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Stabilization of Tetravalent Cobalt in an Isolated Six-Coordinated Site of an Oxide Lattice: A Magnetic and ESR Characterization

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The prediction that low-spin Co(+IV) is likely to be stabilized in the environment of a strongly elongated octahedron of oxygen atoms has been illustrated by synthesis of $Sr_{0.5}La_{1.5}Li_{0.5}Co_{0.5}O_4$, whose structure and composition favor such a distortion. The magnetic and ESR properties of the material have been interpreted in terms of covalency and symmetry and lead to the first complete characterization of isolated six-coordinated Co(+IV) ions in an oxide lattice.

Few tetravalent cobalt oxides have been reported so far. To our knowledge the only known examples are the ternary alkali or alkali–earth oxides A_2CoO_3, ACo_2O_4 (A = K, Rb, Cs), $K_6Co_2O_7$, Li_8CoO_6, Na_4CoO_4, and Ba_2CoO_4 (*1–6*) in which Co(+IV) accommodates a tetrahedral site owing to the strong ionic character of the competing bonds, and the hexagonal perovskites with formulae $Ba_3Co_2CO_9$, $SrCoO_{3-x}$, and $BaCoO_3$ (*6–8*) containing six-coordinated Co(+IV). In the latter case delocalization of the d electrons resulting from short Co–Co distances makes difficult a precise characterization of the unusual oxidation state of cobalt.

It was therefore considered worthwhile to try to stabilize Co(+IV) in an isolated six-coordinated site of an oxide and to determine some of its characteristic physical properties.

Use of a theoretical model previously described (*9*) giving the variation of the energy levels of a six-coordinated M (d^n) ion with axial distortion of the MO_6 octahedron ($\theta = d_{M\text{-}O}(z)/d_{M\text{-}O}(xy)$) and average crystal field ($\overline{Dq}/B$) allowed us to determine the stability areas of the ground terms of a d^5 ion, e.g., Co^{4+} (Fig. 1). Such a diagram shows that the $^2B_{2g}$ term, corresponding to the expected low-spin configuration of Co(+IV) ($d_{yz}^2 d_{zx}^2 d_{xy}^1$) ($\overline{Dq}/B \gg 3$ for Co(+IV) in oxides) can more easily be stabilized in a slightly elongated site ($\theta > 1$) than in a pure O_h one ($\theta = 1$). The energy gain in $\overline{Dq}/B$ units brought about by a distortion θ can be defined by the parameter

$$\eta(\theta) = \frac{E/B(\theta) - E/B(1)}{\overline{Dq}/B}$$

where $E/B(\theta)$ represents the relative energy of the $^2B_{2g}$ term in presence of a θ distortion

$$E/B(\theta) \simeq 56 - 3\,\frac{\overline{Dq}}{B}\,\frac{18.28\theta^5 + 1.72}{2\theta^5 + 1}.$$

The $\eta(\theta)$ curve, drawn in Fig. 2 for the $^2B_{2g}$ term, illustrates the large stabilizing effect of an elongation of the CoO_6 octahedron.

The two-dimensional K_2NiF_4 structure is

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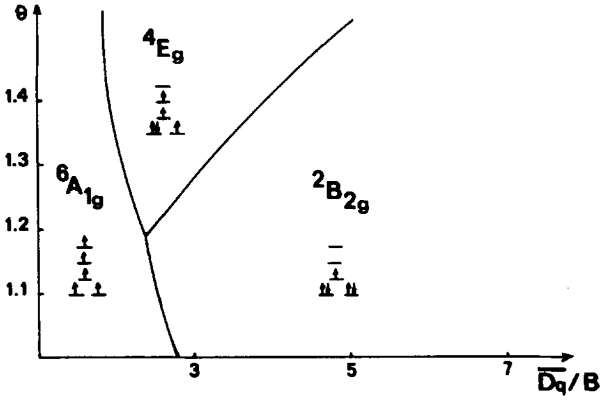

FIG. 1. Stability areas of the fundamental terms of a d^5 (Co + IV) ion vs θ and $\overline{Dq}/B$.

known to be particularly suitable for inducing a large elongation of the MO_6 octahedron. Moreover, the introduction in the perovskite layers of weak Li–O bonds competing with the Co–O ones was likely to enhance the Co–O covalency in the *xOy* plane and thus to increase the distortion while isolating the cobalt atoms from each other. These structural and chemical bonding considerations led to a $Sr_{0.5}La_{1.5}Li_{0.5}Co_{0.5}O_4$ composition.

Preparation and Chemical Analysis

This material has been obtained in two steps. Firstly, a mixture of the corresponding nitrates was calcined at 670°C in a stream of oxygen for 24 hr. As Li_2O sublimes at this temperature, an excess of $LiNO_3$ was added. The second step was a heat treatment at 525°C and 120 bar of oxygen for 48 hr.

Chemical analysis of the product (disso-

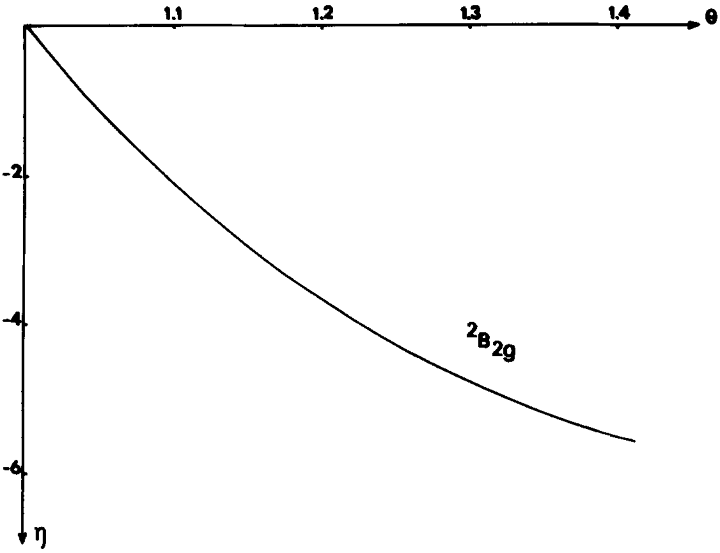

FIG. 2. Stabilization energy of the $^2B_{2g}$ term of a d^5 ion vs θ in $\overline{Dq}/B$ units.

lution in an acidified KI solution followed by redox titration) specified the oxidation state for cobalt as 4.02 ± 0.05.

X-Ray Diffraction Study

The X-ray diffraction of $Sr_{0.5}La_{1.5}Li_{0.5}Co_{0.5}O_4$, using Cu$K\alpha$ radiation, yielded a tetragonal K_2NiF_4-type structure with a_0 = 3.762 Å and c_0 = 12.66 Å. However, Guinier photographs revealed very weak superstructure lines which could be indexed in a supercell ($a = a_0\sqrt{2}$, $c = c_0$) arising probably, as in the homologous phase with Fe(+IV) (*10*), from an ordering of Li and Co ions in the perovskite layers. At room temperature the c_0/a_0 ratio is 3.36, i.e., intermediate between that generally observed for an isotropic electronic structure (3.25–3.30) and that characterizing a Jahn–Teller effect due to an asymmetric population of e_g orbitals ($c_0/a_0 \simeq 3.45$) (*11*). This confirms the low-spin configuration of cobalt(+IV) ($d_{yz}^2 d_{zx}^2 d_{xy}^1$).

Magnetic Investigation

The magnetic susceptibility of $Sr_{0.5}La_{1.5}Li_{0.5}Co_{0.5}O_4$ has been measured between 4.2 and 300 K using a Faraday balance. After correction for the diamagnetic contribution, the variation of χ_m^{-1} with temperature appears to fit with a Curie–Weiss law for 50 K < T < 200 K (Fig. 3). The Curie constant calculated in the paramagnetic region ($C_{exp} = 0.40 \pm 0.05$) is close to the theoretical spin-only value for one unpaired electron (C_{theor} = 0.375; $\mu_{eff} = 1.73\mu_B$). This result is accounted for by the axial field component resulting from the elongation of the CoO_6 octahedra, which lifts the orbital degeneracy of the $^2T_{2g}$ term to give rise in D_{4h} symmetry to an orbital singlet $^2B_{2g}$ as the ground term (Table I), and tends to move the temperature dependence of the magnetic moment towards the spin-only value. One may notice that some t_{2g} electron transfer onto the oxygen atoms, which is likely to occur due to the strong covalency of the equatorial Co(+IV)–O bonds,

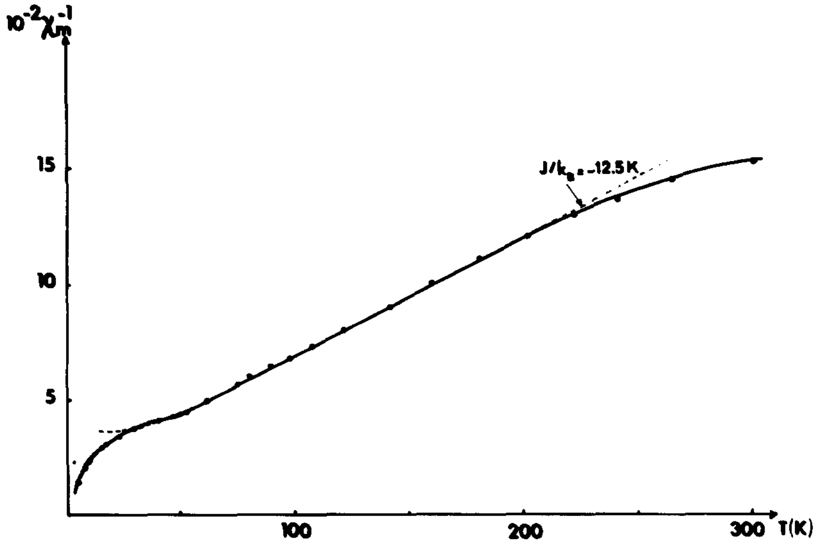

FIG. 3. Reciprocal molar susceptibility vs temperature: —— experimental curve; --- theoretical curve for $J/k_B = -12.5$ K.

quenches the orbital angular momentum in a similar way (*12*).

It was worthwhile therefore, in interpreting the magnetic behavior of $Sr_{0.5}La_{1.5}Li_{0.5}Co_{0.5}O_4$, to modify Kotani Hamiltonian ($\mathcal{H} = \mathcal{H}_0 + \lambda\hat{L}\hat{S} + \beta(\hat{L} + g_e\hat{S})\mathbf{H}$) to take into account the axial ligand-field component $\mathcal{H}_{\mathrm{ttgl}}$, and an orbital reduction factor k:

$$\mathcal{H} = \mathcal{H}_0 + (\mathcal{H}_{\mathrm{ttgl}} + \lambda k\hat{L}\hat{S}) + \beta(k\hat{L} + g_e\hat{S})\mathbf{H}.$$

As the effects of the axial ligand-field component and of the spin–orbit coupling are likely to be of the same order of magnitude, $\mathcal{H}_{\mathrm{ttgl}}$ and $\lambda k\hat{L}\hat{S}$ must be treated as simultaneous perturbations of $\mathcal{H}_0$. The result of this calculation is that the sixfold degenerate $^2T_{2g}$ term is split by the elongation and the spin–orbit coupling into a set of three doubly degenerate levels (*13*), of respective energies:

$$E_1 = \Delta - \frac{k\lambda}{2}$$

$$E_2 = \frac{1}{2}\left(\left(\frac{k\lambda}{2} + \Delta\right) + \left(\Delta^2 + k\lambda\Delta + \frac{9k^2\lambda^2}{4}\right)^{1/2}\right)$$

$$E_3 = \frac{1}{2}\left(\left(\frac{k\lambda}{2} + \Delta\right) - \left(\Delta^2 + k\lambda\Delta + \frac{9k^2\lambda^2}{4}\right)^{1/2}\right),$$

Δ being defined in Table I.

A further calculation is then necessary to introduce the influence of the magnetic field perturbation $\beta(k\hat{L} + g_e\hat{S})\mathbf{H}$, and to obtain the theoretical variation of μ_{eff} with k_BT/λ, for various values of the k and Δ/λ parameters. The comparison of these calculated values reported by Figgis (*14*) with the experimental ones obtained for Co(+IV) (for which the free-ion value -650 cm^{-1} has been taken for λ (*12*)) showed that this model, with approximately $k \leq 0.7$ and $\Delta/\lambda \leq -1$, was much more representative of the observed magnetic behavior than that of Kotani (Fig. 4). However, it appeared impossible, with only magnetic susceptibility data, to determine even roughly the values of k and Δ for Co(+IV). This observation led us to investigate the ESR properties of $Sr_{0.5}La_{1.5}Li_{0.5}Co_{0.5}O_4$.

TABLE I

TERM SPLITTING OF A d^5 ION IN D_{4h} SYMMETRY AND CORRESPONDING ELECTRONIC CONFIGURATIONS

O$_h$	D_{4h}		Electronic configurations
$^6A_{1g}$ →	$^6A_{1g}$		$d_{zx}^1 d_{yz}^1 d_{xy}^1 d_{x^2}^1 d_{x^2-y^2}^1$
$^4T_{2g}$	$\nearrow$ $^4B_{2g}$		$d_{zx}^1 d_{yz}^1 d_{xy}^2 d_{z^2}^1 d_{x^2-y^2}^0$
	$\searrow$ ^4E_g		$(d_{zx}d_{yz})^3 d_{xy}^1 d_{z^2}^1 d_{x^2-y^2}^0$
$^2T_{2g}$	$\nearrow$ ^2E_g	$\updownarrow$ Δ	$(d_{zx}d_{yz})^3 d_{xy}^2 d_{z^2}^0 d_{x^2-y^2}^0$
	$\searrow$ $^2B_{2g}$		$d_{zx}^2 d_{yz}^2 d_{xy}^1 d_{z^2}^0 d_{x^2-y^2}^0$

At high temperature the χ_m^{-1} vs T curve departs from the spin-only behavior. That can be explained by partial populating of levels arising from the orbital doublet ^2E_g, lying at an energy Δ above the $^2B_{2g}$ ground term in D_{4h} symmetry (Table I).

For $T < 50$ K, the χ_m^{-1} vs T curve suggests a two-dimensional magnetic behavior, perturbed at very low temperature by magnetic impurities. Such a behavior is not surprising if one considers the layer structure of the material and the d_{xy}^1–d_{xy}^1 magnetic couplings inside the perovskite planes as being the only possible ones. The estimated paramagnetic Curie temperature ($\theta_p \simeq -40$ K) denotes the existence of predominant antiferromagnetic couplings, which can be attributed to super-superexchange interactions between the half-filled d_{xy} orbitals of Co(+IV) through two different oxygen atoms (Fig. 5). As shown in the first part of this study, the susceptibility values for $50\text{ K} < T < 200$ K are very close to the spin-only ones. With the approximation of

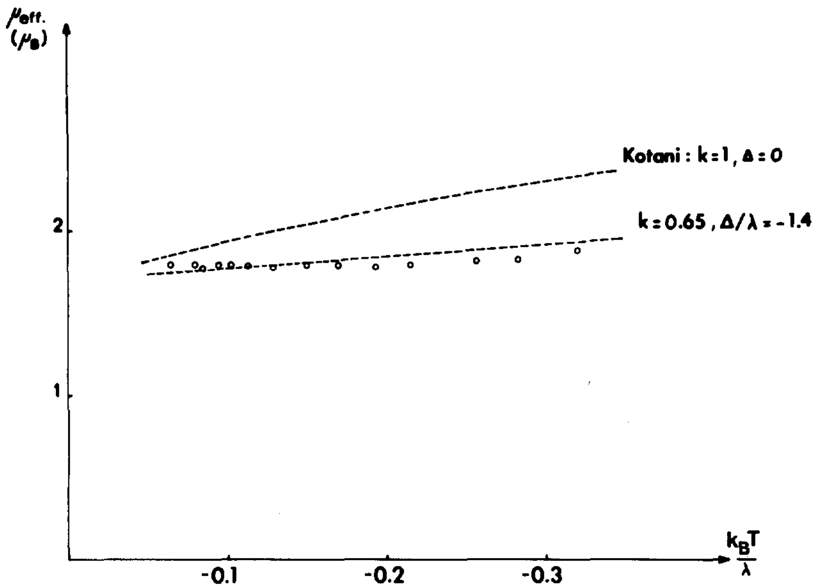

FIG. 4. Experimental and theoretical variations of the effective magnetic moment with k_BT/λ.

a Heisenberg model this permits the determination of the exchange integral J/k_B from the susceptibility curve without additional correction, using the high-temperature expansion-series method (*15*).

For a quadratic-layer Heisenberg antiferromagnet with exchange Hamiltonian $\mathcal{H} = \Sigma_{i,j}\ 2J\ \hat{S}_i\hat{S}_j$, the Rushbrooke and Wood equation for magnetic susceptibility can be written as

$$\frac{Ng^2\mu_B^2}{2\chi|J|} = 3x + \sum_{n=1}^{\infty} \frac{C_n}{x^{n-1}}$$

with

$$x = \frac{k_BT}{2|J|S(S+1)}.$$

The C_n coefficients have been calculated up to $n = 6$ by Lines (*16*). The introduction of these values in previous equation leads to

$$\chi_m^{-1} = \frac{4|J|}{Ng^2\mu_B^2}\left(3x + 4 + \frac{2.667}{x} + \frac{1.185}{x^2} + \frac{0.149}{x^3} - \frac{0.191}{x^4} + \frac{0.001}{x^5}\right)$$

for the theoretical value of reciprocal molar susceptibility. Fitting of the experimental χ_m^{-1} vs T curve using this equation leads to $g \simeq 2$ and $J/k_B = -12.5$ K (Fig. 3).

This value is much lower than those mentioned by Le Flem *et al.* (*17*) for other K_2NiF_4-type oxides with $AA'BO_4$ formulae. This can be of course attributed to the fact that Li–Co ordering in $Sr_{0.5}La_{1.5}Li_{0.5}Co_{0.5}O_4$ implies much longer Co–Co distances and weaker interactions (super-superexchange)

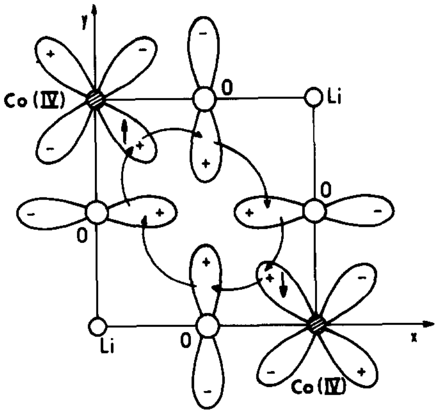

FIG. 5. Super-superexchange coupling mechanism.

than the *B–B* ones in the above mentioned oxide.

The calculation of the Stanley–Kaplan temperature, given by $T_{SK} = \frac{|J|}{5k_B}(Z - 1)(2S(S + 1) - 1)$ (*18*) (where Z is the number of nearest neighbors of the magnetic ion) leads for this Co(+IV) oxide to $T_{SK} = 3.75$ K. Such a value shows that if 3D-magnetic ordering exists it may only appear at very low temperature ($T < 3.75$ K) and justifies the use of Heisenberg formalism (which supposes the absence of a magnetic ordering temperature) rather than that of an Ising model.

ESR Measurements

The ESR spectrum of $Sr_{0.5}La_{1.5}Li_{0.5}Co_{0.5}O_4$ at 4.2 K was obtained with a Brucker-ER 200 tt X-band spectrometer (Fig. 6). Though the upper field ($H_{max} \simeq 8000$ G) did not allow us to obtain the $g_\parallel$ signal, the spectrum shows the absence of magnetic ordering at 4.2 K, thus corroborating the results of the magnetic study, and is characteristic of an anisotropic electronic distribution ($2.32 \leq g_\perp \leq 2.55$, $g_\parallel \leq 0.85$). The g values, though not very precise, are consistent with those previously obtained for Co(+IV) by Townsend and Hill in Al_2O_3: Co^{4+}, Mg^{2+} ($g_\perp \simeq 2.58$, $g_\parallel$ unobserved) and lie well outside the theoretical limits for octahedral Co^{2+} (*19*). This is another confirmation of the oxidation state +IV of cobalt with a low-spin configuration ($d^2_{yz}d^2_{zx}d^1_{xy}$).

The theoretical g values for a $^2T_{2g}$ term split by axial-symmetry field have been reported by several authors (*14, 19–21*). They follow the equations

$$g_\perp = 2 \cos \omega(\cos \omega - k\sqrt{2} \sin \omega)$$

$$g_\parallel = 2(\cos^2 \omega - (1 + k) \sin^2 \omega)$$

with

$$\tan(2\omega) = \frac{\lambda\sqrt{2}}{\Delta + \lambda/2}.$$

Their variation with k and λ/Δ shown in Fig. 7 leads to an estimation of a lower limit for the ratio Δ/λ : $g_\parallel \leq 0.85 \rightarrow \lambda/\Delta \leq -0.65$, i.e., $\Delta/\lambda \geq -1.54$.

The comparison of this value with those resulting from the above magnetic investigation shows that the best agreement between experimental and theoretical μ_{eff} and g values is obtained for $\Delta/\lambda \simeq -1.4$, giving $\Delta \simeq 900$ cm^{-1} and $k \simeq 0.65$. With such a set of parameters, the calculated g values become $g_{\perp theor} = 2.32$, $g_{\parallel theor} = 0.80$.

The value of k deduced is much smaller than that found in Al_2O_3 doped with Co^{4+}

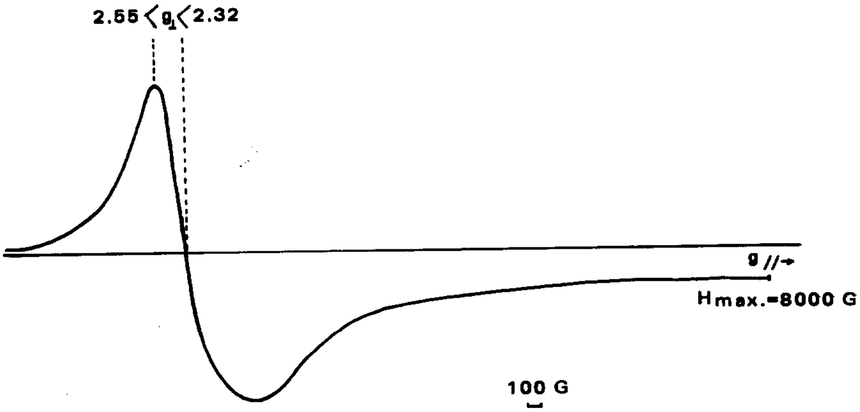

FIG. 6. ESR spectrum at 4.2 K.

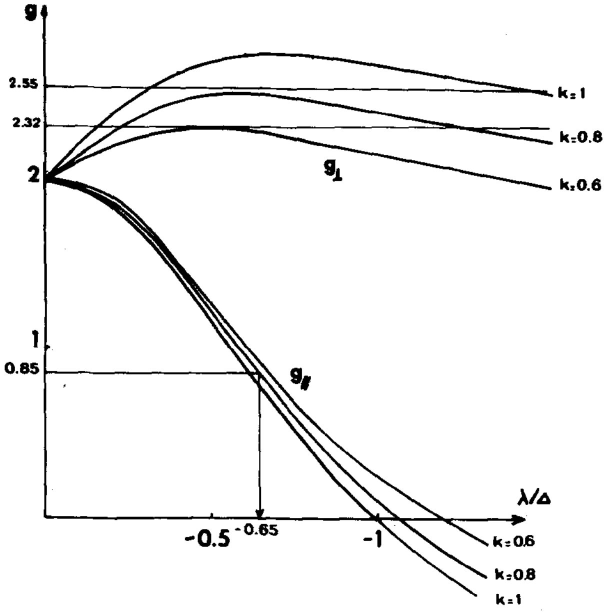

FIG. 7. Theoretical variations of the g values of a low-spin d^5 ion with k and λ/Δ.

($k = 0.94$–1.00) (*19*) and those generally observed for oxides. It can possibly be attributed to enhancement of the covalency of the Co(+IV)–O bond due to a surrounding of four weak Li–O bonds. We notice that a similar decrease of the k factor has already been observed in $NaCrO_2$ (*22*) ($k = 0.7$) in which the Cr(+III)–O bond is in competition with the weak Na–O one. The high Δ value, which is of the same order of magnitude as the spin–orbit coupling constant λ, justifies a posteriori the treatment of $\mathcal{H}_{\mathrm{ttgl}}$.

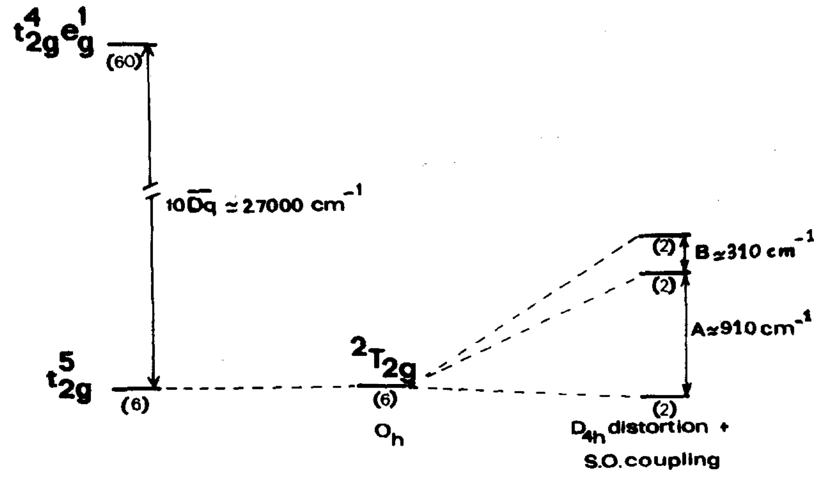

FIG. 8. Spectroscopic characterization of Co(+IV) in $Sr_{0.5}La_{1.5}Li_{0.5}Co_{0.5}O_4$.

$$A = \left(\Delta^2 + k\lambda\Delta + \frac{9k^2\lambda^2}{4}\right)^{1/2} \qquad B = 1/2\left(\Delta - \frac{3k\lambda}{2} - A\right).$$

and $\lambda k\hat{L}\hat{S}$ as simultaneous perturbations of $\mathcal{H}_0$. It is also a good confirmation of the influence of the anisotropic Li environment on the distortion of the CoO_6 octahedron.

Conclusion

As shown by the previous discussion on the stability of the $d_{yz}^2 d_{zx}^2 d_{xy}^1$ configuration, isolated Co^{4+} ions can be stabilized in elongated six-coordinated sites of a K_2NiF_4-type structure. The $Sr_{0.5}La_{1.5}Li_{0.5}Co_{0.5}O_4$ oxide, in which this distortion is enhanced by Li–Co ordering in the perovskite-type layers, has been prepared under a high pressure of oxygen. The oxidation state (+IV) of cobalt and the low-spin configuration have been established by redox titration, magnetic susceptibility, and ESR measurements. A model taking into account the influence of a tetragonal distortion of the CoO_6 octahedra and the covalency of the Co(+IV)–O bonds allowed us to evaluate the magnitude of the distortion ($\Delta \simeq 900\ \mathrm{cm}^{-1}$) and of the electronic delocalization factor ($k \simeq 0.65$). An interpretation of the low-temperature magnetic behavior has been performed using a high-temperature expansion-series method with a Heisenberg model. It led us to determine the exchange integral: $J/k_B = -12.5$ K.

The main results of this study are summarized in Fig. 8 in which we have added an estimate of $10\,\overline{Dq}$ obtained by extrapolation of a plot of crystal field vs oxidation state of cobalt (*23*). They constitute the first complete spectroscopic characterization of six-coordinated Co(+IV) in oxides.

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