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A Neutron Diffraction Study of $LaCoO_3$ in the Temperature Range $4.2 < T < 1248$ K

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The structure of $LaCoO_3$ has been reexamined using high-intensity and high-resolution powder neutron diffraction, the latter measurements being made at 4, 71, 293, 668, 1143, and 1248 K. Only in the 668 K data is there evidence for $R\bar{3}$ instead of $R\bar{3}c$ symmetry, found at other temperatures. Previous X-ray diffraction work suggested that the $R\bar{3}$ space group was retained from 648 K through a first-order semiconductor–metal transition at 1210 K. The $R\bar{3}c$ cell parameters found are: $a = 5.3416(1)$ Å, $\alpha = 60.990(1)°$ [4 K]; $a = 5.3489(1)$ Å, $\alpha = 60.966(1)°$ [71 K]; $a = 5.3778(1)$ Å, $\alpha = 60.798(1)°$ [293 K]; $a = 5.4355(1)$ Å, $\alpha = 60.599(1)°$ [668 K]; $a = 5.5001(2)$ Å, $\alpha = 60.357(2)°$ [1143 K]; $a = 5.150(2)$ Å, $\alpha = 60.296(2)°$ [1248 K]. The $R\bar{3}$ cell parameters obtained from the 668 K data are $a = 5.4354(1)$ Å, $\alpha = 60.599(1)°$. These results are in accord with our previously reported differential thermal analysis (DTA) and electrical conductivity data and with a model based on collective 3*d*-electron behavior over the temperature range studied.

Introduction

There is a continued interest in the $RECoO_3$ perovskites which arises from their catalytic and electronic properties (*1–5*). In particular, there have been numerous studies of the bulk (*1–4*) and surface characteristics (*4–7*) of $LaCoO_3$, attention being focused on the role of Co 3*d* electrons. Available experimental data of various types (e.g., X-ray and neutron diffraction, DTA, Mössbauer) have, until recently, been interpreted as follows: at low temperature (4.2 K) the Co 3*d* electrons are localized having the low-spin configuration $t_{2g}^6 e_g^0$; with increasing temperature the high-spin configuration $t_{2g}^4 e_g^2$ is populated; at 648 K long-range ordering of the spin states occurs; charge-transfer between the spin states to form Co^{II} and Co^{IV} species also

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takes place around and above this temperature; finally, at 1210 K there is a transition from localized to itinerant 3*d* electron character (*1–4*).

The interpretation of structural data played an important part in construction of the above model. Neutron (*8*) and X-ray diffraction (*9*) work suggested that the low-temperature structure of $LaCoO_3$ can be described as a rhombohedral distortion of the simple cubic perovskite cell, with a low-temperature $R\bar{3}c$ space group in which there is only one cobalt site.

A transition from $R\bar{3}c$ to $R\bar{3}$, which contains two cobalt sites, suggesting an ordering transition was claimed at 648 K (*9*). The $R\bar{3}$ space group was said to be maintained through a first-order localized-to-itinerant electron transition at 1210 K (*9*). The latter observation was interpreted as an indication of t_{2g} orbital localization through the transition, but with localized e_g orbitals being transformed into a σ^* band. The electron phase transition was supposed to be the cause of the accompanying semiconductor-to-metal transition.

In a previous publication (*4*), we presented neutron diffraction, DTA, and electrical conductivity data which did not reveal the first-order localized-to-itinerant 3*d*-electron phase transition at 1210 K. However, a higher order semiconductor-to-metal transition was observed (*4*) in electrical conductivity data between 520 and 750 K. Differences between our data and those previously reported (*1–4, 8 ,9*) are attributed to the presence of impurity phases in earlier work. More recently (*10*), a comparison of the conductivity versus temperature behavior of several rare-earth cobaltates has permitted the behavior of all the materials studied to be united within a single model which assumes collective-electron behavior for both π^* and σ^* orbitals over the whole temperature range studied. The purpose of the present communication is to describe in detail the results of our neutron diffraction study of $LaCoO_3$.

Sample Preparation

$LaCoO_3$ samples were prepared from $LaCl_3$ (99%) and $K_3Co(CN)_6$ (99%) (BDH Ltd.) using the precursor method of Gallagher (*11*). This involves decomposition of the complex cyanide precursor and annealing to 1273 K in air. It is known that this preparative method yields an essentially stoichiometric product, although it should be noted that, in general, the annealing temperature is critical (*10*). No evidence of impurity phases could be found in either X-ray or neutron diffraction patterns of the samples.

Neutron Diffraction

Two types of measurement were employed, both using diffractometers at the Institut Laue-Langevin. One involved use of the D2 diffractometer (*12*) which is a high-intensity, low-resolution instrument. Diffraction data (λ = 1.221 Å) were collected at several sample temperatures (4.3, 70.5, 278, 694, 1168, and 1243 K). A vanadium-tailed cryostat was used for measurements below room temperature, the sample being contained in a vanadium can. Measurements at higher temperatures employed a molybdenum element furnace and a Pt/13% Rh sample can. The latter had an electron-beam-welded cap, thus guaranteeing constant stoichiometry to the highest temperature (1243 K).

High-resolution diffractometry was performed using the DIA instrument (*13*). Data were again collected at several sample temperatures (4, 71, 293, 668, 1143, and 1248 K). The sample containers and cryostat used were those employed in the D2 experiments. However, a vanadium element furnace was used for measurements above

room temperature. A neutron wavelength of $\lambda = 1.511$ Å was used for the 4 and 71 K measurements, and $\lambda = 1.387$ Å for the remainder. Data were collected in the range $6° < 2\theta < 160°$.

The data were refined using a modification (*14*) of the Rietveld profile-refinement routine (*15*), with diffraction peaks arising from the Pt/13% Rh sample can being omitted from the refinements. All structure pa-

TABLE I

POSITIONAL AND ANISOTROPIC TEMPERATURE FACTORS

The coefficients of the anisotropic temperature factor are those for a complete temperature factor: $\exp[-0.25(a_1^{*2}U_{11}h^2 + a_2^{*2}U_{22}k^2 + a_3^{*2}U_{33}l^2 + 2a_1^*a_2^*U_{12}hk + 2a_1^*a_3^*U_{31}hl + 2a_2^*a_3^*U_{23}kl)]$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}
$LaCoO_3$, $R\bar{3}c$, 4 K									
La 2(a)	0.25	0.25	0.25	0.16(2)	0.16(2)	0.16(2)	−0.03(1)	−0.03(1)	−0.03(1)
Co 2(b)	0.0	0.0	0.0	0.26(5)	0.26(5)	0.26(5)	−0.13(4)	−0.13(4)	−0.13(4)
O 6(e)	0.1978(1)	0.3021(1)	0.75	0.30(2)	0.30(2)	0.45(3)	−0.16(2)	−0.08(1)	−0.08(1)
			R(profile) = 8.3% R(expected) = 10.5%						
$LaCoO_3$, $R\bar{3}c$, 71 K									
La 2(a)	0.25	0.25	0.25	0.08(2)	0.08(2)	0.08(2)	−0.01(1)	−0.01(1)	−0.01(1)
Co 2(b)	0.0	0.0	0.0	0.24(5)	0.24(5)	0.24(5)	−0.09(4)	−0.09(4)	−0.09(4)
O 6(e)	0.1982(1)	0.3018(1)	0.75	0.24(2)	0.24(2)	0.39(3)	−0.16(2)	−0.05(2)	−0.05(2)
			R(profile) = 8.7% R(expected) = 7.3%						
$LaCoO_3$, $R\bar{3}c$, 293 K									
La 2(a)	0.25	0.25	0.25	0.36(1)	0.36(1)	0.36(1)	−0.11(1)	−0.11(1)	−0.11(1)
Co 2(b)	0.0	0.0	0.0	0.33(3)	0.33(3)	0.33(3)	−0.10(1)	−0.10(1)	−0.10(1)
O 6(e)	0.2003(1)	0.2997(1)	0.75	0.51(1)	0.51(1)	0.79(3)	−0.32(2)	−0.12(1)	−0.12(1)
			R(profile) = 7.9% R(expected) = 9.8%						
$LaCoO_3$, $R\bar{3}c$, 668 K									
La 2(a)	0.25	0.25	0.25	0.89(2)	0.89(2)	0.89(2)	−0.28(1)	−0.28(1)	−0.28(1)
Co 2(b)	0.0	0.0	0.0	0.92(5)	0.92(5)	0.92(5)	−0.32(3)	−0.32(3)	−0.32(3)
O 6(e)	0.2025(1)	0.2972(1)	0.75	1.26(2)	1.26(2)	1.73(4)	−0.56(2)	−0.40(2)	−0.40(2)
			R(profile) = 9.4% R(expected) = 17.6%						
$LaCoO_3$, $R\bar{3}$, 668 K									
La 2(c)	0.2514(2)	0.2514(2)	0.2514(2)	0.92(2)	0.92(2)	0.92(2)	−0.29(1)	−0.29(1)	−0.29(1)
Co 1(a)	0.0	0.0	0.0	0.2(2)	0.2(2)	0.2(2)	−0.1(1)	−0.1(1)	−0.1(1)
Co 1(b)	0.5	0.5	0.5	1.4(4)	1.4(4)	1.4(4)	−0.5(2)	−0.5(2)	−0.5(2)
O 6(f)	0.2043(6)	0.2979(6)	0.759(1)	1.4(1)	1.1(1)	1.55(6)	−0.62(2)	−0.35(8)	−0.38(8)
			R(profile) = 8.7% R(expected) = 17.5%						
$LaCoO_3$, $R\bar{3}c$, 1143 K									
La 2(a)	0.25	0.25	0.25	1.73(3)	1.73(3)	1.73(3)	−0.56(2)	−0.56(2)	−0.56(2)
Co 2(b)	0.0	0.0	0.0	1.33(7)	1.33(7)	1.33(7)	−0.43(5)	−0.43(5)	−0.43(5)
O 6(e)	0.2067(4)	0.2930(4)	0.75	2.51(3)	2.51(3)	3.27(8)	−1.61(3)	−0.48(3)	−0.48(3)
			R(profile) = 11.4% R(expected) = 27.2%						
$LaCoO_3$, $R\bar{3}c$, 1248 K									
La 2(a)	0.25	0.25	0.25	2.00(3)	2.00(3)	2.00(3)	−0.66(2)	−0.66(2)	−0.66(2)
Co 2(b)	0.0	0.0	0.0	1.27(7)	1.27(7)	1.27(7)	−0.42(6)	−0.42(6)	−0.42(6)
O 6(e)	0.2076(4)	0.2923(4)	0.75	2.82(3)	2.82(3)	3.8(1)	−1.86(4)	−0.55(4)	−0.55(4)
			R(profile) = 12.6% R(expected) = 31.1%						

rameters were refined as well as anisotropic temperature factors, the counter-zero-point, reflection half-width and asymmetry parameters, and cell parameters. Trial models based on the space groups $R\bar{3}$ and $R\bar{3}c$ were used, the starting parameters being those obtained from the earlier neutron diffraction study (*8*). The scattering lengths used were $b_{La} = 0.83$, $b_{Co} = 0.25$, and $b_o = 0.58$ ($\times 10^{-12}$ cm) (*16*).

Results

The principle reason for making high-intensity diffraction measurements was to test for the presence of a (111) reflection (cubic ($\frac{111}{222}$)). This reflection is allowed in space group $R\bar{3}$ but not in $R\bar{3}c$. In fact, a (111) reflection could not be detected in any of the data sets collected using the D2 instrument. This suggests that any distortion to $R\bar{3}$ must be very small.

Profile refinements of the high-resolution data indicate that there is no reason to prefer $R\bar{3}$ to $R\bar{3}c$ symmetry at any temperature studied, except 668 K. At other temperatures, refinement in $R\bar{3}$ does not give a significant improvement in the reliability factor over that obtained from refinement in $R\bar{3}c$. In addition, refinements in $R\bar{3}$ result in a negative cobalt temperature factor. The results of $R\bar{3}c$ refinements are shown in Table I along with those for $R\bar{3}$ refinement of the 668 K data, the lattice parameters being given in the abstract. Important interatomic distances and angles obtained from the data are shown in Table II. The experimental and calculated profiles in $R\bar{3}c$ of a representative portion of the data for $LaCoO_3$ at 4 K are shown in Fig. 1. The *R* factors in Table I are those defined by Rietveld (*15*).

Discussion

The results described above indicate that at all temperatures studied, except possibly 668 K, $LaCoO_3$ has $R\bar{3}c$ symmetry with only one cobalt site. The derived 1143 K structure based on the simple cubic unit cell is shown in Fig. 2. The principal cause of the rhombohedral distortion, tilting of adjacent octahedra along the cubic axes, is easily observed, although there is only a small distortion of the simple cubic CoO_6 octahedra. The derived Co–O bond distances (1.92–1.97 Å) are in line with those obtained by summing tabulated ionic radii (*17*)

TABLE II

INTERATOMIC DISTANCES (Å) AND ANGLES (°)

	$R\bar{3}c$						$R\bar{3}$
	4 K	71 K	293 K	668 K	1143 K	1248 K	668 K
Co–O	1.924	1.926	1.932	1.948	1.963	1.968	1.956
Co(2)–O							1.940
La–O	2.428	2.432	2.451	2.483	2.527	2.535	2.487
	2.686	2.689	2.702	2.730	2.760	2.767	2.691
	2.994	2.995	2.992	3.002	3.003	3.005	2.769
O–Co–O	88.55	88.58	88.77	88.96	89.24	89.34	88.76
	91.45	91.42	91.23	91.02	90.76	90.66	91.24
	180.00	180.00	180.00	180.00	180.00	180.00	180.00
O–Co(2)–O							86.78
							93.22
							180.00
Co–O–Co	163.08	163.21	163.91	164.68	166.06	166.29	164.52

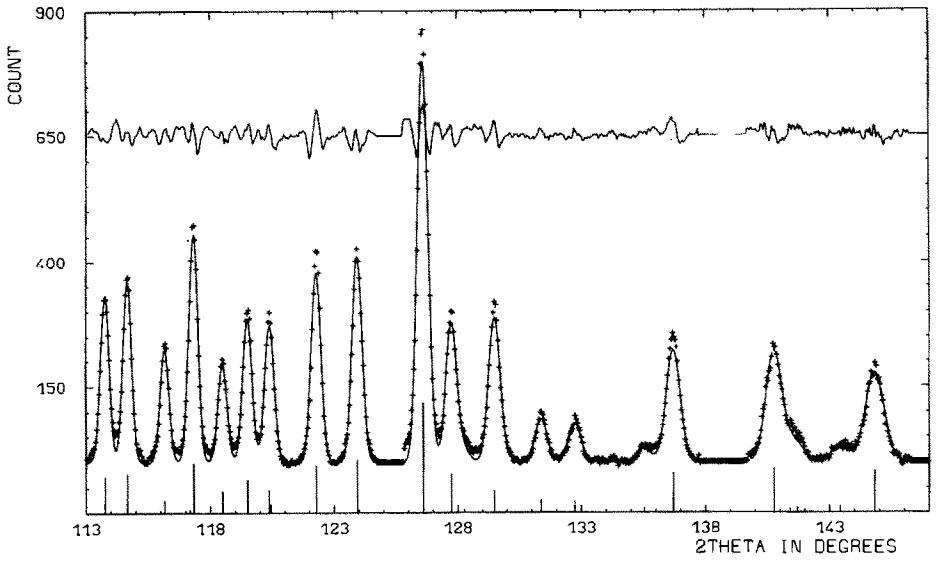

FIG. 1. High angle portion of the powder neutron diffraction (D1A) profile for $LaCoO_3$ at 4 K. The experimental points are marked (+), and the full curve passes through the calculated points. The vertical lines mark the positions of the Bragg reflections and the upper trace is the difference profile.

(high-spin Co^{III}, 1.95 Å; low-spin, Co^{III}, 1.89 Å).

The results of $R\bar{3}$ refinements indicate that there is a near-linear change in the structural parameters of $LaCoO_3$ over the temperature range studied (Fig. 3). In par-

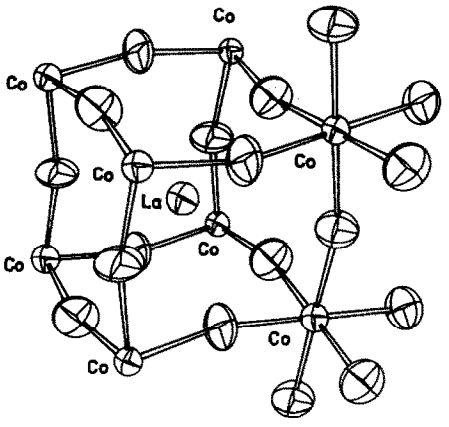

FIG. 2. The structure of $LaCoO_3$ at 1143 K based on a simple cubic unit cell. Only two CoO_6 polyhedra are shown for clarity. The atoms not labeled are oxygen anions.

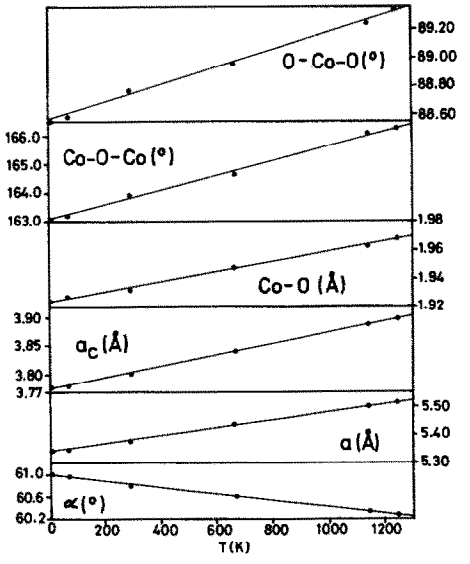

FIG. 3. The variation in rhombohedral cell parameters (a,α), pseudo-cubic cell parameter ($a_c = a/\sqrt{2}$), and important bond distances and angles of $LaCoO_3$ with temperature.

ticular, there is no discontinuity in the cell parameters or temperature factors through the proposed first-order transition at 1210 K as previously evidenced (*3–9*). This is consistent with DTA and electrical conductivity data which show no evidence of such a transition (*4*).

Evidence of possible cobalt(III) spin-state ordering is restricted to the positive temperature factors obtained by profile refinement of 668 K data in $R\bar{3}$. In $R\bar{3}$, adjacent cobalt atoms are inequivalent and lanthanum can move from the body center. The earlier X-ray powder diffraction data (*9*) were interpreted as revealing, at 673 K, a small displacement of lanthanum atoms as expected, but a very large separation in Co–O distances by ca. 0.45 Å as the oxygens move toward the low-spin cobalt(III) ion and away from the high-spin ion. This latter shift is surprisingly large, as the tabulated difference in ionic radii of the spin states is only 0.06 Å. In fact, the 668 K neutron data yields a difference of only 0.016 Å in Co–O distances, and the displacement of lanthanum atoms from the body-center positions is only 0.0024 Å. The discrepancy between the neutron and X-ray results (*9*) must arise because of the difficulty in accurately locating oxygen positions using integrated intensities of X-ray powder diffraction. Refinement of the 668 K neutron data in $R\bar{3}$ produces cobalt temperature factors which are anomalous in that one is high and the other low. In addition, relatively large estimated standard deviations of oxygen positions are obtained (0.0006 Å). The (111) reflection, the presence of which would indicate $R\bar{3}$ symmetry, could not be detected above background (ca. 5000 counts per 0.1° interval) in the 694 K D2 data. However, on the basis of structural parameters obtained from the 668 K data refinement in $R\bar{3}$, the (111) peak height should be only ca. 300 counts per 0.1° interval. Given the above, there must be some uncertainty regarding the existence of an ordering transition at 648 K.

The changes observed in the structure of $LaCoO_3$ with increasing temperature are

(i) CoO_6 polyhedra move toward perfect octahedra;

(ii) the rhombohedral distortion decreases (as evidenced by the increase in Co–O–Co angle toward 180°, and the decrease in rhombohedral angle);

(iii) the Co–O distances increase following the thermal expansion of the lattice.

The former two factors will increase the Co $3d$–O $2p$–Co $3d$ overlap, and hence the crystal field splitting, while the latter will cause a decrease. Since $LaCoO_3$ undergoes a high-order semiconductor-to-metal transition below 750 K, the net effect of the three factors must be to populate the σ^* band, which is synergistic with an increasing Co–O distance and a decreasing crystal-field splitting.

This behavior is consistent with delocalized σ^* and π^* orbitals through the whole temperature range. Spin-state ordering is still, in principle, possible but will only occur in a situation where the crystal-field splitting is of sufficient magnitude to induce a significant difference in Co–O distances between high- and low-spin ions. The results of the present work indicate that there is only marginal evidence, at one temperature only, for a change in space group from $R\bar{3}c$ to $R\bar{3}$. For $LaCoO_3$ therefore, the evidence supporting spin-state ordering is equally marginal.

Summary

The structure of $LaCoO_3$ in the temperature range $4 < T < 1250$ K has been reexamined. There is possible evidence of cobalt(III) spin-state ordering at 668 K, but at other temperatures studied only one cobalt site is present. The data are consistent with a gradual removal of the rhombohedral distortion from simple cubic symmetry as the

temperature is raised. In particular, no evidence of a previously reported first-order transition at 1210 K could be found. These results are in accord with our previously reported DTA and electrical conductivity data (*4*) and with a model assuming collective electron σ^* and π^* orbitals over the whole temperature range studied.

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