

Crystallographic Study of $\text{YCo}_{1-2x}^{3+}\text{Co}_x^{2+}\text{Pt}_x^{4+}\text{O}_3$ and $\text{DyCo}_{1-2x}^{3+}\text{Co}_x^{2+}\text{Pt}_x^{4+}\text{O}_3$

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Received November 21, 1986; in revised form March 5, 1987

The crystal structures of single crystals of $\text{YCo}_{1-2x}^{3+}\text{Co}_x^{2+}\text{Pt}_x^{4+}\text{O}_3$ and $\text{DyCo}_{1-2x}^{3+}\text{Co}_x^{2+}\text{Pt}_x^{4+}\text{O}_3$ have been examined at room temperature, and shown to be isostructural with GdFeO_3 , which belongs to space group *Pbnm*. The overall expansion of octahedra caused by substitution of platinum enhances the distortion of rare-earth dodecahedra by moving 4 out of 12 oxygens further away from the rare-earth ions, as shown by the rotation of octahedra along the [110] axis. No order has been found for Co^{2+} , Co^{3+} , and Pt^{4+} . © 1987 Academic Press, Inc.

Introduction

Rare-earth transition metal perovskites have been studied extensively at room temperature and at high and low temperatures, both for scientific and technological reasons: the chemical stability and high electrical conductivity (1), the crystallographic and electronic structures and related magnetic interactions (2), the metal-insulator transitions (3), the electrochemical characteristics (e.g., (4)), and the catalytic properties (5). The general formula of the perovskites is ABO_3 with a relatively simple structure. The transition metal ions are oc-

tahedrally coordinated by oxygen ions, and the rare-earth ions fit into the oxygen dodecahedral interstices. The structures may assume different symmetries, e.g., rhombohedral LaCoO_3 and orthorhombic LaFeO_3 .

The crystal structure of gadolinium orthoferrite, GdFeO_3 , was first determined by Geller (6) to have four distorted GdFeO_3 units in the orthorhombic cell and has been taken as the prototype for the orthorhombic perovskites. The space group was determined to be *Pbnm*. Many rare-earth transition metal perovskites are known to be isostructural with GdFeO_3 , as are all the rare-earth orthochromites, orthovanadites, orthorhodites, orthoferrites, and orthoaluminates (from Sm to Lu), orthocobaltites (from Pr to Eu), and also YCoO_3 , YFeO_3 , YCrO_3 , and YAIO_3 . However, NaCoF_3 and NaNiF_3 , which are orthorhombic, were re-

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fined in the space group $P2_12_12_1$ (7) instead of $Pbnm$ because of the existence of weak extra reflections which violated the systematic absence rule $h + l = 2n$ for $h0l$ and $k = 2n$ for $Ok\bar{l}$ ($n = \text{integer}$) in $Pbnm$. In another study, the redetermination of the crystal structures of LuFeO_3 and LaFeO_3 by Marezio *et al.* (8) confirmed the space group to be $Pbnm$, and the existence of the forbidden reflections of the type $h0l$ with $h + l = 2n + 1$ for LaFeO_3 were attributed to twinning. This kind of twinning was observed again in SmAlO_3 (9). They were also able to refine all the rare-earth orthoferrites in the space group $Pbnm$ (10).

Rare-earth cobaltite perovskites. These perovskites (general formula: $M\text{CoO}_3$, $M = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu}$) have been the subject of recent extensive investigations because of their use in catalytic processes (11–12) and because cobalt can occur in either high- or low-spin states (13–16). Both of these aspects of the rare-earth cobaltites have been shown to be dependent on the composition of the material and the temperature at which the measurements are made. Some attempt has been made to correlate the measured catalytic activity of compounds with structures; Shimizu (11) proposed a relationship between the well-known perovskite tolerance factor (calculated from the ionic radii of Shannon and Prewitt (17)) and the oxygen binding energy. Casalot (18) and Demazeau *et al.* (19) have studied powder patterns of the compounds in the rare-earth cobaltite series at high temperatures and determined their cell dimensions. Raccach and Goode-nough's (20) original X-ray powder diffraction study indicated that the Co in LaCoO_3 is in the low-spin state at room temperature and transforms to the high-spin state at 375°C. However, the reported structural phase transition at that temperature was not observed in a neutron powder diffraction study, and was attributed to the insensitivity of X-ray diffraction intensities to

the oxygen atoms in the presence of heavy atoms in the structure (21). This had been noticed earlier by Okazaki *et al.* (7) when no distinct peaks corresponding to oxygens were observed in the electron density map of GdFeO_3 .

Attention has also been focused on the perovskites with *A*-cation and/or *B*-cation substitutions, as they show a great diversity of electronic and magnetic properties, and also improved characteristics as catalysts. Phase transformations as functions of the amount of substitutions were observed, as for $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, which transform from rhombohedral to cubic structures at $x = 0.4$ (22–23). It was also shown that perovskites with the formula $\text{LaNi}_{1-x}\text{M}_x\text{O}_3$, where $M = \text{Mn, Cr, and Fe}$, change from rhombohedral to orthorhombic structures when $x > 0.2$, $x > 0.35$, and $x > 0.5$, respectively (3). Khattak *et al.* (24) refined the orthorhombic structure of LaCrO_3 and the rhombohedral structure of $\text{La}_{0.75}\text{Sr}_{0.25}\text{CrO}_3$ with neutron powder data, but little else has been done with regard to the detailed crystal structure study of these solid solution perovskites, as compared to the unsubstituted ABO_3 .

We have obtained a complete series of rare-earth cobaltite samples (La through Lu, plus Y) from J. Remeika of AT&T Bell Laboratory. Preliminary examination of crystals thought to be GdCoO_3 with low-spin Co shows that Co is in the high-spin state and the octahedral site contains about 30% Pt, apparently coming from the platinum crucible used for the synthesis. Although most of the samples remain to be examined, this series appears to represent a fascinating set of problems, i.e., the nature of the spin state of Co, the substitution of Pt for Co (with implications for studies of these and other oxides containing Co where the chemical composition was not determined after synthesis), and how the chemistry, structures, and properties of these perovskites change within the series.

The results recently obtained by Rao and co-workers (e.g., (15, 25)) suggest that the mechanism of the spin-state transitions is likely to be different for the lighter (Pr,Nd,Tb) rare-earth cobaltites. Differences in catalytic activity have been observed throughout the series (12).

In this communication, we report the results of the detailed structural study of two solid solution perovskites: $\text{YCo}_{1-x}\text{Pt}_x\text{O}_3$ and $\text{DyCo}_{1-x}\text{Pt}_x\text{O}_3$.

Experimental

Data Collection

A preliminary study of single crystals of the series of $\text{ACo}_{1-x}\text{Pt}_x\text{O}_3$ perovskites ($A = \text{La}$ through Lu , and Y) using the precession camera showed that they all have orthorhombic symmetry. For all of the samples except yttrium perovskite, weak reflections of the type $k = 2n+1$ for Ok_l were observed. Two crystals from the series, $\text{YCo}_{1-x}\text{Pt}_x\text{O}_3$ and $\text{DyCo}_{1-x}\text{Pt}_x\text{O}_3$ with dimensions of $30 \times 30 \times 100$ and $40 \times 40 \times 320$ (in microns), respectively, were mounted on the glass fibres for single-crystal diffractometer study. The experiments were carried out at room temperature.

The single-crystal X-ray data were collected on a Picker four-circle diffractometer using MoK radiation (fine-focus tube, take-off angle 1.7° , 50 kV, 14 mA) with a flat graphite-monochromator ($\lambda = 0.70926 \text{ \AA}$) and a scintillation detector. The $\omega - 2\theta$ scanning method and a constant-precision mode were used in data collection; the scan width on $2\theta(^\circ)$ was $2.0 + 0.7 \tan \theta$. The reflections with 2θ up to 70° in a quarter of reciprocal space were collected for both samples, and there was 1355 reflections for $\text{YCo}_{1-x}\text{Pt}_x\text{O}_3$ and 1289 for $\text{DyCo}_{1-x}\text{Pt}_x\text{O}_3$. Lorentz and polarization corrections were applied. Between 55° and 70° , 19 reflections for $\text{YCo}_{1-x}\text{Pt}_x\text{O}_3$ and 24 reflections for $\text{DyCo}_{1-x}\text{Pt}_x\text{O}_3$ were centered at eight equiv-

alent positions and the average positions were used in least-squares refinement to obtain the cell parameters. The results are shown in Table I, together with the cell parameters for YCoO_3 and DyCoO_3 for comparison.

Space Group Determination

For $\text{YCo}_{1-x}\text{Pt}_x\text{O}_3$, all the reflections of types $k = 2n + 1$ for $0kl$ and $h + l = 2n + 1$ for $h0l$ ($n = \text{integer}$) were absent if a reflection was taken to be unobserved when $I(\text{obs}) < 3\sigma_1$. It is probably isostructural with GdFeO_3 , as is YCoO_3 , and belongs to the space group $Pbnm$.

For $\text{DyCo}_{1-x}\text{Pt}_x\text{O}_3$, reflections for all classes of indices were observed. Five reflections of the type $h00$, $0k0$, and $00l$ ($h, k, l = 2n + 1, n = \text{integer}$) were 100, 010, 001, 030, and 050. These reflections plus three reflections, 011, 013, 015 of $0kl$ type with $k = 2n + 1$, were further measured by means of the azimuth-scanning method (26) in order to see whether they originated from the Umweganregung process of multiple diffraction. In this measurement, intensities were recorded as a function of the rotation of the crystal around its reciprocal lattice vector for a particular reflection in question. These measurements showed that all five $h00$, $0k0$, and $00l$ reflections were of the result of multiple reflections, while none of the $0kl$ reflections with $k = 2n + 1$ could be attributed to this cause.

TABLE I
CELL PARAMETERS

Compound	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$
$\text{YCo}_{1-x}\text{Pt}_x\text{O}_3$	5.2512(5) ^a	5.6571(7)	7.5337(8)	223.80(4)
$\text{DyCo}_{1-x}\text{Pt}_x\text{O}_3$	5.2627(7)	5.6447(9)	7.5396(7)	223.98(4)
YCoO_3^b	5.133	5.412	7.360	
DyCoO_3^b	5.165	5.404	7.407	

^a Errors in parentheses refer to the least significant decimal.

^b See Jakobs *et al.* (31).

It was noted that all the $0kl$ reflections could be divided into two groups, one with $k = 2n$ and the other $k + l = 2n$, reflections with $k = 2n + 1$ and l even were absent. This feature of having two sets of systematic absence rules was observed among the rare-earth orthoaluminates (9), and has been attributed to twinning by a 90° rotation around the c axis. The similarity between intensities of all the reflections other than those of the class $0kl$ with k odd were noted when Y and Dy perovskites were compared. As the ionic radii for Y^{3+} and Dy^{3+} are nearly equal, it is unlikely to have $DyCo_{1-x}Pt_xO_3$ in a space group other than that of $YCo_{1-x}Pt_xO_3$, as long as the amount of Pt substitution is comparable between the two.

We think that the Dy perovskite sample is most probably twinned, and from intensity ratios, the twinned volume is less than 10%. In conclusion, both samples are isostructural with $GdFeO_3$ and in space group $Pbnm$.

Refinement

The crystal structures of $YCo_{1-x}Pt_xO_3$ and $DyCo_{1-x}Pt_xO_3$ were refined in space group $Pbnm$. A prismatic absorption correction was applied using the program ABSORB (L. Finger, unpublished), with the absorption coefficients of 508.3 and 590.8 cm^{-1} , respectively. This gave the range of transmission factors from 0.23 to 0.37 and from 0.12 to 0.30, respectively. The least-squares program PROMETHEUS (27) was used. Reflections with intensities less than $3\sigma_I$ were considered to be unobserved and were rejected. All the parameters, including the occupancy, x , of Pt in the octahedral site were refined simultaneously. The residuals of the sum of $w_i(|F_{obs}| - |F_{calc}|)^2$ were minimized where w_i is the weight which equals the reciprocal of σ_F . Atomic scattering factors and anomalous dispersion coefficients were taken from *International Ta-*

bles for X-Ray Crystallography (Vol. IV, 1974). After applying a secondary extinction correction following Becker and Coppens (28) the reflections were combined, giving 629 and 673 independent reflections, including the rejected ones, for $YCo_{1-x}Pt_xO_3$ and $DyCo_{1-x}Pt_xO_3$, respectively. The initial values were taken from that of $GdFeO_3$ (6). No twin correction was applied to the Dy intensity data because of the difficulty in monitoring those weak reflections of $0kl$ type with $k = 2n + 1$ which could be used to define the relative orientation of the twin. Eleven reflections at low 2θ angles with medium intensities had $w_i|F_{obs} - F_{calc}|$ larger than 2θ ; this was most probably caused by the twin, and these reflections, together with those unobserved reflections, were rejected in the final refinement. The final refinement results for all the parameters are shown in Table II. The observed structure factors after absorption and extinction correction, the calculated structure factors, and the weights assigned to them are deposited.¹

As indicated above, the platinum occupancies were obtained by the refinement, simultaneously with other variables. A chemical analysis was initially conducted in order to fix the stoichiometries. The samples of Y crystals from the same batch as supplied by Remeika were electron probe analyzed. It showed that the platinum content for different crystals, although from the same batch, are different, spanning over a region of at least $0.28 < x < 0.40$. The same observed for the Dy crystals except with a region of $0.25 < x < 0.35$. This variable platinum content is attributed to

¹ See NAPS Document No. 04500 for 12 pages of supplementary materials from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 up to 20 pages plus \$.30 for each additional page. All orders must be prepaid.

TABLE II
FRACTIONAL ATOMIC COORDINATES, THERMAL PARAMETERS, AND OCCUPANCY NUMBER x FOR $\text{YCo}_{1-x}\text{Pt}_x\text{O}_3$
AND $\text{DyCo}_{1-x}\text{Pt}_x\text{O}_3$ FROM THE REFINEMENTS

	(1) $\text{YCo}_{1-x}\text{Pt}_x\text{O}_3$				(2) $\text{DyCo}_{1-x}\text{Pt}_x\text{O}_3$			
	Y	Co/Pt	O(1)	O(2)	Dy	Co/Pt	O(1)	O(2)
x	.9780(1)	0	.1173(10)	.6852 (7)	.9784(1)	0	.1151(18)	.6869(12)
y	.0756(1)	1/2	.4570 (9)	.3072 (6)	.0740(1)	1/2	.4598(16)	.3075(12)
z	1/4	0	1/4	.0587 (5)	1/4	0	1/4	.0545(10)
β_{11}	.0089(2)	.0044(1)	.0121(17)	.0095(11)	.0087(2)	.0039(2)	.0135(30)	.0100(18)
β_{22}	.0044(2)	.0029(1)	.0067(17)	.0069(10)	.0066(1)	.0054(2)	.0046(24)	.0086(19)
β_{33}	.0043(1)	.0018(1)	.0024 (8)	.0059 (7)	.0028(1)	.0006(1)	.0017(15)	.0034(13)
β_{12}	-.0006(2)	.0004(2)	.0013(13)	.0000 (9)	-.0005(1)	.0003(2)	-.0054(22)	-.0020(15)
β_{13}	0	.0000(1)	0	.0020 (8)	0	.0002(2)	0	-.0007(13)
β_{23}	0	.0002(1)	0	-.0024 (7)	0	.0000(1)	0	-.0002(12)
equi. B	.84(1)	.42(1)	.91(8)	1.09 (6)	.81(1)	.42(1)	.82(14)	.99(11)
x		.325(2)			.321(3)			
Ref.'s (meas.)		629			595			
(used.)		508			541			
$R(\%)$		4.4			4.6			
$R(w)(\%)$		2.5			4.4			

Note. The β_{ij} 's are as defined by $\exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$.

the uncontrollable platinum contamination from the crucible in synthesis, with those crystals close to the crucible wall probably having more platinum. We did not, however, analyze the very samples used for the data collections, and both refinements were started with an initial x value of 0.30 and the refined results nevertheless fell within the observed range of platinum contents.

It is noticed in Table II that temperature factors β_{33} of Dy and Co/Pt in Dy crystal are much smaller than β_{11} and β_{22} , and are only about half of that of Y crystal, while the rest of the temperature factors for both crystals are comparable. This may result from the inaccuracy of the absorption model used. For the needle-like crystals with the dimensions shown before, the orientation matrixes showed that both crystals have their c axis lying along the long dimension. For Dy crystal, this dimension (320 μm) is three times as long as that of Y crystal (100 μm). Errors in measuring the crystal dimensions and/or orientations result in

errors in the absorption models, especially for reflections with large components along the c axis. Heavy atoms as Dy, Y, and Pt would respond to such under- or overestimation of absorption by the corresponding change of temperature factors, especially β_{33} of the Dy crystal in our case.

Discussion

The cell distortion factor, d_c , describing the departure of the structure from an ideal cubic model (for which $d_c = 0$) is defined as (29)

$$d_c = 10^4 x \{ (a/\sqrt{2} - a_p)^2 + (b/\sqrt{2} - a_p)^2 + (c/2 - a_p)^2 \} / 3a_p^3,$$

where $a_p = (a/\sqrt{2} + b/\sqrt{2} + c/2)/3$. It is 10.60 for $\text{YCo}_{.68}\text{Pt}_{.32}\text{O}_3$ and 9.44 for $\text{DyCo}_{.68}\text{Pt}_{.32}\text{O}_3$, compared to that of 5.08 and 3.60 for YCoO_3 and DyCoO_3 , respectively ($d_c = 4.33$ for GdFeO_3 which is comparable with YCoO_3 and DyCoO_3). The difference

in the departure from cubic symmetry shows the difference in the closeness of the packing of ions within the cell through the ratio $R_A/\sqrt{2}(R_B + R_O)$ as first noticed by Yagi *et al.* (30), and later defined by Sasaki *et al.* (29) as the observed tolerance factor, $t_{\text{obs}} = (R_A + R_O)/\sqrt{2}(R_B + R_O)$, where $(R_A + R_O)$ is the mean interatomic distance in dodecahedra and $(R_B + R_O)$ in octahedra; this ratio increases to 1 as the structure approaches cubic symmetry, and gives 0.972 and 0.974 for Y and Dy perovskites, respectively. Because Y^{3+} is a little smaller than, although close to, Dy^{3+} , and because substitution of larger platinum, which is most likely at the Pt^{4+} state, for Co^{3+} expands the octahedra, different distortions result that are consistent with that described by the

cell distortion factor. This suggests that the crystallographic properties of the platinum-substituted rare-earth cobaltites are predictable from the systematic relationships determined for the $GdFeO_3$ -type perovskites (29). If the bond length distortion parameter, d_b , as defined in (29),

$$d_b = 1/n \sum \{(r_i - \bar{r})/\bar{r}\}^2 \times 10^3,$$

is calculated for the dodecahedra, it is 38.7 and 36.2 for Y and Dy perovskites, respectively. The bond length distortion vs t_{obs} shows that both perovskites are close to $TmFeO_3$, as far as this distortion is concerned.

It is interesting to note how the distortion proceeds by adding Pt^{4+} . As shown in Table III, the 12 oxygens bonded to the rare-earth

TABLE III
INTERATOMIC DISTANCES (Å) AND ANGLES (°) OF OCTAHEDRA AND DODECAHEDRA

(1) $YCo_{.675}Pt_{.325}O_3$				(2) $DyCo_{.679}Pt_{.321}O_3$			
Co/Pt	O(1) 1 × 2		1.996(2)	Co/Pt	O(1) 1 × 2		1.993(3)
	O(2) 2 × 2		2.029(3)		O(2) 2 × 2		2.016(6)
	O(3) 3 × 2		2.040(3)		O(2) 3 × 2		2.037(6)
		Average	2.022			Average	2.015
O(1) 1	Co/Pt	O(2) 2 × 2	88.87(18)	O(1) 1	Co/Pt	O(2) 2 × 2	89.68(35)
		O(3) 3 × 2	87.34(18)			O(2) 3 × 2	86.95(35)
O(2) 2		O(2) 3 × 2	88.72 (7)	O(2) 2		O(2) 3 × 2	88.65(12)
Y	O(1) 4 × 1		3.575(5)	Dy	O(1) 4 × 1		3.541(9)
	O(1) 5 × 1		2.278(5)		O(1) 5 × 1		2.293(9)
	O(1) 6 × 1		3.197(5)		O(1) 6 × 1		3.189(9)
	O(1) 7 × 1		2.229(5)		O(1) 7 × 1		2.234(9)
	O(2) 8 × 2		2.262(4)		O(2) 8 × 2		2.279(7)
	O(2) 9 × 2		2.482(4)		O(2) 9 × 2		2.503(7)
	O(2) 10 × 2		2.652(4)		O(2) 10 × 2		2.631(7)
	O(2) 11 × 2		3.639(4)		O(2) 11 × 2		3.607(7)
O(1) 4	Y	O(1) 5 × 1	149.46(21)	O(1) 4	Dy	O(1) 5 × 1	149.99(38)
O(1) 5		O(1) 6 × 1	120.85(16)	O(1) 5		O(1) 6 × 1	119.95(32)
O(1) 6		O(7) 7 × 1	150.37(21)	O(1) 6		O(1) 7 × 1	151.57(40)
O(1) 7		O(1) 4 × 1	60.67(16)	O(1) 7		O(1) 4 × 1	61.51(31)
O(2) 8		O(2) 9 × 2	119.33 (8)	O(2) 8		O(2) 9 × 2	119.65(14)
O(2) 9		O(2) 10 × 1	67.22 (5)	O(2) 9		O(2) 10 × 2	66.91 (9)
O(2) 10		O(2) 11 × 2	120.67 (8)	O(2) 10		O(2) 11 × 2	120.23(15)
O(2) 11		O(2) 8 × 2	51.47 (4)	O(2) 11		O(2) 8 × 2	51.73 (6)
O(1) 4		O(2) 8 × 2	54.59(11)	O(1) 4		O(2) 8 × 2	55.34(19)
O(1) 5		O(2) 9 × 2	72.48(14)	O(1) 5		O(2) 9 × 2	72.07(25)
O(1) 6		O(2) 10 × 2	116.98 (8)	O(1) 6		O(2) 10 × 2	117.38(14)
O(1) 7		O(2) 11 × 2	49.98 (9)	O(1) 7		O(2) 11 × 2	50.22(18)

can be divided into 8 first-nearest neighbors and 4 second-nearest neighbors. The average bond lengths for them are 2.412 and 3.513 Å for Y and 2.419 and 3.486 Å for Dy perovskite, respectively; these can be compared with those of 2.468 and 3.411 Å for GdFeO₃ (10). The larger distortion in the platinum-substituted samples is achieved by moving the 4 second-nearest oxygens farther away from the rare-earth while the 8 first-nearest are kept tightly bonded to the rare-earth. This is possible because the second-nearest oxygens are screened out from the rare-earth by those first-nearest oxygens. This distortion resulting from stretching some of the bonds is equivalent to the tilting and/or rotating of cobalt octahedra with respect to each other. This is shown in Fig. 1 for YCo_{0.68}Pt_{0.32}O₃ as viewed along the [110] direction and along the *c* axis, where, for simplicity, yttrium is not shown. It can be seen that the distortion is mainly the tilting of octahedra along the *c* axis together with the rotating around an axis that bisects the *a* and *b* axes; the latter are axes of the pseudomonoclinic cell. With this distortion, the rare-earths are no longer 12 coordinated but 8. Using the ionic radii, for 8 coordination, of 1.019 and 1.027 Å for Y³⁺ and Dy³⁺, respectively, as given by Shannon and Prewitt (17), and 1.38 Å for O²⁻, we get the bond lengths of 2.399 and 2.407 Å, which compare well with the observed 8 coordinated average bond lengths of 2.414 and 2.419 Å, respectively.

For charge balance, the proper formula of the platinum substituted rare-earth cobaltites should be written as ACo_{1-2x}Co_x²⁺Pt_x⁴⁺O₃. For the yttrium and dysprosium perovskites, we found no ordering among Co³⁺, Co²⁺, and Pt⁴⁺; they are randomly distributed in octahedral sites. As is well known now, for the trivalent cobalt ions in the octahedral sites, the energy levels for the diamagnetic low-spin state with electronic configuration $t_{2g}^6e_g^0$, and the paramagnetic high-spin state of $t_{2g}^4e_g^2$ are nearly

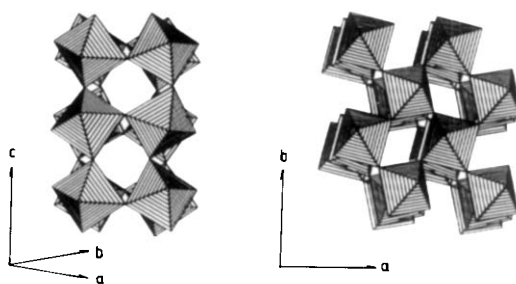


FIG. 1. Distortions of dodecahedra for YCo_{0.68}Pt_{0.32}O₃ seen along the [110] and [001] directions.

equal (20), so that high-spin and low-spin cobalt ions may coexist in the structure. While, on the other hand, the divalent cobalt ions in these sites are assumed to be in the high-spin state (20) because they have a smaller crystal-field splitting associated with the smaller cationic charge compared to that of trivalent cobalt ions, and the relatively larger intra-atomic splitting which competes with the crystal-field splitting makes the low-spin divalent cobalt ions less likely than high-spin ones with electronic configuration of $t_{2g}^5e_g^2$.

The octahedral bond length distortion, d_b , gives 0.086 and 0.080 for Y and Dy perovskites, respectively, much higher than that of 0.029 for TmFeO₃. In accordance with this, the bond angles are distorted as much as 3° from the ideal 90°. We believe that this apparent large distortion of octahedra is largely caused by the positional disordering of Pt⁴⁺, Co²⁺, and Co³⁺, which have significantly different ionic radii. This positional disordering has been reflected in the little high oxygen temperature factor, especially for O(2), as shown in Table II. The ionic radii for octahedral sites cations were given by Shannon and Prewitt (17) as (in Å): 0.745 for Co²⁺(HS), 0.625 for Pt⁴⁺, 0.545 for Co³⁺(LS), and 0.61 for Co³⁺(HS), and that for O²⁻ as 1.38 Å (oxygen coordination number is taken to be 4 instead of 6 because of the severe distortion the coordination polyhedra are experienc-

ing). On the basis of the derived stoichiometries, the average octahedral bond lengths indicated by these data are 2.02 Å, assuming low-spin Co^{3+} , and 2.04 Å, assuming high-spin Co^{3+} . These figures compare well with the observed average bond length of 2.02(3) Å. At this point, the spin state of the Co^{3+} ions cannot be confirmed. It is also noted that our previous assignment of Pt^{4+} state is consistent with the observed octahedral bond lengths. A Pt^{2+} state, with the ionic radius of 0.80 Å, would result in a calculated bond length of 2.08 Å, assuming a low-spin Co^{3+} state.

As for LaCoO_3 , both YCoO_3 and DyCoO_3 are intrinsic semiconductors (32). Rao *et al.* (33) reported electronic properties of $\text{LaCo}_{1-x}\text{M}_x\text{O}_3$ ($M = \text{Ni}, \text{Fe}$), and showed that the spin state of Co^{3+} is markedly affected by the substituents. But to the best of our knowledge, the substitution of Co^{3+} in rare-earth cobaltites by ions in the oxidation state IV has never been reported. The existence of Co^{2+} from the charge compensating for Pt^{4+} may have very possibly changed the electrical transportation properties. It is anticipated that the room-temperature intrinsic end-member YCoO_3 and DyCoO_3 semiconductors may transfer to the extrinsic-type conduction by this substitution, where the hopping of charge carriers from site to site among octahedral sites may dominate the electrical transport, as in the system $\text{Y}_{1-x}\text{M}_x\text{CrO}_3$ ($M = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) (34).

Acknowledgments

We thank J. P. Remeika of AT&T Bell Telephone Laboratory for kindly supplying all the samples and K. J. Baldwin for help during the data collection and processing. This project has been supported by NSF Grant EAR83-19504.

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