# Localized-to-Itinerant Electron Transitions in Rare-Earth Cobaltates

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Mössbauer studies show that cobalt ions in $\mathrm{LaCoO_3}$ exist predominantly in the low-spin $\mathrm{Co^{III}}$ state at low temperatures and partially transform to the high-spin $\mathrm{Co^{3+}}$ state up to 200 K. Above 200 K, $\mathrm{Co^{II}}$ and $\mathrm{Co^{4+}}$ ions are formed by the transfer of *d* electrons from $\mathrm{Co^{3+}}$ to $\mathrm{Co^{III}}$; $\mathrm{Co^{3+}}$ ions completely disappear at the first-order localized-to-itinerant electron transition temperature.

Raccah and Goodenough[1] (RG) showed the coexistence of low-spin and high-spin states of cobalt in $\mathrm{LaCoO_3}$ and observed a first-order phase change at 1210 K due to a unique transition of the $e_g$ electrons from the localized-to-itinerant state (LI transition). RG proposed a mechanism of the LI transition in terms of the temperature variations in the spin-state equilibria, symmetry changes, and ion movements. The observation of the LI transition implies that the crystal field and band limits of *d* electrons are distinct thermodynamic states.[1,2] We have examined the nature of the cobalt spin states and the LI transition in $\mathrm{LaCoO_3}$ by employing Mössbauer spectroscopy. We have also investigated whether the novel phase transitions from LI states of *d* electrons occur in other cobaltates as well.

Magnetic-susceptibility ($\chi_g$) data[1,3,4] of $\mathrm{LaCoO_3}$ indicate that the cobalt ions exist predominantly in the low-spin $\mathrm{Co^{III}}$ state at low temperatures; however, as the temperature is increased, these diamagnetic ions are transformed into paramagnetic high-spin $\mathrm{Co^{3+}}$ ions. An insight into this transformation can be obtained by examining the variation of $\chi_g T$ with $T$. If the transformation is between $\mathrm{Co^{III}}$ and $\mathrm{Co^{3+}}$, we can show that

$$\mathrm{Co^{3+}/Co^{III}} = (N^2\mu^2/3R\chi_g T) - 1\,, \tag{1}$$

where $\mu$ is the moment due to spin only of the $\mathrm{Co^{3+}}$ ion. A plot of $\chi_g T$ for $\mathrm{LaCoO_3}$ is shown in Fig. 1(a).

We sought to investigate this variation in the spin-state equilibrium by recording the Mössbauer spectra of $\mathrm{LaCoO_3}$ doped with $\mathrm{Co^{57}}$ and matched against a $\mathrm{K_4Fe(CN)_6}$ single-crystal absorber; Fig. 2 shows typical spectra at various temperatures. The spectra are characterized by two resonances whose relative intensities are temperature dependent. Based on the isomer-shift systematics,[5] the higher-energy resonance is attributed uniquely to high-spin $\mathrm{Fe^{3+}}$ arising out of the electron capture decay of $\mathrm{Co^{3+}}$ ($t_{2g}{}^4e_g{}^2$). The lower-energy resonance may be due to $\mathrm{Fe^{III}}$ arising out of low-spin $\mathrm{Co^{III}}$ ($t_{2g}{}^6e_g{}^0$). If this iden-

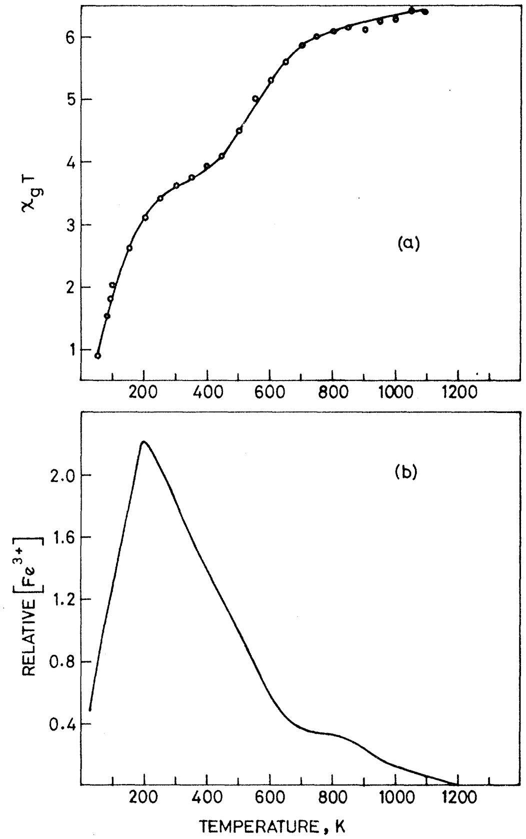

FIG. 1. (a) Plot of $\chi_g T$ against temperature for $\mathrm{LaCoO_3}$. (b) Temperature variation of the relative population of $\mathrm{Fe^{3+}}$ with respect to other states (obtained from Mössbauer data). The ratio of the intensity of the high-energy resonance (due to $\mathrm{Fe^{3+}}$) to that of the low-energy resonance is plotted as the ordinate.

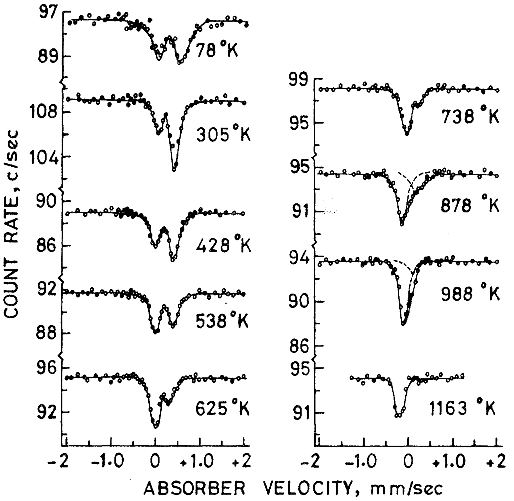

FIG. 2. Typical Mössbauer spectra of $\mathrm{LaCoO_3}$ at different temperatures.

tification is correct, the relative intensities of the two states should comply with (1). We, however, see [Fig. 1(b)] that while up to 200 K, the relative intensities indeed comply with (1),[6] beyond 200 K the relative intensity of the higher-velocity resonance decreases and completely disappears at 1210 K, corresponding to the LI transition. This discrepancy raises a question as to whether the lower-energy resonance can be uniquely attributed to the low-spin $\mathrm{Co^{III}}$ alone, although there is no doubt that at very low temperatures (<200 K), this resonance is essentially due to $\mathrm{Co^{III}}$. We can explain this behavior by assuming that the $e_g$ electrons from $\mathrm{Co^{3+}}$ ions are transferred to $\mathrm{Co^{III}}$ ions, creating divalent $\mathrm{Co^{II}}$ ($t_{2g}^6e_g^1$) and tetravalent cobalt with a configuration $t_{2g}^5e_g^0$ ($\mathrm{Co^{IV}}$), $t_{2g}^3e_g^2$ ($\mathrm{Co^{4+}}$), or $t_{2g}^4e_g^1$ ($\mathrm{Co^{iv}}$, intermediate spin). Since $\chi_gT$ increases rapidly with $T$, it appears likely that $\mathrm{Co^{II}}+\mathrm{Co^{4+}}$ pairs are formed. Electron capture decay of these cobalt ions would give $\mathrm{Fe^{II}}$ ($t_{2g}^6e_g^0$) and $\mathrm{Fe^{4+}}$ ($t_{2g}^3e_g^1$) in the Mössbauer spectra.[7] The isomer shifts of both these states are near the zero-velocity position and would overlap the resonance due to $\mathrm{Fe^{III}}$ ($t_{2g}^5e_g^0$). Electron transfer *via* $e_g$ orbitals rather than *via* $t_{2g}$ orbitals is compatible with $\Delta_{cac}^{\sigma} > \Delta_{cac}^{\pi}$.[1] The nature of the spin-state equilibria consistent with the RG mechanism for the LI transition is discussed in the footnotes.[8]

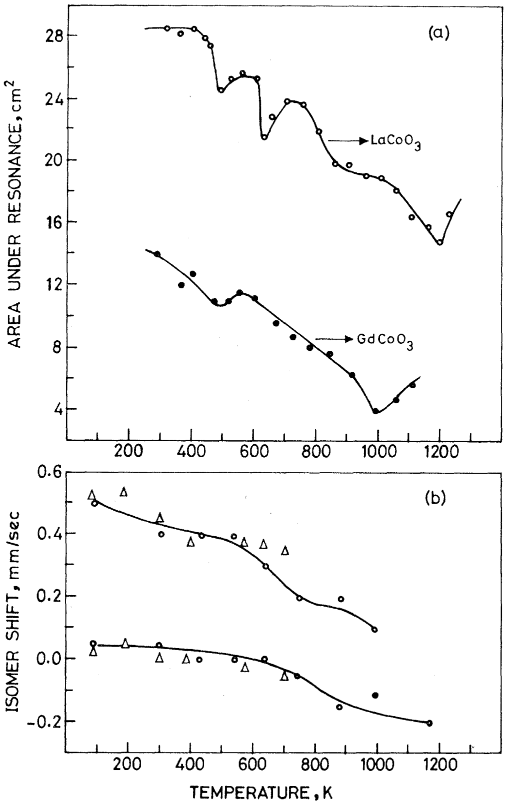

FIG. 3. (a) Area under resonance (obtained by using a stainless-steel absorber) for $\mathrm{LaCoO_3}$ and $\mathrm{GdCoO_3}$ plotted against temperature. (b) Isomer shifts of (1) $\mathrm{Fe^{3+}}$, and (2) the low-energy resonance for $\mathrm{LaCoO_3}$ and $\mathrm{NdCoO_3}$: circles, $\mathrm{LaCoO_3}$; triangles, $\mathrm{NdCoO_3}$.

RG have examined the crystal-symmetry changes in $\mathrm{LaCoO_3}$ employing x-ray diffraction. They observed an increase in the Debye-Waller factor in the $400<T<650$-K range followed by a symmetry change from $R\bar{3}C$ to $R\bar{3}$ due to an ordering of the $\mathrm{Co_I}$ and $\mathrm{Co_{II}}$ sites of the $R\bar{3}$ cell.[9] We have examined these and other structural changes by investigating the variation of the Lamb-Mössbauer (LM) factor (area under resonance) with temperature [Fig. 3(a)]. Our Mössbauer data agree excellently with the x-ray data of RG on $\mathrm{LaCoO_3}$. The LM factor seems to be more sensitive than x-ray diffraction or differential-thermal analysis (DTA) in identifying phase transitions. The LM factor shows transitions around 500, 650, 900, and 1210 K, of which the last three are shown by DTA as well; in the DTA the 1200-K transition is seen as a large endothermic peak with a $\Delta H$ of 1 kcal mole$^{-1}$. At 500 K, there is the onset of short-range order and a break in the resistivity-temperature curve. At 650 K, the plateau in the $(1/\chi_g)$-$T$ curve ends and the plateau in the $[\mathrm{Fe^{3+}}]$ curve [Fig. 1(b)] starts; above this temperature the Seebeck coefficient and resistivity become essentially constant. Metallic behavior of the resistivity is, however, seen only above the LI transition at 1210 K.

Above the transition at 1210 K, the LM factor increases with temperature, indicating establishment of long-range order. The decrease in the LM factor in the 970–1210-K range shows occurrence of large ionic vibrations.

An insight into the nature of the LI transition is also obtained through center-shift changes with temperature for the $Fe^{3+}$ state and to some extent for the other resonance as well. The center shift [Fig. 3(b)] decreases substantially in the region $650 < T < 900$ K, indicating either (a) a change in the mean square velocity, and/or (b) a change in the chemical shift. The observed changes cannot be entirely accounted for by (a) since these changes should have been reflected prominently in the LM factor changes. If we assume that the observed changes are due to a chemical shift, then the reduction in isomer shift would imply a greater covalency resulting in an increase in the overlap integrals. As already mentioned, $\Delta_{cac}{}^{\sigma} > \Delta_{cac}{}^{\pi}$; the increase in overlap integrals would initiate the delocalization of the $e_g$ electrons to form the $\sigma^*$ band (perhaps with the $t_{2g}$ electrons still localized). This provides a distinction between the various valence states at the two sites.

Having clarified to some extent the nature of the spin-state equilibria and the LI transition in $LaCoO_3$, we next examined several other rare-earth cobaltates, $RCoO_3$, employing magnetic susceptibility, Mössbauer spectroscopy, x-ray diffraction, DTA, and electron transport measurements. Our observations on these cobaltates are as follows: (i) The $(1/\chi_g)$-$T$ curves of all the cobaltates show the essential features of $LaCoO_3$, but the plateau region (where $1/\chi_g$ is temperature independent) varies from one cobaltate to another. (ii) Mössbauer spectra show temperature variations similar to $LaCoO_3$. Plots of the relative intensity of the high-velocity resonance (population of $Fe^{3+}$) against temperature, as in Fig. 1(b), show that $[Fe^{+3}]$ increases up to ~200 K and then decreases with increase in temperature, completely disappearing at relatively high temperatures corresponding to the LI transition temperatures (1030 and 980 K, respectively, when $R$ is Nd and Gd). (iii) Both the LM factor and DTA measurements show phase transitions at the LI transition temperatures[10] [see Fig. 3(a) for $GdCoO_3$]. The LM factor sharply increases after the transition temperature in all the cases. (iv) Isomer shifts vary continuously through the LI transitions [Fig. 3(b)] indicating that the transitions are not associated with large ionic displacements. (v) There are no significant changes in crystal structure or volume through the first-order LI transitions. (vi) Electrical-resistivity data of all the cobaltates are generally similar to those of $LaCoO_3$ with low activation energy (~0.1 eV) in the low-temperature region ($T < 200$ K), where a $t_{2g}$ electron is promoted to the $\sigma^*$ band of itinerant $e_g$ electrons. The resistivity, as well as the Seebeck coefficient, remains low and constant at relatively high temperatures, indicating metal-like behavior.

These observations on several of the cobaltates point out that the first-order LI transitions are essentially caused by the change in the entropy of $d$ electrons, as first suggested by RG in the case of $LaCoO_3$. We are presently continuing our investigations on all these cobaltates and intend publishing detailed reports in the near future.

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[5] We have established that low-spin $Co^{III}$ ions yield low-spin $Fe^{III}$ ions, while high-spin $Co^{3+}$ ions yield high-spin $Fe^{3+}$ ions. When $Co^{57}$ doped in $RFeO_3$ was used as the source, we only saw high-spin $Fe^{3+}$ spectra as in the orthoferrites [M. Eibshütz, S. Shtrikman, and D. Treves, Phys. Rev. 156, 562 (1967)], clearly showing that low-spin $Fe^{III}$ in the spectra of $RCoO_3$ arises from the existence of the low-spin $Co^{III}$ ions and not from electron capture effects. Our assignments of the isomer shifts to the two spin states are consistent with the earlier studies on cobalt compounds: G. K. Wertheim, Phys. Rev. 124, 761 (1961); V. G. Bhide and G. K.Shenoy, Phys. Rev. 147, 306, 309 (1966); W. Triftshäuser and P. P. Craig, Phys. Rev. 162, 274 (1967); J. G. Mullen and H. N. Ok, Phys. Rev. 168, 550, 563 (1968), and 181, 986(E) (1969).

[6] We have obtained the energy difference, $E(Co^{3+}) - E(Co^{III})$, from the Mössbauer data in the low-temperature region, and find it to be about 0.05 eV, a value close to that reported from susceptibility data (see Refs. 1, 3, and 4). In the low-temperature region (< 200 K), the activation energy for conduction is $\leq 0.1$ eV.

[7] There is also a possibility of exciton transfer in the 400–650-K region, as suggested by RG, to create $Co^{III}$ $(t_{2g}{}^5e_g{}^1)$ intermediate spin states. There seems to be no evidence from the Mössbauer data for the $Co^{2+}$ and $Co^{IV}$

states proposed by RG.

[8] In the range $650 < T < 1210$ K, the configurations of $Co_I$ and $Co_{II}$ sublattices would be $Co_a^{III}\,Co_b^{II}\,Co_c^{iii}\,Co_d^{4+}$ and $Co_a^{3+}\,Co_b^{4+}\,Co_c^{iii}\,Co_d^{II}$, respectively. At 650 K, $d \approx 0$. The preferential excursions of $La^{3+}$ ions towards $Co_I$ found by RG in the $650 < T < 925$-K range in $b > d$; the $Co_I$-O and $Co_{II}$-O separations are similar in this temperature range. Further, in this temperature range, it is likely that $a \approx b + c + d$, so that the $e_g$ electrons spend equal time at all Co ions, a behavior which is reasonable near the LI transition. As $T \rightarrow 1210$ K, $b \approx d \approx 0$, and the $La^{3+}$ ions are midway between the $Co_I$ and $Co_{II}$ subarrays. When $T > 925$ K, $a < c$ and the $Co_I$-O separation should be smaller than the $Co_{II}$-O separation, as observed by RG (Ref. 1). At $T \geqslant 1210$ K, the configurations of the two cobalt sites are likely to be $(t_2^{\,6}\sigma^{*\xi})_a(t_2^{\,5}\sigma^{*1})_{1/2-a}$ and $(t_2^{\,4}\sigma^{*2-\xi})_a(t_2^{\,5}\sigma^{*1})_{1/2-a}$.

[9] This is consistent with our Mössbauer results, except that we find that ordering occurs after the transfer of $\sigma$-bonding $d$ electrons from $Co^{3+}$ to $Co^{III}$ ions.

[10] $GdCoO_3$ shows transitions around 500 and 980 K, the latter corresponding to the LI transition. Our results on $GdCoO_3$ significantly differ from those of A. Casalot, P. Dougier, and P. Hagenmuller [J. Phys. Chem. Solids 32, 407 (1971)], who failed to see the first-order transition at 980°K.

# Effect of Pressure and Alloying on the Itinerant Antiferromagnetic Ordering in Cr-Fe Alloys

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We have investigated the effect of hydrostatic pressure on chromium-rich iron alloys with Ru and Mn additions. The results show that addition of Fe to Cr rotates the commensurate-incommensurate phase boundary and causes the reversal in the ordering sequence of the magnetic transitions observed in Cr-Fe alloys. Many other anomalous characteristics of Cr-Fe alloys are explained.

The itinerant antiferromagnetic transitions in chromium-rich alloys containing a wide variety of transition metals have been studied extensively at atmospheric pressure[1-9] and also at high pressure.[10-12] Of these, the behavior of Cr-Fe alloys[3-5, 10, 12] is unique and also poorly understood. The anomalous situation with regard to Cr-Fe alloys[4,5] is the following: (1) the lowering of $T_N$ when Fe is added; (2) the appearance of only the incommensurate (I) phase at low Fe concentration (<2%); (3) the appearance of the commensurate (C) phase at higher concentration of Fe, but at a lower temperature than the I phase; (4) the sharp and large resistivity rise ($\Delta\rho/\rho \approx 40\%$) at the I-C transition; and (5) the presence of local magnetic moment on Fe, which is only weakly coupled to the antiferromagnetic (AF) state of Cr. In this study we have investigated, under pressure, Cr-Fe alloys with Ru or Mn additions. The important finding is that a triple point between paramagnetic (P), I, and C phases exists in Cr-Fe alloys as in Cr-Mn or Cr-Ru alloys,[11] but the addition of Fe to Cr twists the I-C phase boundary and reverses the magnetic ordering sequence P-C-I observed in the latter alloys.[11] It is suggested that the sharp resistance anomaly at the I-C transition and the progressive loss of sharpness[10, 12] with pressure may be due to the closeness of the latter to the P-I transition at low pressure, and their separation at higher pressure.

Hydrostatic pressure was generated as described earlier.[13] The resistivity anomaly was used to follow the transitions. Figure 1 shows the resistivity as a function of temperature at various pressures, for Cr-3% Fe-0.5% Ru. In the inset the resistivity-temperature data for Cr-3% Fe is shown.[12] The addition of 0.5% Ru has raised the $T_N$ by 125°, and has broadened the sharp resistivity anomaly seen in Cr-3% Fe alloy. We believe this transition to be the P-C transition. When pressure is applied, $T_N$ falls at a rate of about 15°/kbar. In the range 9-11 kbar the resistance anomaly becomes almost as steep as that seen for the I-C transition in Cr-3% Fe alloy and has a clearly identifiable inflection point, which we be-