] and the lattice parameters were further least-squares refined. Figure 1 shows the concentration dependence of the lattice parameters of  $\text{La}_2\text{Co}_{17-x}\text{V}_x$  compounds (also see table 1). A linear increase of  $a$  and  $c$  with  $x$ , the V content, in the range  $0.8 \leq x \leq 1.2$  is observed, which implies that the homogeneous range in the  $\text{La}_2\text{Co}_{17-x}\text{V}_x$  series is  $0.8 \leq x \leq 1.2$ .

The Rietveld powder diffraction profile fitting technique [7] was used to refine the XRD pattern of  $\text{La}_2\text{Co}_{16}\text{V}$  using the program DBW-9411 [8]. The space group is  $R\bar{3}m$ . There are four crystallographic positions (18f, 18h, 9d and 6c) which V can possibly occupy. The crystal structure of  $\text{R}_2\text{Co}_{17}$  compounds is considered to be derived from that of  $\text{RCO}_5$  compounds by substituting the dumb-bell pair of Co atoms (6c crystallographic position) on the rare-earth site of every third unit cell.  $\text{LaCo}_5$  exists but  $\text{La}_2\text{Co}_{17}$  does not exist because the ratio of La atomic radius to Co atomic radius is large. Therefore, substitution of V for part of the Co in dumb-bell sites is necessary to stabilize the  $\text{La}_2\text{Co}_{16}\text{V}$  phase because the atomic radius of V is larger than that of Co. So we suggest that V atoms should occupy the 6c crystallographic position. The values of  $R$  factor for the V occupancy in different



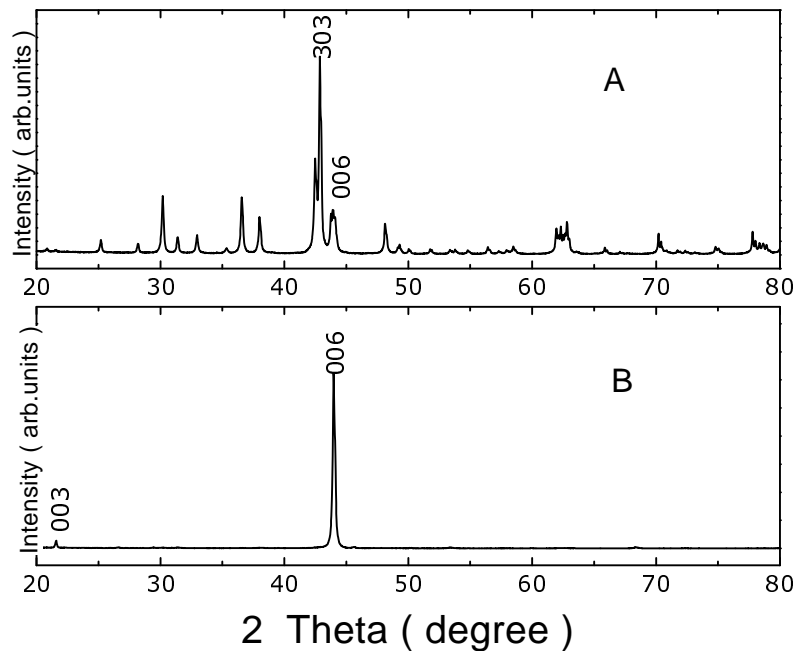
**Figure 3.** The temperature dependence of magnetization of  $\text{La}_2\text{Co}_{17-x}\text{V}_x$  measured at low fields by vibrating sample magnetometer.



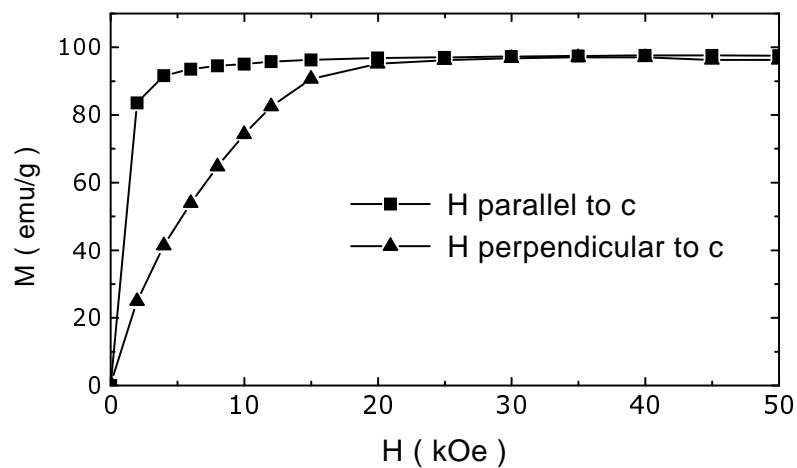
**Figure 4.** The field dependence of magnetization of  $\text{La}_2\text{Co}_{17-x}\text{V}_x$  measured by extraction sample magnetometer at 1.5 K.

crystallographic positions are shown in table 2. The small difference between  $R$  factors is due to the small difference between  $f$  factors for Co and V atoms. The pattern factor  $R_p$  and the weighted pattern factor  $R_{wp}$  is smallest for the V occupancy in the 6c position, which also suggests that V atoms preferentially occupy the 6c crystallographic position. The final refinement results are shown in table 3 and figure 2.

Magnetic balance measurement indicates that  $\text{La}_2\text{Co}_{17-x}\text{V}_x$  compounds are ferromagnetic with Curie temperature higher than 820 K in composition range of  $x = 0.8$ –1.2.



**Figure 5.** The x-ray diffraction patterns for sample  $\text{La}_2\text{Co}_{16}\text{V}$  before (A)/after (B) field alignment at room temperature.



**Figure 6.** Magnetization as a function of magnetic field at 1.5 K for the aligned powder sample of  $\text{La}_2\text{Co}_{16}\text{V}$ . The upper curve is parallel to the aligned direction ( $c$  axis) and the lower curve is perpendicular to the aligned direction.

Figure 3 shows the temperature dependence of magnetization. The magnetization curves at 1.5 K, measured by an extraction sample magnetometer in a field of 7 T, are shown

in figure 4. The results that the Curie temperature  $T_C$ , the saturation moment  $\mu_s$  of  $\text{La}_2\text{Co}_{17-x}\text{V}_x$  and the magnetic moment per Co atom  $\mu_{Co}$  decrease with increase V substitution may be due to the combination of contributions from the magnetic dilution of the Co sublattice by the nonmagnetic V and additional reduction of the Co moment resulting from V substitution (see table 1).

The x-ray diffraction patterns for the aligned and random original powder samples at room temperature are plotted in figure 5 for  $\text{La}_2\text{Co}_{16}\text{V}$ . It can be seen that the compound  $\text{La}_2\text{Co}_{16}\text{V}$  exhibits a uniaxial anisotropy and the easy magnetization direction is the  $c$  axis.

In order to evaluate the uniaxial anisotropy, the powder samples of  $\text{La}_2\text{Co}_{16}\text{V}$  were made to align in a magnetic field of 1 T and fixed by epoxy resin. Figure 6 shows the magnetization measured with the applied field parallel to or perpendicular to the easy axis ( $c$  axis) of the aligned powder sample, respectively. By linearly extrapolating  $M$  to zero from the  $M$  ( $=M_{\parallel} - M_{\perp}$ )- $H$  curve, the anisotropy field  $H_A$  of 19 kOe was derived. The value of  $H_A$  is low because the contribution of La without a magnetic moment to the magnetocrystalline anisotropy is negligible.

Compared to  $\text{R}_2\text{Co}_{17}$  compounds, the Co sublattice anisotropy in  $\text{La}_2\text{Co}_{16}\text{V}$  compound is easy axis instead of easy basal plane. This phenomenon can be explained by the following factor. One of the characteristic structural features of the  $\text{R}_2\text{Co}_{17}$  compounds is the presence of so-called dumb-bell pairs of Co atoms. These Co atoms occupy the crystallographic 6c position. The so-called dumb-bell Co atoms are commonly considered to be responsible for the easy-plane anisotropy of the Co sublattice in the  $\text{R}_2\text{Co}_{17}$  compounds, compared to the easy-axis anisotropy in the parent  $\text{RCo}_5$  compounds, where the Co dumb-bell atoms are absent [2]. For the  $\text{La}_2\text{Co}_{16}\text{V}$  compound V preferentially occupies the dumb-bell sites (6c positions) from x-ray diffraction analysis. The substitution of V for Co in dumb-bell sites weakens the easy-plane anisotropy resulting from Co dumb-bell atoms, thus resulting in a favourable uniaxial anisotropy.

In conclusion, new compounds  $\text{La}_2\text{Co}_{17-x}\text{V}_x$  with  $\text{Th}_2\text{Zn}_{17}$ -type structure were synthesized and the homogeneous range of  $\text{La}_2\text{Co}_{17-x}\text{V}_x$  compounds is  $0.8 \leq x \leq 1.2$ . The Curie temperature and magnetic moment of  $\text{La}_2\text{Co}_{17-x}\text{V}_x$  compounds are still high and large, and comparable to those of preceding  $\text{R}_2\text{Co}_{17}$  compounds. Furthermore,  $\text{La}_2\text{Co}_{17-x}\text{V}_x$  compounds favour uniaxial anisotropy due to preferentially occupied 6c positions of V. Therefore,  $\text{La}_2\text{Co}_{17-x}\text{V}_x$  compounds can be expected to be potential candidates for permanent magnets.

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