

Spin State Equilibria and Localized versus Collective *d*-Electron Behaviour in Neodymium and Gadolinium Trioxocobaltate(III)

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Magnetic susceptibility measurements and Mössbauer spectra show that NdCoO_3 and GdCoO_3 contain predominantly low-spin Co^{III} ions at low temperatures which transform partially to high-spin Co^{3+} until a certain temperature. Beyond this temperature, there is a transfer of e_g electrons from Co^{3+} to Co^{III} giving rise to di- and tetra-valent Co species followed by short-range ordering. Co^{3+} ions completely disappear at about 1000 K where there is a gradual transition from localized electron behaviour to collective behaviour. The cobaltates are semi-metals beyond this transition. The spin state equilibria and the electronic transition described here find support from electron transport properties, Mössbauer parameters as well as differential thermal analysis and X-ray data.

Transition metal oxides with perovskite structure exhibit metallic conductivity and Pauli paramagnetism if the spin of the transition metal ion $S \leq \frac{1}{2}$. The outer *d*-electrons in such systems are well described by band theory.¹⁻³ Typical examples of oxides exhibiting collective *d*-electron behaviour are LaTiO_3 and LaNiO_3 ($S = \frac{1}{2}$). If $S \geq 2$, however, these oxides show an atomic moment which is described by crystal field theory and Jahn-Teller distortion is found in the case where there are four *d*-electrons ($S = 2$). Thus, *d*-electrons in oxides like LaMnO_3 and LaFeO_3 generally exhibit localized behaviour.⁴ The factors which determine the spin state of the transition metal ion are the crystal field splitting, Δ_{cf} , and the exchange energy, Δ_{ex} . Ions exist in the low-spin or the high-spin state depending on whether Δ_{cf} is greater or less than Δ_{ex} . When $\Delta_{\text{cf}} \approx \Delta_{\text{ex}}$, however, both the spin states can coexist; in terms of overlap integrals,⁵ this situation would be found when the integrals $\Delta_{\text{cac}}^{\sigma}$ and $\Delta_{\text{cac}}^{\pi}$ are of the right order. In oxides where there is coexistence of the low- and the high-spin states, it becomes possible to study their properties in terms of the localized versus collective behaviour of *d*-electrons. Such a coexistence of high- and low-spin states is found in lanthanum trioxocobaltate(III), LaCoO_3 .

The properties of LaCoO_3 were first investigated in detail by Raccach and Goodenough⁶ who identified the plateau in the inverse magnetic susceptibility against temperature curve in the 400-650 K range with the variation of the population of the low versus high spin cobalt ions and establishment of short range order. Evidence for such ordering is found by the observation of phase transitions in differential thermal analysis as well as in other measurements. After the establishment of short range order, LaCoO_3 undergoes a symmetry change from $R\bar{3}c$ to $R\bar{3}$. While in $R\bar{3}c$, the two cobalt spin states do not occupy unique sites, in $R\bar{3}$ they do.⁶ Raccach and Goodenough⁶ also showed that LaCoO_3 undergoes a first-order transition around 1210 K due to a change from localized behaviour of *d*-electrons to collective behav-

ion; beyond this transition, LaCoO_3 becomes metallic. Raccach and Goodenough interpreted electron transport and other properties of LaCoO_3 in terms of the temperature-variation of spin- and valence-state equilibria of cobalt ions. We investigated the spin state equilibria in LaCoO_3 by employing Mössbauer spectroscopy and other measurements.⁷ These studies establish that cobalt ions exist predominantly in the low-spin ($t_{2g}^6 e_g^0$) Co^{III} state ($^1A_{1g}$) at low temperatures which transform partially to the high-spin ($t_{2g}^4 e_g^2$) Co^{3+} state ($^5T_{2g}$) up to 200 K. Mössbauer data indicate that above 200 K, there is electron transfer from Co^{3+} to Co^{III} producing divalent and tetravalent cobalt ions, causing a decrease in the relative population of Co^{3+} . Magnetic susceptibility data show a continuous increase in χT even beyond 200 K, since di- and tetra-valent Co ions are paramagnetic. At high temperatures, the population of Co^{3+} decreases significantly and completely disappears at the localized-collective electron transition temperature, 1210 K. All these changes are reflected in the electron transport properties of LaCoO_3 . These results seem to show that the crystal field and band limits of d -electrons may be distinct thermodynamic states. We have recently investigated⁸ the spin state equilibria in HoCoO_3 . In this cobaltate, the populations of Co^{III} and Co^{3+} equalize above ~ 300 K leading to an ordered phase and there is no evidence for electron transfer from Co^{3+} to Co^{III} . The temperature-variation of the Mössbauer [Co^{3+}] population as well as χT of HoCoO_3 are identical, both remaining constant above 300 K over a wide temperature range. Accordingly, the resistivity of HoCoO_3 is considerably higher than that of LaCoO_3 . This marked effect of the size and acidity of the central rare earth ion on the spin state equilibria in cobaltates has prompted us to take up a detailed investigation of neodymium and gadolinium trioxocobaltate(III) employing magnetic susceptibility, Mössbauer spectroscopy, X-ray diffraction, differential thermal analysis (d.t.a.) and electron transport properties.

EXPERIMENTAL

NdCoO_3 and GdCoO_3 were prepared by the decomposition of the respective hexacyanocobaltates. Both the cyanocobaltates decompose completely to the trioxocobaltates around 965 K. The trioxocobaltates are stable up to 1225 K without any measurable loss of oxygen as shown by thermogravimetry. D.t.a. was carried on the cyanocobaltates and trioxocobaltates using an Aminco differential thermal analyzer.

Lattice parameters of NdCoO_3 and GdCoO_3 were determined at different temperatures in the range 300–1080 K employing a General Electric XRD-6 diffractometer fitted with a furnace assembly. X-ray Debye–Waller factors were calculated using the diffraction profiles where the temperature factor $2M$ is given by,

$$2M = \frac{2}{m} \int_0^m f(v) dv \left(\frac{1}{2} + 1/\exp(hv/kT) - 1 \right) v^{-2} dv \bigg/ \int_0^m f(v) dv. \quad (1)$$

Magnetic susceptibilities of the samples were measured by the Gouy technique over the temperature range 80–1030 K for NdCoO_3 and 80–1200 K for GdCoO_3 .

For Mössbauer effect studies, the trioxocobaltates were used as ^{57}Co sources. In preparing the Mössbauer sources, a few drops of an aqueous solution of $^{57}\text{CoCl}_2$ were dropped on a disc of the trioxocobaltate and ^{57}Co diffused thermally into the trioxocobaltates at about 800 K for about 4 h. After thermal diffusion of ^{57}Co , the samples were cooled to room temperature. These sources were matched against enriched $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ single crystal absorbers. Lamb–Mössbauer factor data at various temperatures were obtained using a 310 enriched stainless steel absorber. All the Mössbauer spectra were recorded on a mechanical drive spectrometer.

Electrical resistivities of NdCoO_3 and GdCoO_3 were measured at 300–1250 K on pressed pellets (sintered at 1000 K) employing the four-probe technique. Seebeck coefficients relative to platinum were measured in the range 350–1200 K on pressed sintered pellets.

RESULTS AND DISCUSSION

Magnetic susceptibility data on NdCoO_3 and GdCoO_3 and LaCoO_3 are shown in fig. 1. Just as in LaCoO_3 , NdCoO_3 exhibits three regions in the $1/\chi_g$ against T curve: (i) a low temperature region where $1/\chi_g$ is essentially linear with temperature giving a lower effective magnetic moment; (ii) an intermediate temperature region where $1/\chi_g$ is independent of temperature and (iii) a high temperature region where $1/\chi_g$ is again linear with temperature, but gives a higher effective magnetic moment.* It appears that the cobalt ions exist predominantly in the low-spin Co^{III} state at low temperatures. As the temperature is increased, the diamagnetic Co^{III} ions are transformed progressively into paramagnetic high-spin Co^{3+} ions. The plateau in the susceptibility curve in the intermediate temperature region in NdCoO_3 may be associated with the spin state equilibrium and ordering of cobalt ions just as in LaCoO_3 . If so, we would expect to find an ordering transition in NdCoO_3 in the 400-600 K range. GdCoO_3 does not show a plateau region distinctly, but there is a change in

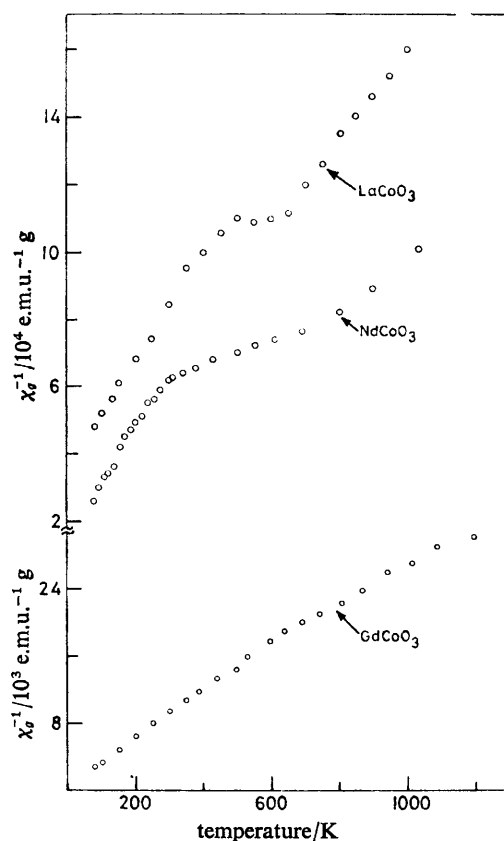


FIG. 1.—Plots of reciprocal susceptibility, $1/\chi_g$, against temperature for LaCoO_3 , NdCoO_3 and GdCoO_3 .

* The magnetic moments of NdCoO_3 and GdCoO_3 in the low-temperature region (where the cobalt is essentially diamagnetic) are found to be around 3.6 and $8.4 \mu_B$ respectively; the spin-only values for Nd^{3+} and Gd^{3+} are 3.80 and 7.94 respectively. In the high-temperature region the moments of NdCoO_3 and GdCoO_3 are 5.1 and $11.7 \mu_B$ respectively.

the slope of the susceptibility curve around 550 K (fig. 1) where there could be an ordering transition as noted earlier by Casalot and coworkers.⁹

Lattice parameters and unit cell volumes of NdCoO_3 and GdCoO_3 are shown as functions of temperature in fig. 2. Lattice parameters of NdCoO_3 show no significant changes other than those due to thermal expansion. Lattice parameters of GdCoO_3 show a change in slope around 580 K, a temperature close to that at which the susceptibility curve shows a change in slope.* We have not been able to establish any changes in crystal symmetry in NdCoO_3 and GdCoO_3 in the 400–600 K region similar to that found in LaCoO_3 by Raccach and Goodenough.⁶ However, Debye–Waller factor measurements do indicate the presence of transitions around 550 and 430 K respectively in NdCoO_3 and GdCoO_3 ,† the variation of the Debye–Waller factor in the transition region being quite similar to that found in the ordering region of LaCoO_3 .

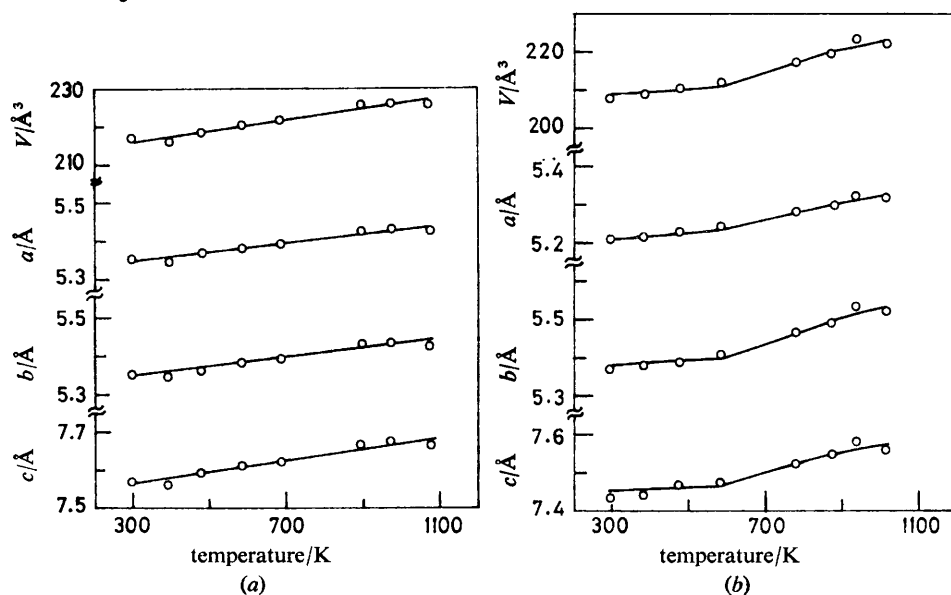


FIG. 2.—Variation of lattice parameters and unit cell volume of (a) NdCoO_3 and (b) GdCoO_3 with temperature.

D.t.a. curves of NdCoO_3 and GdCoO_3 show the presence of small endothermic transitions ($\Delta H \approx 1.5 \pm 0.2 \text{ kJ mol}^{-1}$) around 600 and 530 K respectively. These may correspond to the ordering transitions referred to earlier. The d.t.a. curve of LaCoO_3 also exhibits such endothermic ordering transitions.^{6, 7} D.t.a. curves of NdCoO_3 and GdCoO_3 also show endothermic transitions ($\Delta H \approx 1.5 \pm 0.4 \text{ kJ mol}^{-1}$) around 1030 and 970 K respectively. These high temperature transitions, which were also seen in the Debye–Waller factor data, arise from the electronic transition similar to that in LaCoO_3 as will be shown later.

The spin-state equilibria and the nature of ordering of cobalt ions can be under-

* Another change in slope may be present at higher temperatures ($> 900 \text{ K}$) in GdCoO_3 as reported by Casalot and coworkers,⁹ but this does not appear distinctly in the temperature range studied by us.

† Debye–Waller factor measurements show the presence of high-temperature transitions around 1000 K in both NdCoO_3 and GdCoO_3 and these transitions are discussed later.

stood by an examination of the variation of the magnetic susceptibility with temperature. Ordinarily, $\chi_g T$ of substances does not vary with temperature (eqn (2)):

$$\chi_g T = N^2 \mu^2 / 3R. \quad (2)$$

However, when the proportion of the paramagnetic species varies with temperature, $\chi_g T$ does not remain constant, but obeys relation (3) where n and m represent the proportions of the paramagnetic (high-spin) and the diamagnetic (low-spin) ions respectively:

$$\chi_g T = \frac{N^2 \mu^2}{3R} \times \frac{n}{n+m}. \quad (3)$$

Relation (3) can be rewritten as:

$$\frac{n}{m} = \frac{1}{(N^2 \mu^2 / 3R \chi_g T - 1)}. \quad (4)$$

In the present situation, therefore, the ratio $\text{Co}^{3+}/\text{Co}^{\text{III}}$ should keep increasing with temperature. Plots of $\chi_g T$ against temperature for NdCoO_3 and GdCoO_3 are shown in fig. 3 along with the curve for LaCoO_3 . These curves show that $\chi_g T$ increases with temperature as expected, although not in a uniform manner. There is a distinct change in slope at about 400 K for NdCoO_3 and 600 K for GdCoO_3 . The above treatment of the magnetic susceptibility data is justified for the following reasons: (i) all the rare earth trioxocobalates give the spin-only values of the magnetic moments of the rare earth ions from the low-temperature susceptibility data; (ii) at very low temperatures, cobalt is almost entirely in the diamagnetic low-spin state. The behaviour of NdCoO_3 is very similar to that of LaCoO_3 where La^{3+} is diamagnetic. As such, the temperature-variation of χT represents the spin- and valence-state populations of cobalt and cannot be due to the rare earth ion. (iii) The susceptibility

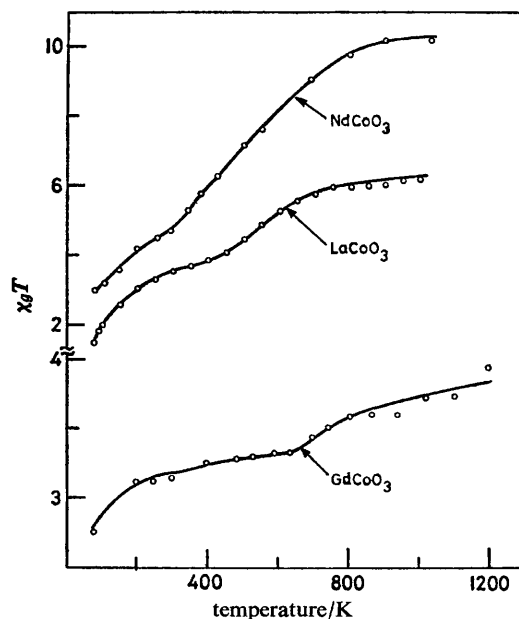


FIG. 3.—Plots of $\chi_g T$ against temperature.

curve shows the same general features such as the plateau in the intermediate temperature region after subtracting the contribution due to the rare earth ion. (iv) χT has been found to be invariant over a wide temperature range (above 300 K) in HoCoO_3 where $\text{Co}^{3+}/\text{Co}^{\text{III}}$ is constant. (v) Studies on rare earth metal trioxoferrates¹⁰ has clearly shown that there is no interaction between the rare earth ion and Fe^{3+} . (vi) There is no evidence for magnetic ordering in any of these trioxocobaltates and the Curie Law (rather than the Curie-Weiss law) is, therefore, applicable.

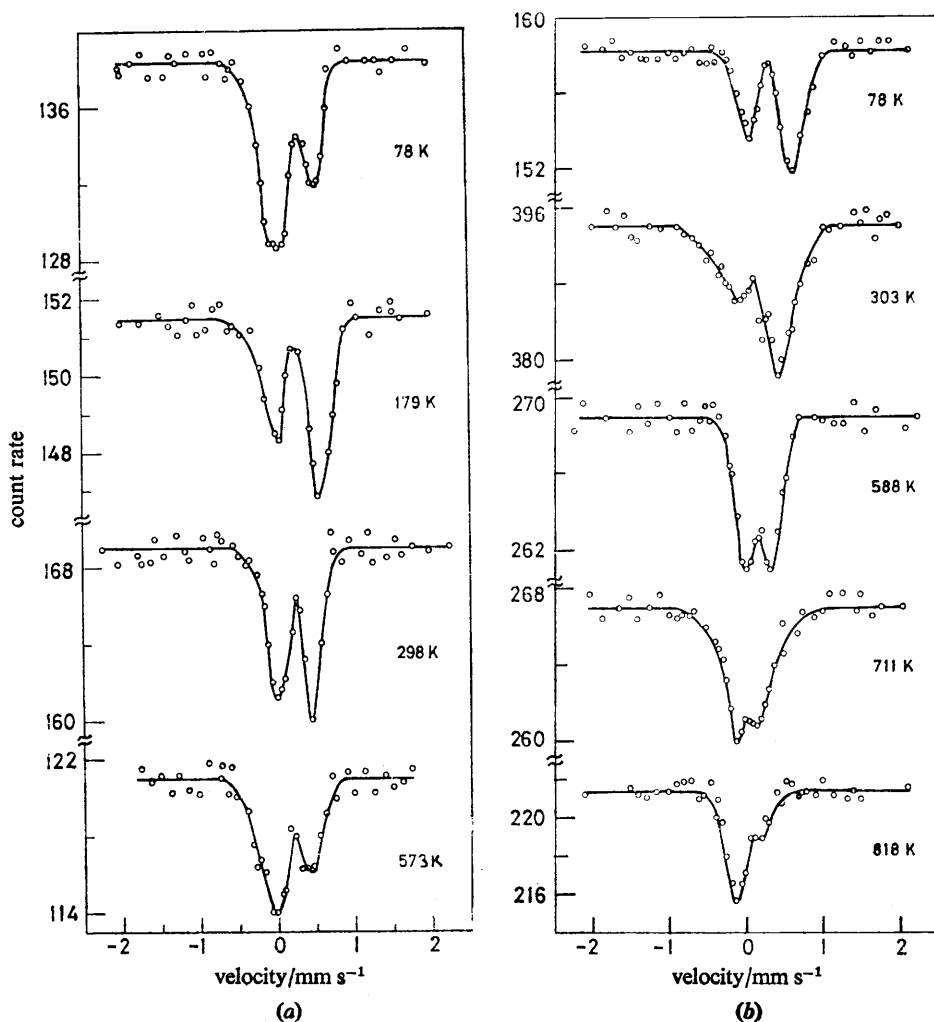


FIG. 4.—Mössbauer spectra of (a) NdCoO_3 and (b) GdCoO_3 ; ^{57}Co matched against $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ single crystal absorber.

We sought to further investigate the spin-state equilibria in NdCoO_3 and GdCoO_3 by recording Mössbauer spectra at different temperatures. Typical Mössbauer spectra obtained by using NdCoO_3 and GdCoO_3 as sources are shown at different temperatures in fig. 4. The spectra show two resonances, one centred close to 0.0 mm s^{-1} and another around 0.5 mm s^{-1} . Based on isomer shift systematics as well

as by analogy with LaCoO_3 and HoCoO_3 , we can safely assign the high energy resonance to Fe^{3+} and the low energy resonance to Fe^{III} arising out of electron-capture decay of Co^{3+} and Co^{III} respectively.⁷ The intensities of the two resonances were determined from the row dips as well as the area under resonances assuming that the Debye–Waller factor for the two states are identical. Based on this assignment, we would expect the relative intensities of the two resonances to comply with eqn (3). However, a plot of the relative proportion of Fe^{3+} (as measured by the intensity of the high energy resonance) shows that in both NdCoO_3 and GdCoO_3 , $[\text{Fe}^{3+}]$ increases up to a certain temperature and then decreases, eventually becoming zero at a high temperature (fig. 5). This behaviour is similar to that in LaCoO_3 , which shows an increase of $[\text{Fe}^{3+}]$ up to 200 K followed by a progressive decrease, reaching zero concentration at 1210 K where the first-order localized-itinerant electron transition is observed⁷ (see fig. 5). We thus see that the $\chi_g T$ data and Mössbauer data show similar behaviour only in the low-temperature region (ascending portions of the curves in fig. 5).

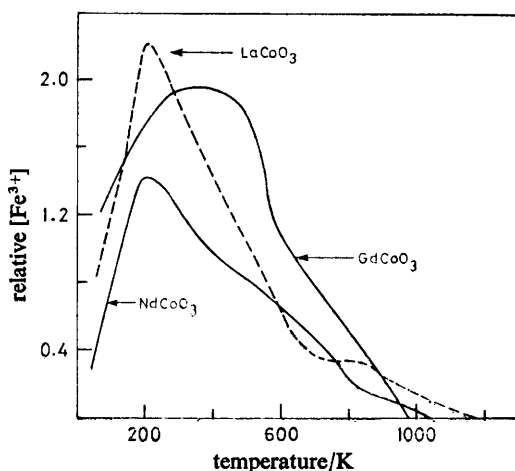


FIG. 5.—Temperature-variation of the relative population of high spin Fe^{3+} (in NdCoO_3 and GdCoO_3) with respect to the other states of Fe. Here, the ratio of the intensity of the high-energy resonance due to Fe^{3+} to that of the low-energy resonance (due to Fe^{III} and other states) is plotted as the ordinate. The dotted line in the figure gives the temperature-variation of Fe^{3+} in the case of LaCoO_3 .

This apparent discrepancy between the susceptibility and the Mössbauer data can be understood if we propose that at high temperatures (beyond the temperature where $[\text{Fe}^{3+}]$ reaches a maximum in fig. 5), there is electron-transfer from Co^{3+} to Co^{III} giving rise to divalent Co^{II} ($t_{2g}^6 e_g^1$) and tetravalent Co^{IV} ($t_{2g}^4 e_g^1$) which are paramagnetic. The corresponding states of iron, Fe^{II} and Fe^{IV} , would however, have isomer shifts near the zero velocity position just as Fe^{III} . Such electron-transfer via orbitals of e_g symmetry is compatible with $\Delta_{\text{cac}}^{\sigma} > \Delta_{\text{cac}}^{\pi}$. We do not see in the Mössbauer spectra evidence for the formation of Co^{2+} and Co^{IV} proposed by Raccah and Goodenough⁶ in the case of LaCoO_3 ; Fe^{2+} produced by Co^{2+} would have given rise to a large isomer shift of the order of 1.0 mm s^{-1} which we have not detected. We, therefore, conclude that at low temperatures, both NdCoO_3 and GdCoO_3 contain mainly diamagnetic Co^{III} ions which are partly transformed to paramagnetic Co^{3+} ions up to a particular temperature. Above this temperature, an e_g electron is transferred from Co^{3+} to Co^{III} to form Co^{IV} (or Co^{4+}) and Co^{II} ion pairs. At very high

temperatures, the concentration of Co^{3+} decreases to below the limit of detection. The spin state equilibria of NdCoO_3 and GdCoO_3 are therefore very similar to those of LaCoO_3 and not to those of HoCoO_3 . The very small size and the high acidity of the holmium ion are apparently responsible for its unique behaviour.

An examination of fig. 5 shows that the temperature at which Co^{3+} (or Fe^{3+}) reaches a maximum (200 K in LaCoO_3 and NdCoO_3 and 400 K in GdCoO_3) is lower than the ordering temperatures evidenced in magnetic susceptibility and Debye-Waller factor measurements or in d.t.a. curves. Apparently, the ordering of the different spin-states of cobalt takes place after the electron-transfer from Co^{3+} to Co^{III} . However, there seems to be some relation between the ordering temperatures seen in the various measurements and the temperatures at which the relative proportion of Fe^{3+} becomes unity in fig. 5 (500, 400 and 600 K in LaCoO_3 , NdCoO_3 and GdCoO_3 respectively). Similarly, in HoCoO_3 ordering begins when Co^{3+} and Co^{III} states are equally occupied.⁸

In the light of our Mössbauer studies, we find that some of the conclusions of Casalot and coworkers⁹ regarding the spin state equilibria in GdCoO_3 are in error. For example, these workers suggest that the concentration of Co^{3+} is about 30 % at 270 K which increases to 100 % in the range 500–570 K. The present results are not fully consistent with the model employed by Bari and Sivardiere¹¹ to explain the second and first order low spin-high spin transitions in trioxocobaltates since we do not see evidence for increasing high-spin Co^{3+} population up to the transition temperatures. Further, ordering sets in after the thermal population of Co^{3+} state.

Examination of fig. 5 shows that $[\text{Co}^{3+}]$ eventually becomes zero at 1210 K in LaCoO_3 corresponding to the first-order localized \rightleftharpoons collective electron transition. At this temperature, LaCoO_3 shows a significant thermal anomaly. A ΔH value of $\sim 4.2 \text{ kJ mol}^{-1}$ was estimated earlier⁷ for this transition, but there is a recent report¹² based on e.m.f. measurements that ΔH is close to 15 kJ mol^{-1} . Beyond this 1210 K transition, LaCoO_3 becomes metallic. NdCoO_3 and GdCoO_3 show similar thermal anomalies at 1030 and 970 K respectively around which temperatures, $[\text{Co}^{3+}]$ becomes zero; the ΔH of these transitions is, however, considerably smaller than in LaCoO_3 as mentioned earlier. It appears that these high temperature transitions in neodymium and gadolinium trioxocobaltate(III) also correspond to the localized-collective electron transition although the nature of the transition may be different. We shall discuss this transition later when we examine the results from other measurements. It is relevant to note at this point that after the high-temperature transition, the trioxocobaltates exhibit only a single resonance (corresponding to the lower energy resonance assigned to Co^{III} , Co^{4+} , Co^{IV} or Co^{II}). Under the second conditions, there would be no localized e_g electrons, but σ^* bands. A possible description of the two cobalt sites at very high temperatures would be, $(t_{2g}^5 \sigma^{*1}) (t_{2g}^5 \sigma^{*1})_{\frac{1}{2}-g}$ and $(t_{2g}^4 \sigma^{*2-e})_a (t_{2g}^5 \sigma^{*1})_{\frac{1}{2}-g}$ where the $t_{2g}^5 \sigma^{*1}$ corresponds to the intermediate Co^{III} state with $t_{2g}^5 e_g^1$ configuration.

Changes in the centre shifts of the two Mössbauer resonances of NdCoO_3 and GdCoO_3 with temperature are shown in fig. 6. We see that the centre shifts, particularly of the high energy resonance due to Fe^{3+} , decrease appreciably in the ordering region just as in LaCoO_3 .⁷ In the case of NdCoO_3 , this occurs before 400 K when the ordering sets in and the relative proportion of $[\text{Co}^{3+}]$ is unity. In GdCoO_3 , the decrease in centre shift is much more marked and occurs below 600 K where the relative $[\text{Co}^{3+}]$ reaches unity. The decrease in centre shifts indicates a greater covalency resulting from an increase in the overlap integrals ($\Delta_{\text{cac}}^{\sigma} > \Delta_{\text{cac}}^{\pi}$). Such an increase in the overlap integrals would be responsible for the delocalization of e_g electrons to form σ^* bands. It appears that the compounds become more and more

SPIN STATE EQUILIBRIA

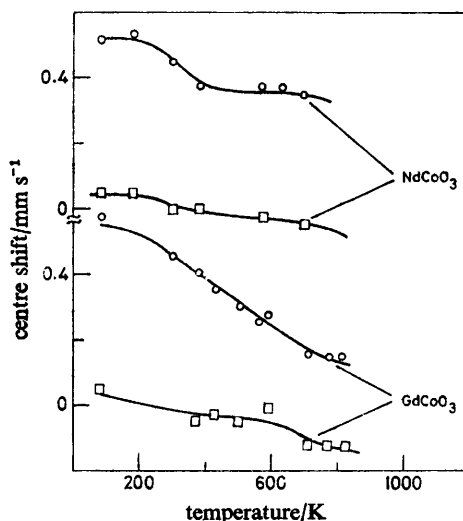


FIG. 6.—Variation of centre shift with temperature: \circ , high energy resonance due to Fe^{3+} ; \square , low energy resonance due to Fe^{III} and other states.

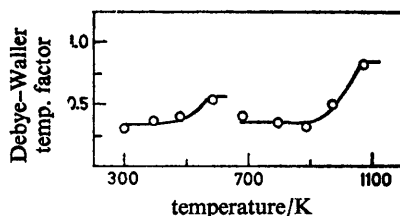


FIG. 7.—Variation of Debye-Waller factor of NdCoO_3 with temperature.

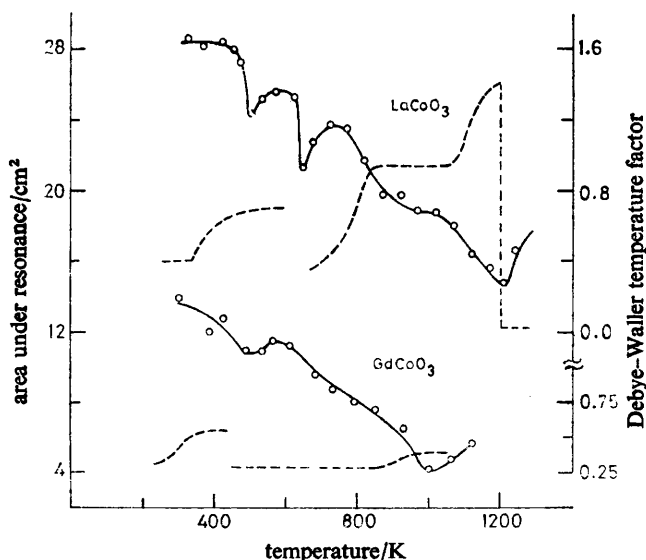


FIG. 8.—Area under the resonance (obtained by using a stainless steel absorber) of GdCoO_3 plotted against temperature. For purpose of comparison data on LaCoO_3 (from ref. (7)) are shown. Variation of Debye-Waller factor with temperature is shown by dotted lines.

covalent with increase in temperature, thus setting the stage for the localized \Rightarrow itinerant electronic transition where $[\text{Co}^{3+}]$ becomes zero. It is likely that both the large decrease in centre shift and the change in slope of the lattice parameters in GdCoO_3 around 580 K (fig. 2(b)) have the same cause, namely increased covalency of Co—O bonds in this temperature region. It would, however, be necessary to carry out a detailed study of the variation of bond lengths with temperature to further substantiate this conclusion.

As mentioned earlier, Debye–Waller factors of NdCoO_3 and GdCoO_3 show evidence for phase transitions. In the case of NdCoO_3 (fig. 7), the Debye–Waller factor increases with temperature significantly (~ 550 K) below the d.t.a. transition temperature (~ 600 K), indicating either short range ordering or a temperature region of larger atomic vibrations. In view of the evidence from susceptibility data and also by analogy with LaCoO_3 , this transition indicated by the Debye–Waller factor may be taken to indicate establishment of short range order. The Debye–Waller factor of GdCoO_3 also shows a similar transition at a temperature (~ 430 K) lower than the d.t.a. transition temperature (~ 530 K). Both NdCoO_3 and GdCoO_3 show evidence for high-temperature transitions around 1100 and 1000 K respectively (fig. 7 and 8) where d.t.a. also shows transitions. These phase transitions can be conveniently studied by an examination of the temperature variation of the Lamb–Mössbauer factor (area under resonance). It is pertinent to note here that the Lamb–Mössbauer factor is essentially equal to e^{-2M} while the Debye–Waller factor is $2M$. A plot of the area under the resonance against temperature in the case of GdCoO_3 clearly shows the two transitions around 500 and 1000 K (fig. 8). The Lamb–Mössbauer data agree well with the d.t.a. and X-ray data. It is significant that the transition at 1000 K in GdCoO_3 is preceded by a decrease in the Lamb–Mössbauer factor probably due to the occurrence of large ionic vibrations.⁶ Beyond the transition temperature, the Lamb–Mössbauer factor increases indicating the establishment of long-range order.

We have measured the electrical resistivity and Seebeck coefficient of NdCoO_3 and GdCoO_3 in order to understand the electron transport properties. The $\log \rho$ against $1/T$ plots (fig. 9) clearly show breaks around the same temperatures as the ordering transitions found by the d.t.a. and other techniques. The activation energy for conduction in both these trioxocobaltates in the low temperature region is somewhat higher* (0.2–0.3 eV) than the corresponding value (~ 0.1 eV) in LaCoO_3 . After the ordering temperature, however, the resistivity decreases sharply and shows evidence for an electronic transition (see fig. 9). Although we do not see an increase in resistivity with temperature in the high temperature region, the order of resistivity, low activation energy, as well as the Seebeck coefficient data (fig. 10) indicate collective electron (metal-like) behaviour above ~ 1000 K, around which temperature both these trioxocobaltates exhibit the phase transition.†

In both NdCoO_3 and GdCoO_3 , the transition at about 1000 K is not accompanied by as large an enthalpy effect (or entropy change) as in LaCoO_3 . In fact, d.t.a. curves show that the enthalpy changes in these transitions are of the same order as the

* The activation energy in this region probably represents the energy required to promote a t_{2g} electron to be σ^* band of itinerant e_g electrons at the low spin Co^{III} ions. The resistivity in the low temperature region (78–200 K) markedly increases in the order LaCoO_3 , NdCoO_3 , GdCoO_3 , HoCoO_3 .

† The trioxocobaltates remain p -type throughout the temperature range (78–1300 K) studied; this is obviously determined by the relative mobilities of the holes and electrons. The Seebeck coefficient is, however, small and constant at high temperature; this is typical of metal-like behaviour. It is significant that the decrease in α becomes marked at lower temperatures in NdCoO_3 than in GdCoO_3 ; this decrease is at still lower temperatures in LaCoO_3 . This is in accordance with the ordering temperatures and data in fig. 5 for these trioxocobaltates.

enthalpies of the ordering transitions found at lower temperatures. There appears to be no doubt that the transitions are electronic in origin particularly because of the absence of any structural change in the transition region (fig. 2(b) and 3). The small heat effects and the absence of metallic conduction are indicative of a gradual transition of the localized d -electrons to collective d -electrons. Occurrence of such a higher order electronic transition is indeed interesting. If the crystal field and band limits of d -electrons are distinct thermodynamic states, we can in principle have first or higher order transitions between the two states depending on structural and other factors.¹³

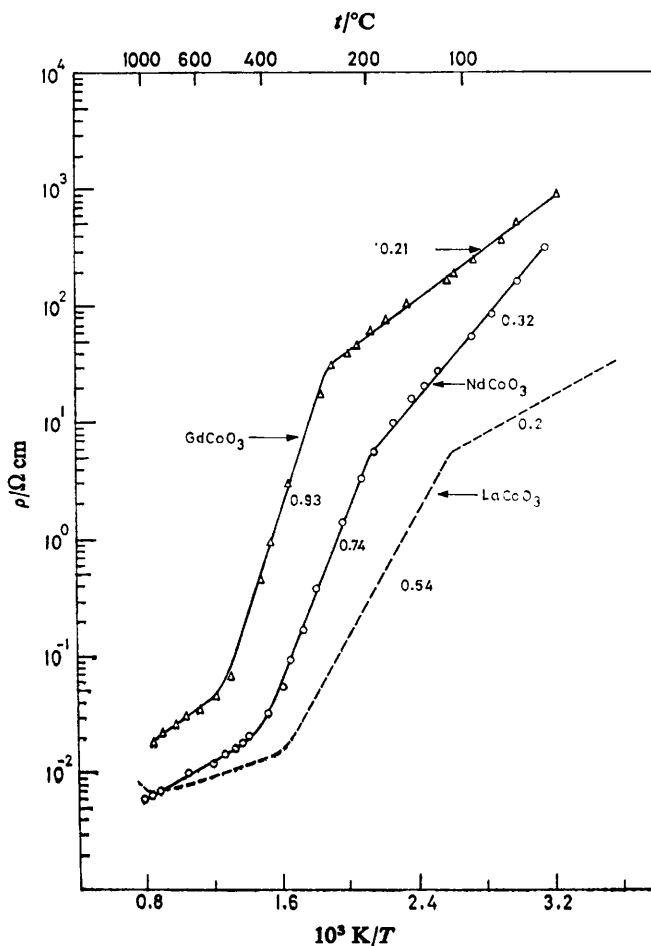


FIG. 9.—Plot of the logarithm of electrical resistivity against reciprocal of absolute temperature for NdCoO_3 and GdCoO_3 . Dotted line represents the data for LaCoO_3 . Values of E_a (in eV) are given against the curves.

In the rare earth metal trioxocobaltates, the acidity of the rare earth ion undoubtedly plays a crucial role in determining the nature of the transition, Nd^{3+} and Gd^{3+} being much more acidic than La^{3+} . The different magnitudes of polarization of the ligand orbitals by the rare earth ions would affect Δ_{cr} and hence the spin-state equilibria. Mössbauer isomer shifts also show the expected trend in these trioxo-

cobaltates. Thus, the Fe^{3+} resonance at 78 K is 0.50, 0.52, 0.57 or 0.65 mm s^{-1} when the rare earth ion is La, Nd, Gd or Ho respectively. The decreasing covalency in this series is also seen in terms of the increasing trend in resistivities of these cobaltates.

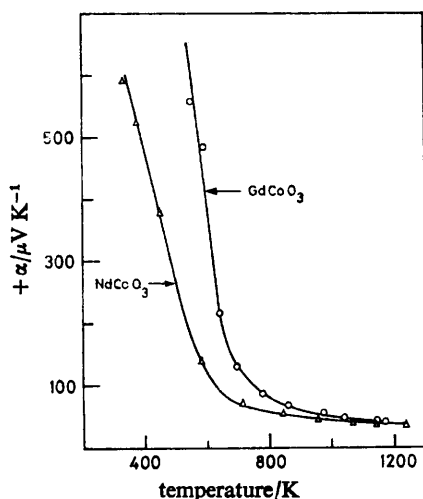


FIG. 10.—Seebeck coefficient data for NdCoO_3 and GdCoO_3 at different temperatures.

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