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Mössbauer Studies of the High-Spin–Low-Spin Equilibria and the Localized-Collective Electron Transition in $LaCoO_3$

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Mössbauer studies combined with magnetic-susceptibility data on well-characterized $LaCoO_3$ in the 4.2–1200-K region show that cobalt ions exist predominantly in the low-spin Co^{III} state at low temperatures which transform partially to high-spin Co^{3+} ions up to 200 K. Above 200 K, Co^{3+} and Co^{III} ion pairs transform to Co^{II} and Co^{4+} pairs. At high temperatures, the population of Co^{3+} decreases significantly and completely disappears at the localized-electron–collective-electron transition temperature at 1210 K. The variations of the Lamb-Mössbauer factor and the center shift with temperature provide valuable information on the high-spin–low-spin equilibria, as well as on the nature of the phase transitions and symmetry changes in $LaCoO_3$. All these changes are reflected in the transport properties of $LaCoO_3$. There appears to be little doubt that the first-order localized-electron–collective-electron transition in $LaCoO_3$ is caused essentially by the change in entropy of the *d* electrons.

I. INTRODUCTION

Transition-metal oxides with ReO_3 perovskite structure have been the subject of intense investigations[1–5] in recent years because of their interesting electrical and magnetic properties.[5c] These studies have led to the inference that if the cationic spins $S \leqslant \frac{1}{2}$, one observes metallic conductivity and Pauli paramagnetism. In such a case, the *d* electrons are well described by band theory and are called collective electrons. On the other hand, if $S \geqslant 2$, then the compounds have an atomic moment which can be described by crystal field theory, and in such cases the *d* electrons behave as localized electrons. The factors which determine whether in a given substance the transition-metal ion exists in the low-spin or in the high-spin state are essentially the crystal field splitting Δ_{cf} and the exchange energy Δ_{ex}. When $\Delta_{cf} > \Delta_{ex}$, the low-spin state is the stable state[3,6] as in WO_3, $LaTiO_3$, $LaNiO_3$, $CaVO_3$, and $ZnCo_2O_4$. On the other hand, when $\Delta_{cf} < \Delta_{ex}$, the transition-metal ion exists in the high-spin state[3,5,6] as in $LaCrO_3$, $LaMnO_3$, $LaFeO_3$, Sr_2CoSbO_6, etc. In the covalent crystal field approach, the parameter which determines whether electrons are localized or collective is the magnitude of the overlap integrals $\Delta_{cac}^{\sigma,\pi}$. If the overlap integrals are large enough, it is appropriate to construct collective electron orbitals out of the various orbitals of e_g and t_{2g} symmetry. These two approaches as shown by Liehr[7] are descriptions of the same phenomenon and suggest the existence of low-spin or collective electrons when Δ_{cf} is large, and that of high-spin or localized electrons when Δ_{cf} is small. Thus crystal field theory and band theory provide two limiting descriptions of the *d* electrons.

As indicated earlier, a variety of transition-metal oxide systems, particularly those possessing the perovskite structure, have been found to exhibit either localized-electron or collective-electron behavior of the *d* electrons. Thus, recent studies of several rare-earth chromites, manganites, and ferrites have established that the *d* electrons are localized in these systems.[5b] However, when $\Delta_{cf} \sim \Delta_{ex}$ (or $\Delta_{cac}^{\sigma,\pi}$ is of the right order), the low-spin and high-spin states can coexist and thereby give rise to interesting electrical and magnetic properties. In such a system, we could also hope to observe a transition from localized-electron to collective-electron behavior. $LaCoO_3$, which exhibits some unique electrical magnetic properties,[4,8–12] is one of the few oxide materials where the localized-electron $\rightleftharpoons$ collective-electron transition has been suggested to occur.[3,8]

Goodenough[3,8,13] has described a unifying model to describe the properties of $LaCoO_3$. He suggests the coexistence of the diamagnetic trivalent cobalt (Co^{III}) state $S=0$ and the paramagnetic trivalent cobalt state (Co^{3+}) $S=2$ in $LaCoO_3$, whereas Heikes *et al.*[12] explain the magnetic susceptibility of $LaCoO_3$ on the basis of a low-temperature low-field state with $S=1$. Raccah and Goodenough[8] observe that the first-order transition at 1210 K in $LaCoO_3$ is a localized-electron $\rightleftharpoons$ collective-electron transition. Goodenough's mechanism for electrical conduction in $LaCoO_3$ presumes the formation of high-spin divalent cobalt and low-spin tetravalent cobalt ion pairs. Although the hopping mechanism of conduction suggested by Goodenough is not consistent with the Hall-effect data of Acket[14a] on

Sr^{2+}-doped $LaCoO_3$, the Hall-effect data of Gerthsen and Hardtl[14b] appear to be in tune with Goodenough's mechanism.

Of the various techniques, Mössbauer spectroscopy provides the most sensitive and direct method to identify the various valence states in the solid through the isomer shift. Not only does it serve as a diagnostic tool[15–19] for determining the valence states, but it also gives valuable information on the degree of covalency and through it information about the variation of Δ_{cac}. In view of the fortunate circumstance that Co^{57} is a Mössbauer isotope, we undertook a detailed and systematic study of well-characterized samples of $LaCoO_3$ employing Mössbauer effect for the 14.4-keV γ rays from Fe^{57} formed out of the electron-capture decay of Co^{57}. We have also studied electron transport and other properties of these samples to fully characterize them and to provide a unified explanation of all the properties based on the results of our Mössbauer studies.

Our Mössbauer studies coupled with magnetic-susceptibility results have unambiguously shown the coexistence of diamagnetic low-spin Co^{III} ($S = 0$) and paramagnetic high-spin Co^{3+} ($S = 2$) ions at low temperatures. Above 200 K, an e_g electron is transformed from the high-spin Co^{3+} ions to the low-spin Co^{III} ions, to produce Co^{II} and Co^{4+} ion pairs. As temperature increases further, the Co^{3+} population decreases progressively to disappear completely above the first-order transition temperature at 1210 K.

The local-symmetry changes reported from x-ray-diffraction studies by Raccah and Goodenough[8] are seen in terms of the corresponding changes in the Lamb-Mössbauer factor. Isomer-shift data coupled with the Lamb-Mössbauer-factor changes occurring at the transition temperature suggest that ΔS_{el} (electronic contribution to entropy change) is the real cause for the observed transition. Further, these studies establish Goodenough's hypothesis that the crystal field and band limits are distinct thermodynamic states.

II. EXPERIMENTAL

$LaCoO_3$ was prepared by the oxalate method reported by Raccah and Goodenough[8] and also by the cobalticyanide method of Gallagher[20] employing Lindsay 99.9% or Johnson and Matthey spectroscopically pure starting materials. The course of formation of $LaCoO_3$ by the two methods was followed by thermogravimetry employing an Aminco recording thermobalance. Oxalate decomposition in air gives $LaCoO_3$ around 1170 K, where cobalticyanide decomposition is complete at 970 K. Considering the lower temperature of formation and the chemical nature of the preparation, we feel that $LaCoO_3$ prepared by the cobalticyanide method yields more stoichiometric samples.

The nature of the phase transitions as studied by differential thermal analysis (DTA) employing an Aminco or DuPont thermoanalyzer of the two samples of $LaCoO_3$ was somewhat different. $LaCoO_3$ obtained by the cobalticyanide method showed two very broad endothermic peaks at 680 K (initiating[21] at 610 and 750 K, respectively) in addition to a sharp peak around 1190 K. In $LaCoO_3$ obtained from oxalate decomposition, the first two transitions are at lower temperatures and are associated with much lower enthalpy changes[3,8]; the high-temperature transition occurs sharply at 1210 K. The enthalpy change associated with this ~1210-K peak was ~1 kcal/mole. It appears that these phase transitions are quite sensitive to the method of preparation, possibly because of differences in the order and stoichiometry in the samples. Similarly, $LaCoO_3$ prepared by mixed-nitrate decomposition gives a very broad DTA peak centered around 870 K and a sharp peak at 1210 K. The phase transitions of $LaCoO_3$ show interesting hysteresis phenomena. Thus, the cooling curves of $LaCoO_3$ (heated above 1220 K) do not show the DTA transition peaks; the DTA curves obtained on reheating such samples show the transitions only after keeping for many hours.

While preparing Mössbauer sources, two different procedures were followed. In one of them, Co^{57} was doped in the corresponding compounds before thermal decomposition leading to $LaCoO_3$. In the other, a few drops of an aqueous solution of $Co^{57}Cl_2$ were dropped on the disk of $LaCoO_3$. Co^{57} was then thermally diffused in $LaCoO_3$ around 1170 K for 4 h. After thermal diffusion of Co^{57}, the sample was slowly cooled to room temperature. Both these sources gave almost the same results. These sources were matched against 310 enriched stainless-steel absorber or against $K_4Fe(CN)_6 \cdot 3H_2O$ single-crystal absorber. With the latter it was possible to resolve the spectra, whereas with the former the absorption was large and although the spectra could not be resolved, it provided useful data on the Lamb-Mössbauer factor.

Mössbauer spectra were obtained on a mechanical linear-drive spectrometer described earlier.[22] The spectra were obtained over a temperature range 4.2–1200 K. The temperature of the sample in the cryostat or in the furnace could be maintained to within ± 2°. The observed spectra were fitted to machine-computed Lorentzian.

We have measured the magnetic susceptibility of one of the samples over the temperature range 78–1000 K (Fig. 1) and the results are in agreement with those published earlier.[12] Four-probe electrical resistivity ρ and Seebeck coefficients α of the pressed pellets of $LaCoO_3$ prepared by different methods were measured in the range 78–1280 K

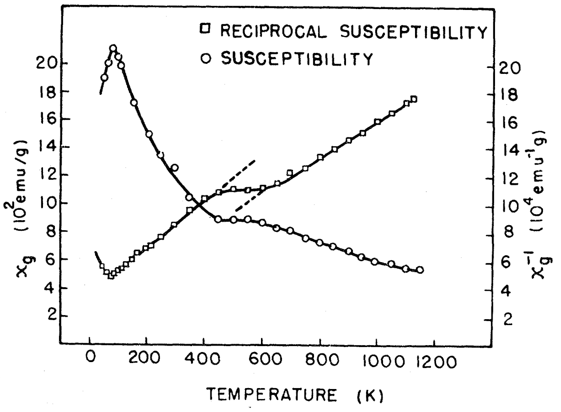

FIG. 1. Plot of susceptibility and reciprocal susceptibility vs temperature for $LaCoO_3$.

(Fig. 2). These measurements of electrical properties and magnetic susceptibility were necessary to fully characterize the samples of $LaCoO_3$ investigated by us. The conductivity data clearly indicate an exponential increase in σ up to ~ 200 K, $\sigma = \sigma_0 e^{-E_a/kT}$, typical of semiconducting behavior with an E_a of ~ 0.1 eV; then in the 200–400-K range the conductivity increases slightly and the E_a is 0.2 eV; σ increases sharply in the 400–650-K range and goes through a broad maximum in the 650–1000-K range. Only a slight decrease in σ is noted above 1210 K. The value of α decreases (from about +350 μV/°C) sharply up to 400 K, followed by a slower rate of decrease in the 400–650-K range and a still lower rate of decrease up to ~ 900 K; α is essentially constant beyond 900 K and through the high-temperature transition at 1210 K.

III. RESULTS AND DISCUSSION

The $1/\chi_g$-T curve of $LaCoO_3$ (Fig. 1) shows three regions: (i) a low-temperature region in which $1/\chi_g$ is almost linear with T, giving a lower effective magnetic moment; (ii) an intermediate-temperature region in which $1/\chi_g$ is almost independent

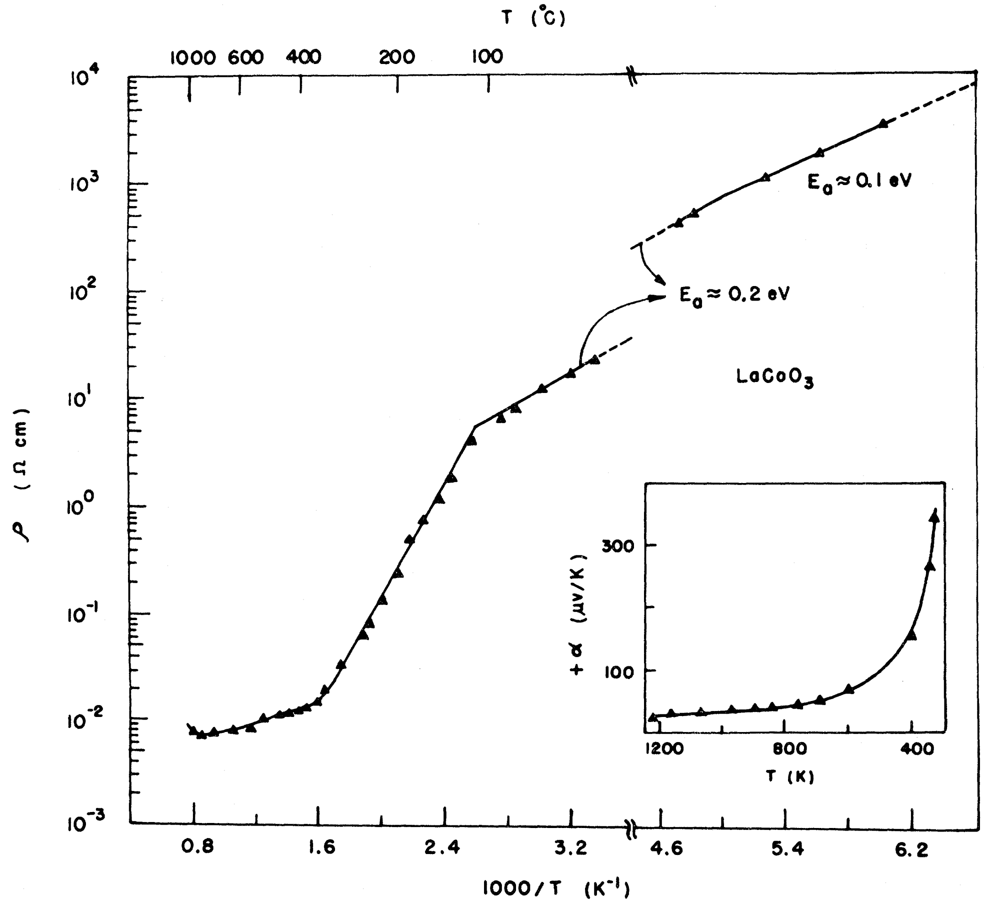

FIG. 2. Plot of the logarithm of electrical resistivity vs reciprocal of absolute temperature, for polycrystalline $LaCoO_3$. Inset shows the Seebeck coefficient vs absolute temperature.

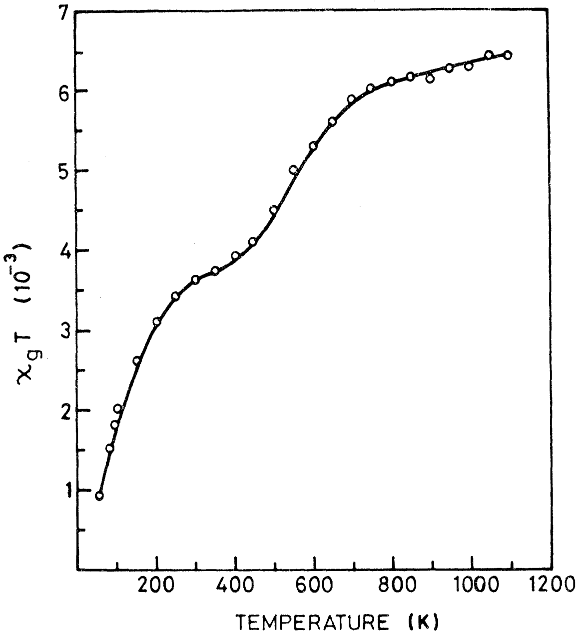

FIG. 3. Plot of $\chi_g T$ against temperature for $LaCoO_3$.

of temperature; (iii) a higher-temperature region in which the $1/\chi_g$-T variation is again almost linear, but gives a higher effective magnetic moment. Such a plateau between two temperature regions exhibiting different slopes has been reported in $MnAs_{1-x}P_x$ and has been identified with a variation in the population of low-spin vs high-spin ions.[4-7] The magnetic susceptibility studies of $LaCoO_3$ show that the cobalt ions exist predominantly in the low-spin Co^{III} state at low temperatures. However, as the temperature is increased, these diamagnetic ions are transformed progressively into paramagnetic (high-spin) Co^{3+} ions. Indeed, Goodenough and Raccah[8] have suggested that in $LaCoO_3$, $E_{Co^{III}}$ is slightly lower than $E_{Co^{3+}}$. A clear insight into this transformation can be obtained (if we neglect the exchange interaction between Co^{3+} ion for which independent evidence exists) by investigating the variation of $\chi_g T$ against T (Fig. 3). If the transformation is between Co^{III} and Co^{3+}, then it can be shown that in $LaCoO_3$

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

where μ is the spin-only moment of Co^{3+} ion. We sought to confirm this variation in the low-spin–high-spin equilibria by studying the Mössbauer spectrum of $LaCoO_3$ as a function of temperature.

Figure 4 shows typical Mössbauer spectra (out of a large number of spectra) obtained with an enriched stainless-steel absorber. The spectrum at room temperature shows asymmetry, indicating the existence of more than one resonance. On resolving this spectrum, we find that it is made up of two resonances, one peaked at 0.0 ± 0.04 mm/sec and the other at 0.45 ± 0.04 mm/sec. With increase in temperature, the intensity of higher resonance decreases and finally above 1210 K it disappears completely. Studies employing a $K_4Fe(CN)_6 \cdot 3H_2O$ absorber give a better insight into what is happening. Figure 5 shows the spectra obtained with $K_4Fe(CN)_6 \cdot 3H_2O$ at various temperatures. The spectra show clearly two resonances, one centered at 0.05 mm/sec and the other at 0.40 mm/sec. It appears likely that the two resonances are due to Fe^{III} and Fe^{3+}, respectively, arising out of the electron-capture decay of low-spin Co^{III} and high-spin Co^{3+} which are shown by Goodenough to coexist in $LaCoO_3$. Before assigning these two resonances to different valence states, we need to exclude other possibilities. One of the possibilities is that these two resonances may be quadrupole partners of a single valence state. This seems most unlikely and can be ruled out since the two resonances are not equally intense. Second, the center of gravity of the spectrum does not correspond with any of the known valence states of iron. The observed temperature variation (Fig. 5) also precludes the possi-

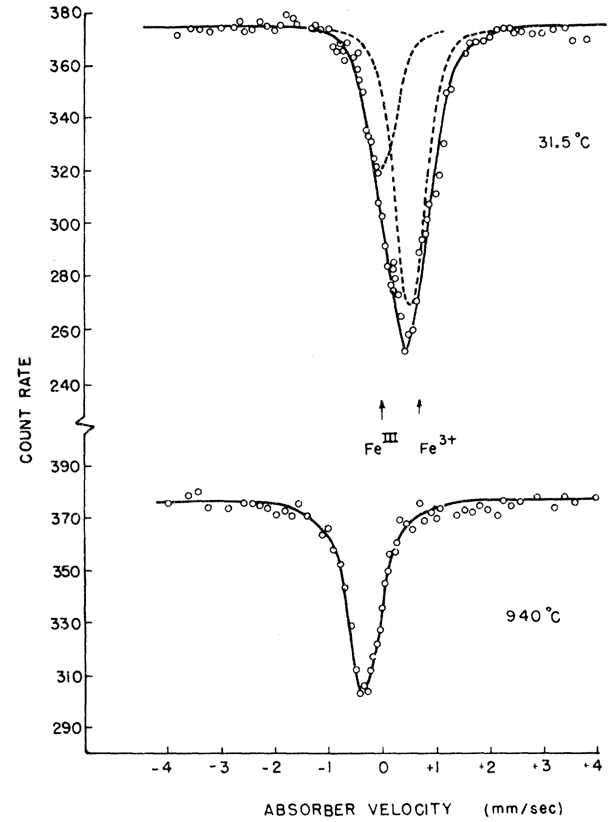

FIG. 4. Typical spectra of $LaCoO_3 : Co^{57}$ matched against 310 enriched stainless-steel absorber: at room temperature and at 940 °C.

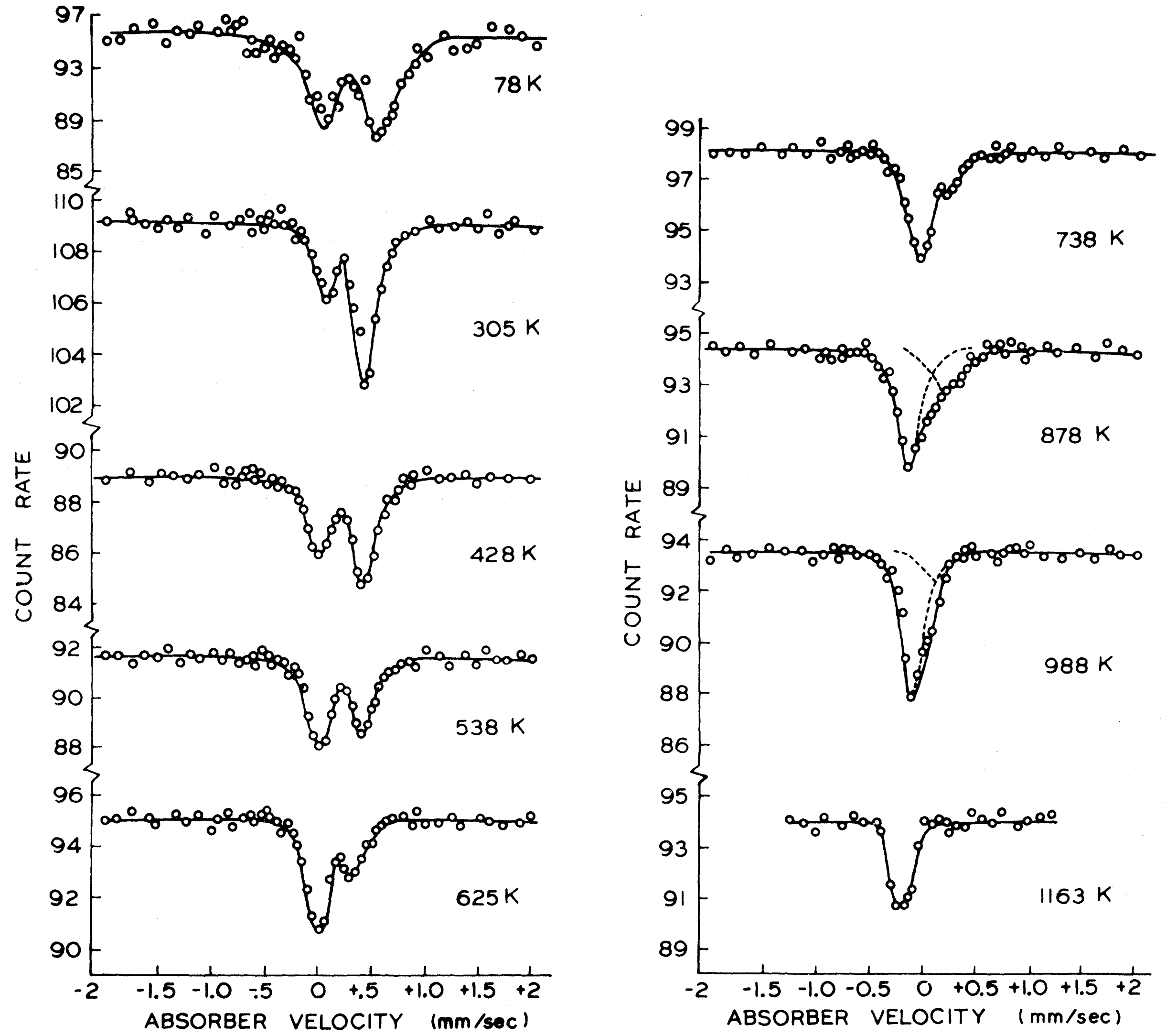

FIG. 5. Series of spectra of $LaCoO_3 : Co^{57}$ matched against $K_4Fe(CN)_6 \cdot 3H_2O$ single-crystal absorber showing the coexistence of Fe^{III} and Fe^{3+}.

bility of the two resonances arising out of the quadrupole splitting of a single valence state. Further, in this structure the quadrupole interaction is expected to be negligible. Having ruled out this possibility, it is tempting to assign the two resonances to Fe^{3+} and Fe^{III} states.

Assuming the validity of this assignment, we plot in Fig. 6 the ratio of the intensities of the two resonances as a function of temperature to give the ratio of Fe^{3+}/Fe^{III}. The intensities were determined from the row dips or by the area under resonance. Implicit in the above is the assumption that the Debye-Waller factors for the two states of cobalt in $LaCoO_3$ are about the same. This assumption is justified to some extent since the two cobalt sites (Fig. 7) in the lattice are occupied by both types of ions. The next question we may examine is whether this ratio of Fe^{3+}/Fe^{III} reflects the ratio of Co^{3+}/Co^{III} in the lattice. In other words, we now examine the question whether Co^{3+} and Co^{III} on electron capture would give Fe^{3+} and Fe^{III} ions. We will presently show by adducing evidence that this is indeed the case.

Co^{57} decays to Fe^{57} by 91% K capture and 9% L capture. As Co^{57} decays to Fe^{57} by electron capture, a hole is created in the K or L shell depending upon whether it is K capture or L capture. On capturing the K or L electron, Co^{57} nucleus goes over to the second nuclear excited state of Fe^{57}. As the K or L hole migrates producing Auger cascades, the nucleus deexcites to the ground state through the emission of γ rays. As a consequence of Auger cascades, there is a possibility of the creation of multiple charge states which are nonequilibrium

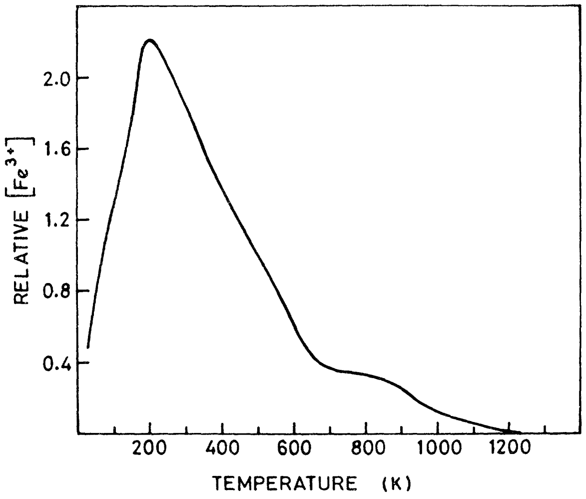

FIG. 6. Temperature variation of the relative population of $Fe^{3+}$with respect to other states of Fe. The ratio of the intensity of the high-energy resonance (due to Fe^{3+}) to that of the low-energy resonance (due to Fe^{III} and other states) is plotted as the ordinate.

charge states. These charge states relax over to the equilibrium charge state in a very short time. Consequently in metals, as well as in most other substances, the Mössbauer spectrum only shows evidence for the equilibrium charge states. However, if the lifetime of the nonequilibrium charge state is comparable with the lifetime of the nucleus in the excited state leading to Mössbauer emission, then the spectrum will show even the nonequilibrium charge states. Wertheim[23] as well as Bhide and Shenoy[24, 25] interpreted the temperature variation of the intensity of Fe^{2+} and Fe^{3+} spectra in CoO : Co^{57} and NiO : Co^{57} systems on the basis that Fe^{3+} is the nonequilibrium charge state formed out of Co^{2+} state. The observation of Fe^{3+} was, however, shown by delayed-coincidence experiments of Triftshauser and Craig[26] to be due to the deviation from nonstoichiometry reflecting more or less the initial Co^{3+} in the lattice. Several experiments since carried out to examine this point[27, 28] have shown that in the lattice where Co exists in the high-spin state, the Mössbauer spectra give only the high-spin iron as in $BaTiO_3$: Co^{57}, Al_2O_3 : Co^{57}, and several other lattices. It has also been shown that in those lattices where Co exists in the low-spin state one obtains the Fe^{III} low-spin Mössbauer spectra. Thus, it is safe to assume that low-spin Co will give on electron capture low-spin Fe and that high-spin Co will lead to high-spin iron.

In order to ensure that the observation of low-spin Fe^{III} spectra is not a mere consequence of the

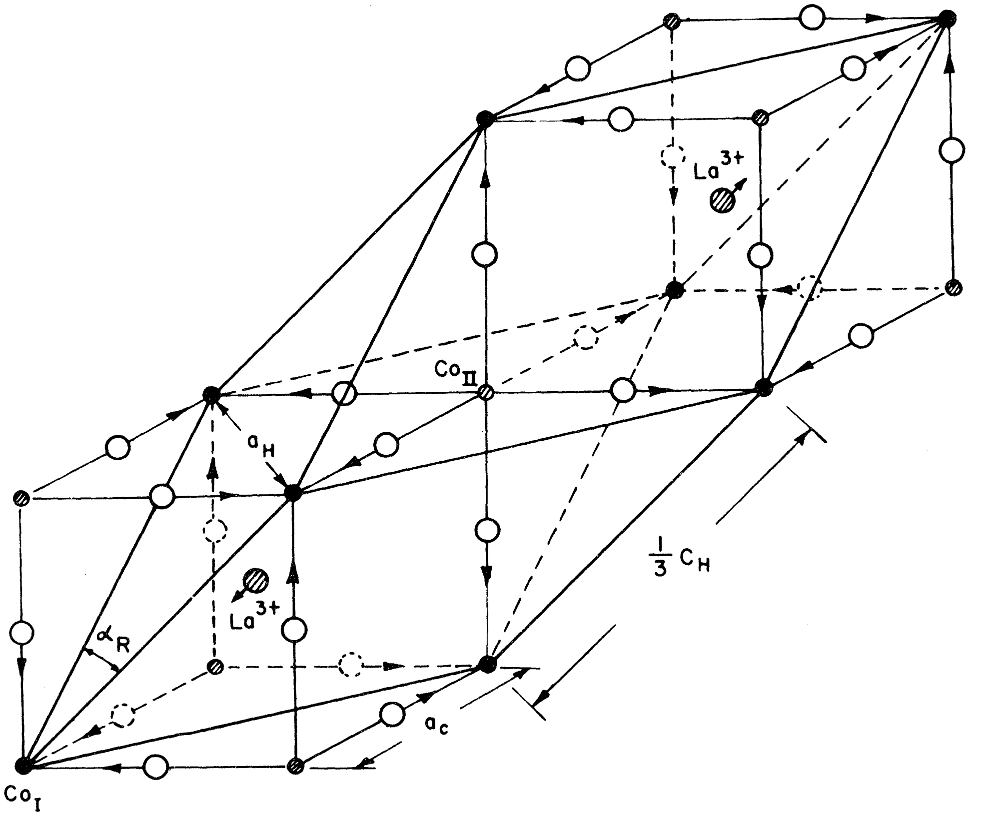

FIG. 7. Rhombohedral unit cell of $LaCoO_3$.

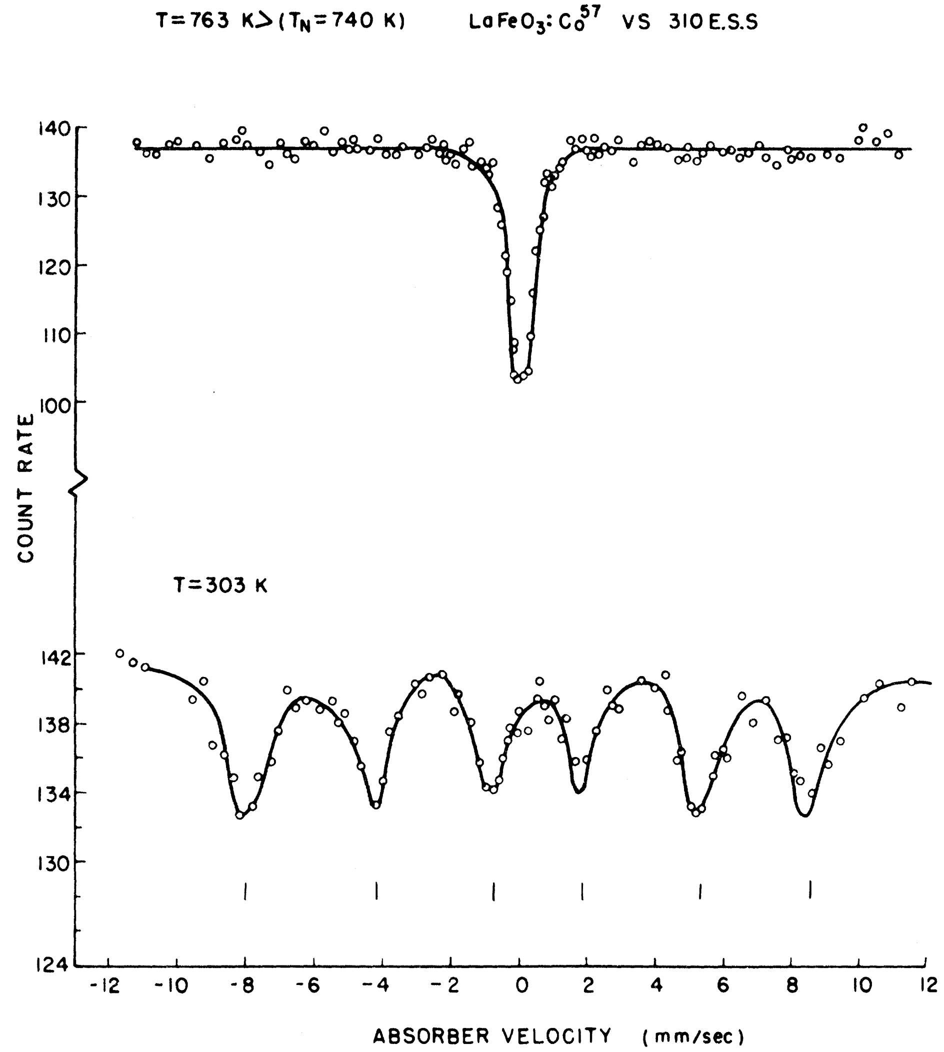

FIG. 8. Typical spectra for $\mathrm{LaFeO_3:Co^{57}}$ matched against 310 enriched stainless-steel (E.S.S.) absorber: at room temperature ($H_n = 514 \pm 2$ KOe, $\delta = 0.36$ mm/sec) and at 760 °K ($\delta = 0.21$ mm/sec).

electron-capture decay of trivalent $(\mathrm{Co}^{57})^{3+}$, but arises from the existence of low-spin cobalt in the lattice, we recorded a few spectra of $\mathrm{LaFeO_3:Co^{57}}$ sources. Figure 8 shows the spectra at two temperatures. These are in agreement with those reported by Eibshutz, Shtrikman, and Treves.[29] In both these spectra, one below the Néel temperature and the other above the Néel temperature, we only see the high-spin $\mathrm{Fe^{3+}}$ spectra, clearly showing that the observation of low-spin $\mathrm{Fe^{III}}$ spectra in $\mathrm{LaCoO_3:Co^{57}}$ is not a mere consequence of electron-capture effects, but arises from coexistence of $\mathrm{Co^{3+}}$ and $\mathrm{Co^{III}}$ in the host lattice. Thus there is little doubt that low-spin $\mathrm{Co^{III}}$ yields low-spin $\mathrm{Fe^{III}}$ while high-spin $\mathrm{Co^{3+}}$ gives high-spin $\mathrm{Fe^{3+}}$. The schematic energy-level diagram shown in Fig. 9 for the various spin states of cobalt and the consequent iron suggests that it is reasonable to assume that on electron capture the high- and low-spin states of cobalt will give rise to the corresponding spin states of iron.

From the above discussion, it becomes clear that there is a coexistence of low-spin $\mathrm{Co^{III}}$ $(t_{2g}^6 e_g^0)$ and high-spin $\mathrm{Co^{3+}}$ $(t_{2g}^4 e_g^2)$ in $\mathrm{LaCoO_3}$ as reflected in the Mössbauer spectrum of $\mathrm{Fe^{III}}$ and $\mathrm{Fe^{3+}}$. Indeed, Goodenough has already suggested this possibility. We do not see any evidence for the $S=1$ paramagnetic states of Co, as suggested by Heikes and coworkers. This state should have led to a medium-spin Fe state with $S=\frac{3}{2}$. On the basis of isomer-shift systematics this should have appeared in between the spectra for high-spin $\mathrm{Fe^{3+}}$ and low-spin $\mathrm{Fe^{III}}$.

If this assignment is correct then the ratio of the two resonances should reflect the ratio of the high-spin $\mathrm{Co^{3+}}$ and the low-spin $\mathrm{Co^{III}}$ in $\mathrm{LaCoO_3}$ in accordance with Eq. (1). It is seen that the ratio of the two resonances agrees with Eq. (1) up to about 200 K. However, beyond 200 K, the higher-energy resonance decreases in relative intensity to disap-

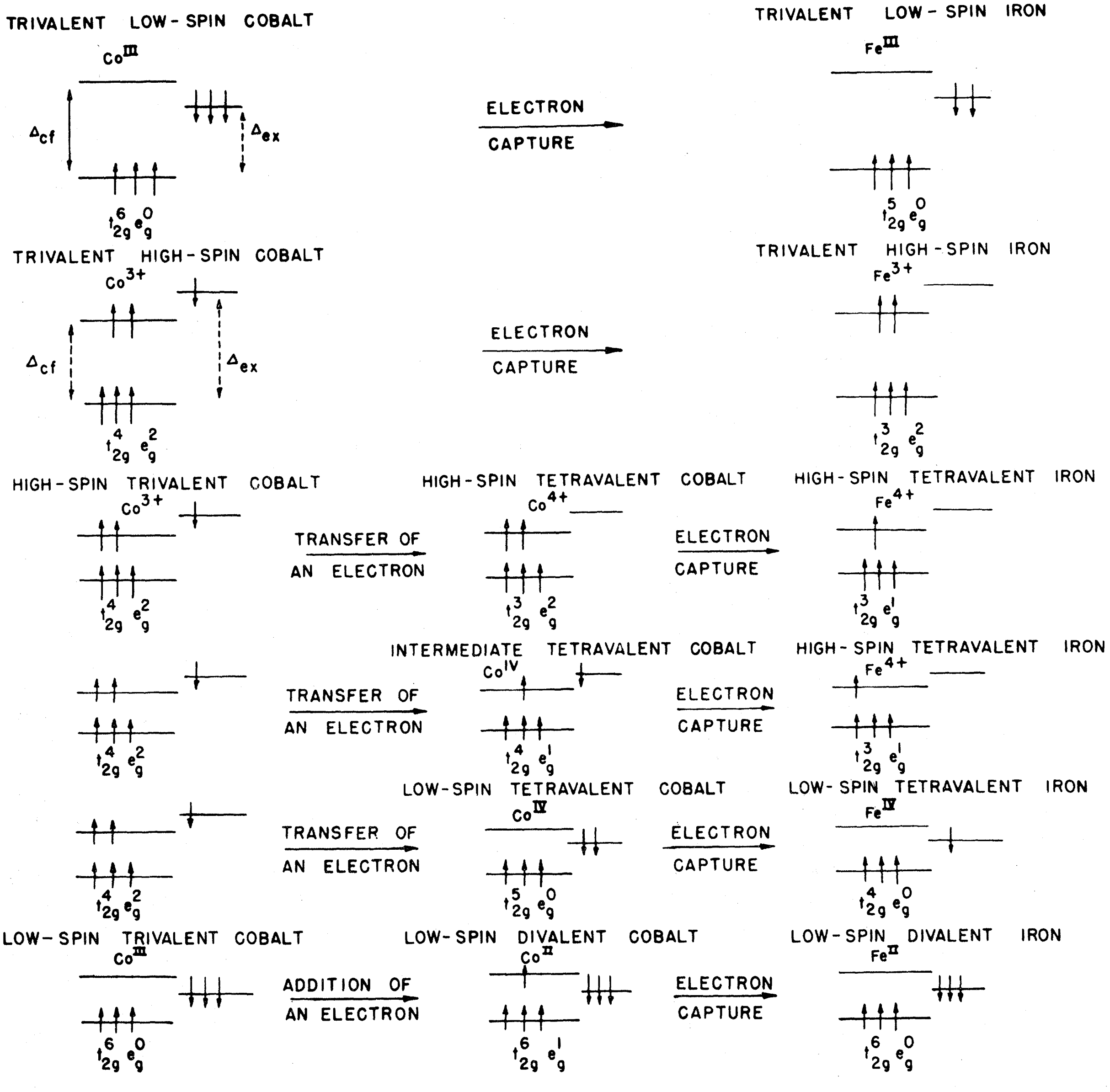

FIG. 9. Spin states of cobalt and consequent iron.

pear completely above 1210 K. This is contrary to what is expected from magnetic-susceptibility data and, indeed, if the assignment is valid, the sample should be diamagnetic at temperatures above 1210 K. This raises a serious doubt about the validity of the assignment of the two resonances to Fe^{3+} and Fe^{III}. There is no ambiguity regarding the assignment of Fe^{3+} to the higher-energy resonance on the basis of isomer-shift systematics. There may, however, be some doubt as to the assignment of lower-energy resonance exclusively to Fe^{III} as other valence states, say Fe^{II} and Fe^{4+}, have almost similar isomer shifts. The magnetic-susceptibility data coupled with Mössbauer data (and as we shall see presently the electrical-conductivity data) all point to the fact that at low temperatures we have the coexistence of Co^{III} and Co^{3+}. But at higher temperatures, the paramagnetic high-spin Co^{3+} state must be getting transformed to some other paramagnetic state which on electron capture would give a resonance round about one due to Fe^{III} state. One of the possibilities, which indeed was suggested again by Goodenough, is that Co^{3+} transfers an e_g electron to Co^{III} to form Co^{2+} and Co^{IV} ion pairs. When an e_g electron is transformed from Co^{3+} to Co^{III} we may get divalent Co^{II} ($t_{2g}^6 e_g^1$) and tetravalent cobalt with a configuration $t_{2g}^5 e_g^0$ (Co^{IV}), $t_{2g}^3 e_g^2$ (Co^{4+}), or $t_{2g}^4 e_g^1$ (Co^{IV} intermediate spin). Since $\chi_g T$ increases rapidly with T (Fig. 3) it is more than likely that out of the various possibilities the $\mathrm{Co^{II}}$ and $\mathrm{Co^{4+}}$ ion pairs are formed. The electron-capture decay of these cobalt ions would give $\mathrm{Fe^{II}}\,(t_{2g}^6 e_g^0)$ and $\mathrm{Fe^{4+}}\,(t_{2g}^3 e_g^1)$ in the Mössbauer spectra. The isomer shift for both these states is near the zero-velocity position and would indeed overlap the resonance due to $\mathrm{Fe^{III}}(t_{2g}^5 e_g^0)$. The electron transfer via orbitals of e_g symmetry rather than via t_{2g} symmetry is compatible with $\Delta_{\mathrm{cac}}^{\sigma} > \Delta_{\mathrm{cac}}^{\pi}$. We have been unable to detect $\mathrm{Co^{2+}}$ and $\mathrm{Co^{IV}}$ states as proposed by Goodenough and Raccah.[8] Indeed, $\mathrm{Co^{2+}}$ on electron capture would have given $\mathrm{Fe^{2+}}$ which has an isomer shift in the vicinity of 1.0 mm/sec and which could have easily been detected. It therefore appears that after 200 K, $\mathrm{Co^{3+}}$ and $\mathrm{Co^{III}}$ ion pairs get transformed to $\mathrm{Co^{4+}}$ and $\mathrm{Co^{II}}$; this transformation seems to proceed progressively up to the transition with the result that, above the transition temperature, we have hardly any high-spin $\mathrm{Co^{3+}}$ left.

Thus these results show that (i) at very low temperatures there is a preponderance of diamagnetic $\mathrm{Co^{III}}$; (ii) as the temperature increases (up to 200 K), the $\mathrm{Co^{3+}}$ state which lies slightly above the $\mathrm{Co^{III}}$ state gets populated; (iii) at temperatures above 200 K, an e_g electron is transferred from $\mathrm{Co^{3+}}$ to $\mathrm{Co^{III}}$ to form $\mathrm{Co^{II}}$ and $\mathrm{Co^{4+}}$ ion pairs; and (iv) above the transition temperature, $\mathrm{Co^{3+}}$ is below the limit of detectability. The preponderance of the $\mathrm{Co^{III}}$ state in the low-temperature region suggests that the low-spin state ${}^1A_1$ $(S=0)$ lies lower than the high-spin paramagnetic ${}^5T_2$ $(S=2)$ state in $\mathrm{LaCoO_3}$. The Mössbauer data indicate that $\mathrm{LaCoO_3}$ should be diamagnetic at 0 K which is well borne out by magnetic-susceptibility measurements.[4,8–12,30] From the variation of the intensities of the $\mathrm{Fe^{3+}}$ state and the $\mathrm{Fe^{III}}$ state in the low-temperature region (up to 200 K) it is possible to determine the energy gap ${}^1A_1 - {}^5T_2$ and we find that $E_{3+} - E_{\mathrm{III}} \simeq 0.02$ eV. Raccah and Goodenough earlier suggested this energy difference to be $\leqslant 0.08$ eV; Jonker[31] and Heikes *et al.*[12] suggested this energy difference to be 0.01 eV. It is interesting to note that in this temperature region, the electrical conductivity has the form $\sigma = \sigma_0 e^{-E_a/KT}$, with E_a nearly equal to the energy separation between the two states. Goodenough has explained the conductivity in this region on the suggestion that an electron is transferred from the t_{2g} level to e_g level. As a result of this process the upper level e_g of the spin-up state becomes populated by electrons while holes are created in the t_{2g} level of the spin-down state.

Goodenough and Raccah[8] have examined the crystal-symmetry changes in $\mathrm{LaCoO_3}$ employing x-ray diffraction. For example, 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 ordering of $\mathrm{Co_I}$ and $\mathrm{Co_{II}}$ sites of the $R\bar{3}$ cell. We sought to study this and other structural changes by investigating the Lamb-Mössbauer-factor variation with temperature. While our results are generally consistent with the ideas of Goodenough, we find that ordering occurs only after the transfer of the σ-bonding d electrons from $\mathrm{Co^{3+}}$ to $\mathrm{Co^{III}}$ (see Figs. 1 and 6). Figure 10 shows the Debye-Waller temperature factor for x rays. The temperature factor $2M$ is given by

$$2M = \frac{2}{m}\int_0^m f(\nu)\,d\nu\left(\frac{1}{2} + \frac{1}{e^{h\nu/KT}-1}\right)\nu^{-2}\,d\nu \bigg/ \int_0^{\nu_m} f(\nu)\,d\nu\,. \tag{2}$$

The Lamb-Mössbauer factor is plotted on the same figure. The Lamb-Mössbauer factor is essentially equal to e^{-2M}. In order to compare the data obtained from x-ray diffraction, we have plotted e^{-2M} with the $2M$ values from the x-ray data of Raccah and Goodenough.[8] The Lamb-Mössbauer factor was determined using a black absorber. Consequently, it is not possible to determine the temperature dependence of the Lamb-Mössbauer factor for each of the valence states. It is interesting that our Mössbauer data agree excellently with the x-ray data. The decrease in the Lamb-Mössbauer factor in the temperature range 970–1210 K is indicative of large ionic vibrations. It is equally significant that above the first-order transition around 1210 K the Lamb-Mössbauer factor increases with temperature. This is in accordance with the long-range order above 1210 K. The temperature variation of the Lamb-Mössbauer factor indicates the occurrence of some transitions at 500, 650, and 900 K as well. In the DTA curve also we see peaks at 650 and 900 K. The transition at 650 K corresponds to the long-range-ordering temperature discussed earlier where electrical resistivity, Seebeck coefficient, and magnetic susceptibility also show significant changes. At 900 K, Raccah and Goodenough[8] have found some structural changes. In the 650–900-K region, the Mössbauer center shift shows marked changes, as will be seen later. The 500-K transition probably corresponds to the onset of short-range order as well as initiation of the plateau in the susceptibility curve and a break in the resistivity curve. We must note here that the Lamb-Mössbauer factor is probably more sensitive than either DTA or x-ray diffraction in identifying transitions due to subtle changes in symmetry or positions of ions. The variations in the temperatures and enthalpies of transitions (as found in our DTA studies) as well as the thermal-hysteresis effects are likely to be associated with the order-disorder nature of these transitions; such transitions are likely to be affected by the method of sample preparation.

Another parameter which provides important information about the displacement of ions as well as

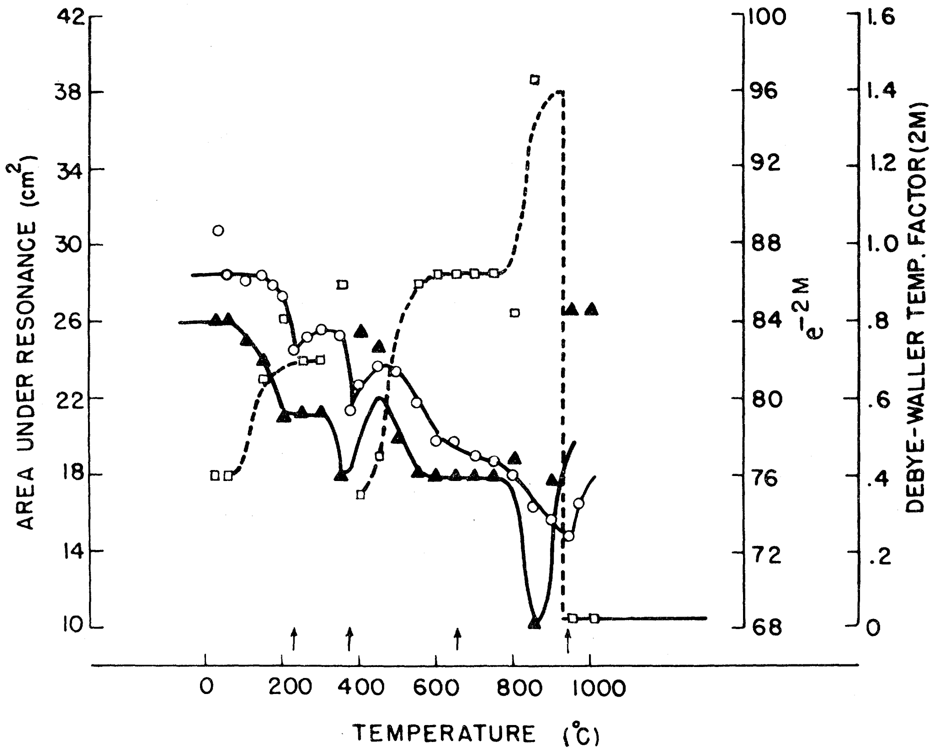

FIG. 10. Variation of (○): area under resonance with temperature for LaCoO$_3$: Co^{57} matched against 310 enriched stainless-steel abosrber, (□): Debye-Waller temperature factor ($2M$) obtained from x-ray studies with temperature [after Raccah and Goodenough (Ref. 8)]; (▲): e^{-2M} vs temperature.

the vibration of ions is the center shift. Figure 11 shows the variation of center shift for high-spin Fe^{3+} resonance and the low-energy resonance (which is probably a composite of Fe^{III} and other states discussed earlier). The center shift decreases rather substantially in the temperature range 650 $< T < 920$ K. This decrease may arise due to the following possibilities: (i) change in the mean-square velocity giving rise to the corresponding changes in the second-order Doppler shift[32] and (ii) change in the chemical shift arising out of the displacement of neighbors. The observed changes cannot be entirely accounted for by (i) since these changes should correspondingly have been reflected in the Lamb-Mössbauer factor. We may note here that x-ray studies[3,8] also indicate interesting ionic displacements in this temperature range. If we assume that the observed changes are due to ionic displacements, then the reduction in the isomer shift would imply greater covalency (causing also increase in the overlap integrals).[6] As already mentioned, $\Delta^{\sigma}_{\text{cac}} > \Delta^{\pi}_{\text{cac}}$; the progressive increase in overlap integrals in this temperature region would initiate the delocalization of the e_g electrons to form σ^* band, perhaps with the t_{2g} electrons still localized. This provides a distinction between various valence states at the two sites even after the transition. It is interesting that the isomer shifts vary continuously through the first-order transition at 1210 K.

Electrical transport properties of LaCoO$_3$ (Fig. 2) show some interesting features. The resistivity data in the 77–200-K range give a small activation energy E_a (~ 0.1 eV), typical of the value expected for promotion of a t_{2g} electron to the σ^* band of itinerant e_g electrons at the low-spin Co^{III} ions. Above 200 K, ρ decreases with T up to ~400 K, the apparent E_a increasing to ~ 0.2 eV. ρ decreases sharply after 500 K up to the long-range-ordering temperature (~ 650 K), the apparent E_a reaching

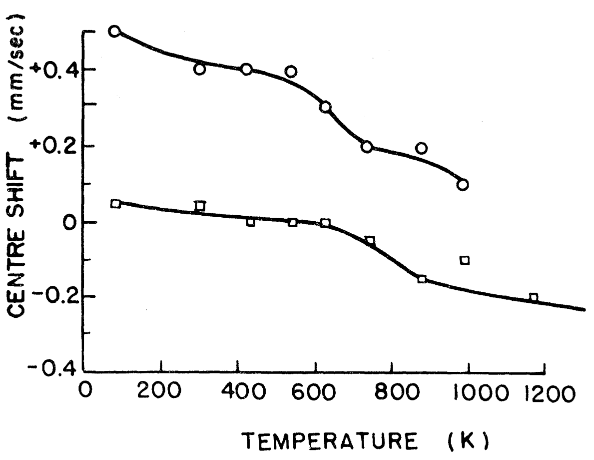

FIG. 11. Variation of center shift with temperature of the high-energy resonance (Fe^{3+}) and the low-energy resonance (Fe^{III} and others). (○): isomer shift for Fe^{3+}; (□): isomer shift for Fe^{III} and other states.

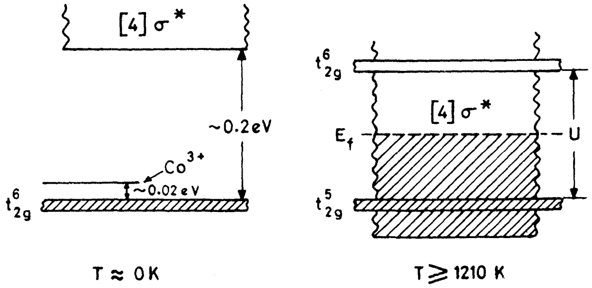

FIG. 12. Band scheme of Co^{III} in $LaCoO_3$.

0.6 eV; ρ becomes constant after 650 K. While the low and nearly constant ρ and α values above 650 K would suggest metal-like behavior, suggesting once again the initiation of delocalization in this temperature region, we could see an increase in ρ with T only above 1210 K corresponding to the localized-collective electron-transition temperature. Raccah and Goodenough[8] have commented on the surprising lack of any discontinuity in ρ across this first-order transition in $LaCoO_3$.

It is noteworthy that $LaCoO_3$ remains p type throughout the temperature range. This means that mobility of holes is greater than that of electrons in the entire temperature range through the first-order localized-electron ⇌ collective-electron transition at 1210 K, a situation similar to that found in Ti_2O_3, which undergoes a higher-order semiconductor-semimetal phase transition.[33] We may point out here that above 1210 K the t_{2g} orbitals are supposed to remain localized according to Raccah and Goodenough[8] since $\Delta^{\pi}_{cac} < \Delta^{\sigma}_{cac} \leq \Delta_c$. We are now in a position to construct an energy diagram for the 3d electrons in $LaCoO_3$ consistent with Mössbauer and other studies. A schematic band scheme for $LaCoO_3$ is shown in Fig. 12 somewhat similar to that of Raccah and Goodenough[34] for Sr^{2+}-doped $LaCoO_3$. In this figure, we have shown the localized t_{2g} levels as a band only for purposes of convenience. Undoubtedly, there is need for further investigation of electron transport and other properties of $LaCoO_3$ for a complete understanding of the electronic structure below and above the localized-electron–collective-electron-transition temperature.

We shall now briefly comment on the nature of the first-order localized-electron–collective-electron transition in $LaCoO_3$ at 1210 K. There are no significant changes in crystal structure or volume through the first-order transition.[8] Mössbauer data show that the isomer shift varies continuously through the transition, whereas the Lamb-Mössbauer factor increases at the transition. While the former implies that the transition is not associated with large ionic displacements, the latter indicates that at the transition temperature the mean-square displacement of the Co ions decreases sharply. Thus, in confirmation of the x-ray data,[8] the Mössbauer results indicate that the entire entropy change (~ 0.8 eu) in this transition is of electronic origin. The confirmation of the nature of the first-order localized-electron–collective-electron transition in $LaCoO_3$ seems to indicate the validity of Goodenough's hypothesis that the crystal field and band limits are distinct thermodynamic states.

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Exchange Interactions and Fluctuations in CeB_6 †

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We report measurements of the low-temperature specific heat of CeB_6 and discuss their significance in the light of earlier studies of this compound. The large specific heat above the antiferromagnetic ordering at 2.31 K is interpreted with the aid of a decorated Ising model. This model permits us to combine exchange and crystal field interactions in a simplified, but exact, calculation of the thermodynamic properties of a magnetic system including the effects of fluctuations. The analysis gives independent support to the proposal by Nickerson and White that the exchange in the crystal field excited state is substantially stronger than the ground-state exchange in CeB_6. We also comment on the possibility of extending such an analysis to other magnetic rare-earth hexaborides.

I. INTRODUCTION

Cerium hexaboride is a metal with an antiferromagnetic transition at 2.3 K. The trivalent Ce ions are in the $4f^1$ configuration, resulting in a $^2F_{5/2}$ ground state, which is further split by a cubic crystal field into a (ground-state) doublet Γ_7 and a quartet Γ_8. With but a single $4f$ electron and a well-known crystal field spectrum, CeB_6 should thus be the simplest of the magnetic rare-earth hexaborides.

The magnetic susceptibility of CeB_6 has been measured a number of times, with consistent results[1,2]: The magnetic susceptibility follows a Curie-Weiss law with a free-ion slope down to 150 K, and rises above the extrapolated Curie-Weiss value below. Nickerson and White[3,4] have given a theoretical interpretation of the magnetic susceptibility. Hull[5] has measured the isothermal magnetization from 1.74 to 7 K, and Fisk obtained the resistivity from 2 to 300 K.[2] The firmest evidence for a Γ_7 crystal field ground-state assignment is in the isothermal magnetization measurements.[5] At the lowest temperature and highest field (60 kOe), the magnetization curve is rather flat and has a value of 0.74 μ_B/atom, in good agreement with the 0.71 μ_B/atom expected from a well-isolated Γ_7 doublet.[6]

We present measurements of the specific heat of CeB_6 from 1 to 22 K and discuss its significance in the context of the earlier work on this compound. Our data were analyzed using a decorated Ising model; the general form of such models has been discussed by Fisher.[7,8] Within this framework we find strong support for the proposal by Nickerson and White[3] that the exchange interactions in the ground and excited states are of different magnitudes, with the excited-state exchange being considerably stronger. The extension of such an analysis to other rare-earth hexaborides, however, is more problematical. We discuss the difficulties further below.