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Relations between Structure and Physical Properties in K_2NiF_4-Type Oxides*

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It is possible to predict the electronic configuration of cations such as Fe(IV), Co(III), and Ni(III) in K_2NiF_4-type oxides on the base of elementary structural and bonding considerations and to describe the more or less two-dimensional character of the magnetic interactions within the layers containing the 3d ions.

The K_2NiF_4-type structure, initially described by Balz and Plieth (*1*) and later by Ruddelsden and Popper (*2*), can be described as a sequence of layers of tetragonally distorted NiF_6 octahedra, the K^+ ions being located in 9-coordinated sites between the layers (Fig. 1). Many compounds belong to this structural type, most of them being halogenides or oxides. A large list of oxides is given in Refs. (*3–29*).

A number of investigations, especially those involving transition ions in the octahedral sites, show the two-dimensional (2D) character of these materials.

In K_2NiF_4 the separation between the layers is almost twice the intraplanar distance between two Ni^{2+} nearest neighbors. The consequences are: (i) a strong tendency for distortion of the octahedral sites along the *c* axis leading to stabilization of a specific electronic configuration for cations occupying these sites, and (ii) relatively weak interplanar interactions between the magnetic ions, so that the magnetic compounds of this type may be expected to show 2D behavior.

In this paper, which is dedicated to Professor Wells, we emphasize such properties, starting from very simple structural considerations. Our aim is (i) to predict the electronic configuration of Fe(IV), Co(III), and Ni(III) in K_2NiF_4-type oxides, and (ii) to describe the more or less 2D character of the magnetic interactions in considering the origin of the interplanar couplings.

As has been done for the perovskite compounds, it is worthwhile to investigate the relationships between crystallographic parameters and size of cations present in oxides with the K_2NiF_4-type structure. In the description given by Ganguli (*15*), the existence conditions of such oxides are deduced from the radii ratio of the cations in both sites as a function of the volume of the unit cell.

Ackerman (*16*) has proposed a tolerance factor similar to the Goldschmidt factor used for perovskites.

More recently the "invariant method"

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* Dedicated to Professor A. F. Wells on his 70th birthday.

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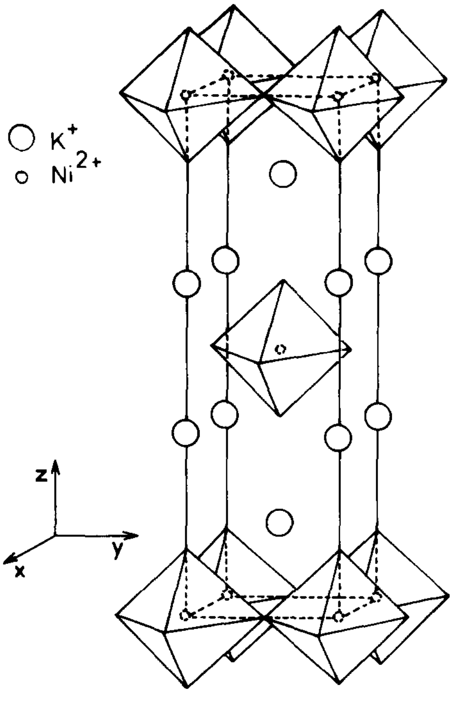

FIG. 1. The structure of K_2NiF_4.

used by Poix (*30*) has led to a rather simple relation between the average cation–oxygen distances associated to the 9- and 6-coordinated sites (ψ_A and β_B) and the volume V of the unit cell:

$$0.99615\ V^{1/3} = \beta_B + \psi_A 2^{1/2}.$$

I. Electronic Configuration of Fe(IV), Co(III), and Ni(III) Ions in K_2NiF_4 Oxides

As a consequence of the tetragonal symmetry of an ideal K_2NiF_4-type lattice, the point group of the octahedral site is D_{4h}. A shift of oxygen atoms along the c axis leads to stabilization of the d_{z^2} orbital if the distortion is an elongation and of $d_{x^2-y^2}$ in the case of compression. Electronic configurations in which the population of both e_g orbitals differs can occur, provided that the distortion of the MO_6 octahedra is strong enough. This is the behavior observed for $La_2Li_{0.5}Ni_{0.5}O_4$, in which nickel(III) (d^7) is stabilized in a low spin configuration ($t_{2g}^6 d_{z^2}^1 d_{x^2-y^2}^0$). Oxygen orbitals ($2p_x$, $2p_y$) participate simultaneously in the Ni–O and Li–O bonds. As a consequence, the weak Li–O bonding increases the covalency of competing Ni–O bonds and thereby enhances the elongation of the NiO_6 octahedra (*25*).

Similar arguments suggest the existence of Fe(IV) in a high-spin configuration in $Sr_{0.5}La_{1.5}Li_{0.5}Fe_{0.5}O_4$ ($d_{yz}^1 d_{zx}^1 d_{xy}^1 d_{z^2}^1 d_{x^2-y^2}^0$) (*24*).

If the distortion of the octahedral sites is not large enough, the electronic distribution is not "frozen" (*31*) and LS–HS transitions may eventually be observed. The "invariant method" used by Poix (*30*) allows us to predict such transitions by comparing the experimental volume of the unit cell with the theoretical value deduced from the average cation–oxygen distances in both sites of the lattice. Table I gives the results observed for phases containing Co(III) or Ni(III).

From the study of the magnetic properties of $SrLaCoO_4$, it was pointed out that about 50% high-spin and 50% low-spin cobalt(III) exists at room temperature (*14*). As shown in the table, the size of the cobalt ion appears to be intermediate between these spin states. At high temperature the proportion of high-spin trivalent cobalt increases. When the size of the present rare earth decreases, shrinking of the unit cell induces a stronger ligand field at the cobalt site and promotes stabilization of the low-spin state.

For the homologous $SrLaNiO_4$ phase, an EPR study proves that the nickel ions exist only with a low-spin configuration (*32*) as a consequence of the increasing crystal field as Co(III) is replaced by Ni(III). When we compare the nickel compounds from $SrLaNiO_4$ to $SrGdNiO_4$, the difference between the theoretical $\beta_B + \psi_A 2^{1/2}$ values calculated for low-spin and high-spin Ni(III) ions decreases, but the data show clearly that

TABLE I

ELECTRONIC CONFIGURATION OF Co(III) AND Ni(III) IN $\mathrm{Sr}LnB\mathrm{O_4}$ COMPOUNDS (Ln = La, Nd, Sm, Eu, Gd; B = Co, Ni)

	$0.99615\ V^{1/3}$	$\beta_B + \psi_A 2^{1/2}$ high spin	$\beta_B + \psi_A 2^{1/2}$ low spin	Reference
$SrLaCoO_4$ 300 K	5.635	5.716	5.605	(*14*)
673 K	5.699			
$SrNdCoO_4$	5.578	5.666	5.556	(*35*)
$SrSmCoO_4$	5.554	5.644	5.533	(*35*)
$SrEuCoO_4$	5.538	5.637	5.527	(*35*)
$SrGdCoO_4$	5.530	5.628	5.517	(*35*)
$SrLaNiO_4$	5.648	5.675	5.645	(*11*)
$SrNdNiO_4$	5.580	5.625	5.595	(*11*)
$SrSmNiO_4$	5.569	5.605	5.575	(*11*)
$SrEuNiO_4$	5.563	5.598	5.568	(*11*)
$SrGdNiO_4$	5.558	5.558	5.558	(*11*)

nickel continues to have a low-spin configuration. A study of the magnetic and electrical properties of $SrLaNiO_4$ has suggested a delocalization of the lone e_g electron in a partly filled $\sigma^*_{d_{x^2-y^2}}$ narrow band. The metallic character is due to the strong covalency of Ni(III)–O bonding (*11*).

II. Dimensionality of Magnetic Interactions in K_2NiF_4-Like Oxides

In K_2NiF_4-type oxides the existence of magnetic ions in the layers induces strong intralayer and weak interlayer magnetic couplings. It is worthwhile to examine whether one can observe a pure 2D magnetism, in other words, to investigate the origin of possible interlayer interactions. With this goal in mind, we have investigated the magnetic structure and properties of oxides containing Cr(III), Mn(IV), or Fe(III), i.e., ions with a spherical electronic configuration and whose magnetic properties can be described in terms of localized electrons. We compared the results with similar ones obtained for perovskite oxides with the same ions, which have a pure 3D-type behavior.

Magnetic Structure of K_2NiF_4-Type Oxides

The magnetic structure of Ca_2MnO_4 has been studied by Cox *et al.* (*33*) and subsequently by Ollivier (*34*). Magnetic ordering appears at 115 K. The Mn(IV) ions are coupled antiferromagnetically in the (001) planes and the spins are parallel to the *c* axis with a net decrease of the magnetic moment ($2\mu_B$/per manganese ion at 4.2 K). Interplanar magnetic ordering results in two possible configurations with or without doubling of the *c* parameter. The magnetic structure of β-Sr_2MnO_4 is given in Fig. 2 (*27*). As for Ca_2MnO_4, the magnetic moments within the layers are parallel to the *c* axis.

For $SrLaCrO_4$, whichever the model considered, the spins are aligned in the (001) planes with a moment of $2\mu_B$ at 4.2 K (*34*).

In the magnetic structure of $CaLaFeO_4$ (Fig. 3), the interplanar couplings between neighboring Fe(III) ions are also antiferromagnetic, but the moments in the (001) plane are aligned along the **a** axis and are equal to $3.75\mu_B$ at 4.2.K (*19*). Magnetic ordering appears at 373 K.

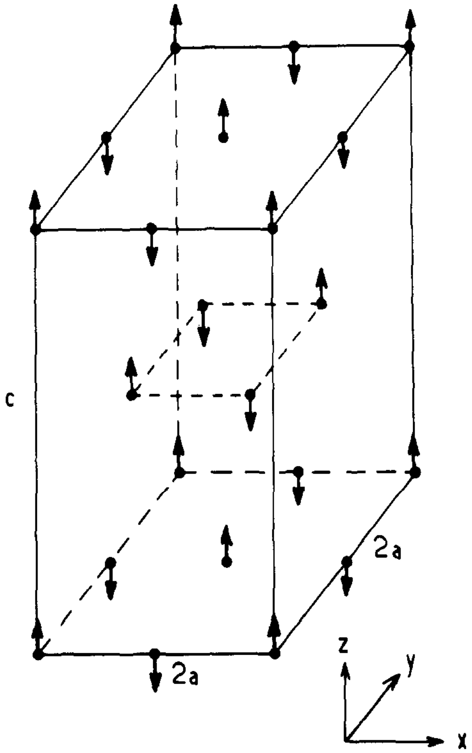

FIG. 2. The magnetic structure of β-Sr_2MnO_4.

In $SrLaFeO_4$ the different magnetic arrangements that may be considered involve all intraplanar antiferromagnetic interactions, the ionic moments being invariably in the (001) planes ($4.23\mu_B$ at 4.2 K), but differing from one another by the interplanar configuration (*20*).

From these results two important conclusions can be drawn: (i) in each compound antiferromagnetic ordering within the layers is in full agreement with the rules of superexchange. (ii) On the other hand, in most cases there is a lack of information concerning the spin orientation. This feature is not surprising since, in the K_2NiF_4-type structure, the strong antiferromagnetic interactions within the layers induce the cancellation of the interaction between neighboring layers. The interplanar interactions are then influenced by the structure as a whole.

Nevertheless, for some of these materials, Ca_2MnO_4, $CaLaFeO_4$, or $SrLaFeO_4$, studies of the critical exponent in the vicinity of ordering temperature and neutron scattering investigations indicate the simultaneous presence of both 2D and 3D magnetic correlations (*34–36*). It was of interest to determine the origin of such interlayer magnetic couplings.

Interlayer Magnetic Coupling in K_2NiF_4 Magnetic Oxides

In Table II are gathered the most significant structural and magnetic data concerning ABO_3 perovskites and K_2NiF_4-type oxides with similar magnetic ions.

Perovskite compounds. The strength of the magnetic interactions depends on the B–B distance between the first magnetic neighbors and on the covalency of the B–O bonds. This strength may be characterized

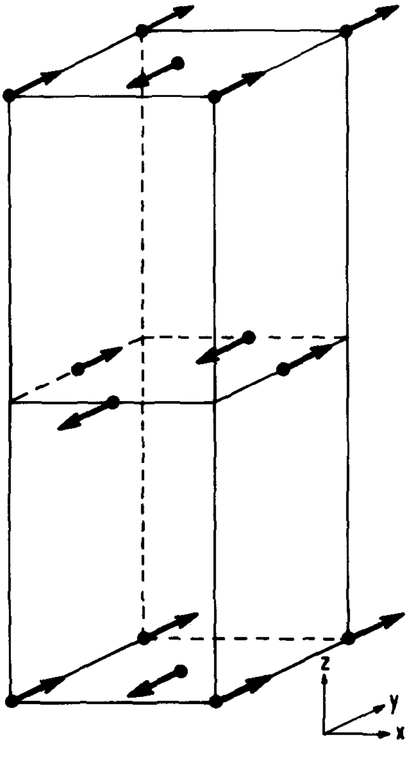

FIG. 3. The magnetic structure of $CaLaFeO_4$.

TABLE II

STRUCTURAL AND MAGNETIC DATA FOR PEROVSKITE AND K_2NiF_4-TYPE OXIDES

	⟨B–B⟩ (Å)	T_N	$\frac{\lvert J \rvert}{k_B}$	μ(4,2K) (μ_B)	Reference
$CaMnO_3$	3.73	130	12	2.64	(*37, 38*)
β-$SrMnO_3$	3.805	260	24	2.66 (77 K)	(*39*)
Ca_2MnO_4	3.667	115	26	2	(*33, 37*) (*40*)
β-Sr_2MnO_4	3.787	170	40	2.42	(*27*)
$YCrO_3$	3.792	140.6	13	2.96	(*3*)
$LaCrO_3$	3.884	282	26.2	2.45	(*3*)
$LuCrO_3$	3.761	112.4	10.3	2.51	(*3, 41*)
$SrLaCrO_4$	3.852	240	52	2	(*35*)
$CaLa_{0.6}Y_{0.4}CrO_4$	3.831		50		(*28*)
$CaYCrO_4$	3.812	120	33		(*28*)
$YFeO_3$	3.831	640	25.5		(*3, 42*)
$LaFeO_3$	3.932	740	29.5	4.65	(*3, 42*)
$LuFeO_3$	3.797	623	24.8		(*3, 42*)
$CaLaFeO_4$	3.867	373	37	3.74	(*19*)
$SrLaFeO_4$	3.880	380	37	4.23	(*20*)
Sr_2FeO_3F	3.864	358			(*43*)

by the value of the ordering temperature or by the exchange integral as far it can be determined. For all compounds with the same B cation given in Table II, $dT_N/d_a > 0$ (a is the average unit cell parameter). As pointed out by Goodenough (*44*), the more basic the A cation the higher the covalency of the π(B–O) bond, which competes with the σ(A–O) bond.

It is worthwhile to observe that the relative variation of the ordering temperature is more important for manganese or chromium compounds than for ferrites. The Mn(IV) and Cr(III) ions are isoelectronic ($t_{2g}^3e_g^0$). They are mainly coupled by t_{2g}–p_π–t_{2g} interactions of correlation and delocalization type. Therefore, the coupling strength is strongly related to the covalency of σ(A–O) bonding. On the other hand, in LnFeO$_3$ compounds (Ln = rare earth) the e_g–p_σ–e_g couplings are largely preponderant on the t_{2g}–p_π–t_{2g} ones and their strength depends essentially on the Fe–Fe distance and on the $\widehat{\text{Fe–O–Fe}}$ angle, which do not change significantly in the phases considered.

K_2NiF_4-type compounds. A similar analysis of the magnetic properties of K_2NiF_4-type oxides leads to significant conclusions with respect to the dimensionality of the magnetic interactions.

The ordering temperatures of the CaLa FeO$_4$ and SrLaFeO$_4$ ferrites are very close and apparently independent of the interlayer distance $|T_N(SrLaFeO_4) > T_N(CaLa FeO_4)|$. They are only slightly influenced by the covalency of the Ca–O or Sr–O bonds (*19, 20*). A recent study of the oxide fluoride Sr_2FeO_3F (T_N = 358 K) confirms this conclusion (*43*). The iron compounds have a prevailing 2D behavior.

For the manganese and chromium phases the situation is different: in absence of e_g electrons and of e_g–p_σ–e_g bonds the competition between the π(Mn, Cr)–O and the σ(Ca, Sr, Ln)–O bonds alters the pure 2D character of the magnetic interactions. Thus β-Sr_2MnO_4, $SrLaCrO_4$, and La-rich $CaLa_{1-x}Y_xCrO_4$ solid solutions (*27, 28, 35*) show a strong 2D behavior, whereas Ca_2MnO_4 and CaYCrO$_4$ (*28, 34*) have a 3D ordering temperature. Such discrepancies can be the result of two factors: (i) decreasing distance between the magnetic $(MnO_4)_n$ or $(CrO_4)_n$ layers due to substitution of one ion by a smaller one in the 9-coordinated site, and (ii) decreasing covalent character of the Mn–O or Cr–O bonds, as revealed by large decrease in $|J/k_B|$. This property results from the higher covalency of the competing bonds between oxygen and CN 9 cations (e.g., as Y is substituted for La or Ca for Sr).

The last contribution obviously prevails: the interlayer distance has already been shown to have no major influence on the ordering temperature in the case of ferrites.

In conclusion, the interlayer couplings in K_2NiF_4-type oxides appear to be mainly related to the covalency of the metal–oxygen bonds between the magnetic layers.

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