

Ground and excited states of KNiF_3 : An *ab initio* cluster-model approach

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Finite cluster models and a variety of *ab initio* wave functions have been used to study the electronic structure of bulk KNiF_3 . Several electronic states, including the ground state and some charge-transfer excited states, have been considered. The study of the cluster-model wave functions has permitted an understanding of the nature of the chemical bond in the electronic ground state. This is found to be highly ionic and the different ionic and covalent contributions to the bonding have been identified and quantified. Finally, we have studied the charge-transfer excited states leading to the optical gap and have found that calculated and experimental values are in good agreement. The wave functions corresponding to these excited states have also been analyzed and show that although KNiF_3 may be described as a ligand-to-metal charge-transfer insulator there is a strong configuration mixing with the metal-to-metal charge-transfer states.

I. INTRODUCTION

The electronic structure of ionic oxides exhibiting a perovskite crystal structure is of importance because of their relationship to the high- T_c superconductor mother compounds such as La_2CuO_4 . The interest in the electronic structure arises from the vinculum of certain features of the electronic structure and the electrical behavior of a given material. Hence, Zaanen, Sawatzky, and Allen proposed that the electrical behavior of a given oxide can be described in terms of the relative energies of some electronic states.¹ In this approach the energy of the pertinent electronic states is usually obtained from model Hamiltonians in which the parameters are estimated from the experiment. An even more simplified approach was used by Torrance *et al.*^{2,3} who assume, as their main physical hypothesis, that the nature of the band gap of these ionic oxides is excitonic or that it can be described through local excitations. These authors used a simple ionic model with the Madelung potential at the ion sites and gas phase atomic data as unique external parameters to compute the energy corresponding to these local excitations. By means of this ionic model Torrance *et al.* were able to classify 76 oxides, in terms of their electric conductivity, as either metals, semiconductors, or insulators.

In the simple ionic model many important physical effects such as exchange, covalency, or electronic correlations are lacking. These effects are indirectly included in the model Hamiltonian approach because the parameters are chosen from experiment. An alternative approach to the use of model Hamiltonians has been presented by Lorda *et al.*⁴ in the framework of the valence-bond (VB) theory. In this approach the crystal is represented by a cluster model and the local excitations correspond to energy differences between many-electron states dominated by different resonating structures. In order to mimic the real crystal, the cluster model is properly embedded to include the Madelung field and the quantum effects of neighboring ions. One of the interesting features of the

ab initio valence-bond cluster-model approach of Lorda *et al.*⁴ is that in the limiting case it reduces to the ionic model of Torrance *et al.* with the only difference being that the energies are computed without any external parameter. This fact permits us to use the model to investigate the importance of the effects introduced when going from the ionic model to a sophisticated *ab initio* configuration interaction wave function.⁵ Also, we notice the close similarity between the *ab initio* valence-bond cluster-model approach⁴ and the model used earlier by Fujimori and Minami.⁶ The main difference between the two approaches is that Fujimori and Minami use the philosophy of the model Hamiltonian approaches and use experimental data to obtain the parameters entering into the Hamiltonian, whereas in the approach of Lorda *et al.* all integrals are explicitly computed using a basis set of atomic orbitals.

The *ab initio* valence-bond cluster-model approach was first applied to alkaline-earth oxides because, from the point view of the ground-state electronic structure, these systems can be considered as closed shells. Therefore, the number of resonating valence-bond structures is rather small; for the electronic ground states there is only one of these structures. The alkaline-earth oxides were a good example to develop the model, although it is not clear that the excited states may be represented by local excitations.⁷ In the case of transition-metal oxides with unfilled *d* shells, it is more likely that the excited states can be properly represented by local excitations in a cluster model. This is because of the local character of the open *d* shell of many of the cations involved in these oxides. However, this character produces a tremendous increase of the number of resonating forms that can be generated from a formal ionic structure and introduces the additional problem of magnetic coupling between different cations. As recently shown⁸ the *ab initio* cluster-model approach permits a reasonable description of this complicated phenomenon.

In this work we will use an *ab initio* cluster-model approach to discuss the electronic structure of a simple

perovskite such as KNiF_3 . First, we will study the nature of the bonding in the electronic ground state and will quantify the importance of covalent contributions. An important conclusion will be that the ground electronic state of this compound can be described as largely ionic. Second, we will discuss the physical nature of the charge-transfer excited states, which, according to Torrance *et al.*^{2,3} are relevant for the electrical behavior of KNiF_3 . Finally, we will discuss the implications of our study to the formulation of model Hamiltonian approaches.

II. CLUSTER MODELS FOR KNiF_3

Three different cluster representations of KNiF_3 have been used. The first one contains explicitly two Ni^{2+} cations and their F^- bridge anion; the four K^+ cations surrounding the F^- anion are represented by nonempirical pseudopotentials, and the remaining of the crystal is simulated by an array of optimized point charges.¹¹ The use of the four K pseudopotentials is important to force the electronic structure of the F^- anion to respond to the presence of the remaining of the crystal. This lattice effect is important for the anions but is almost negligible for the cations electronic structure.¹² The Ni_2F cluster, schematically shown in Fig. 1, is the smallest part of the crystal, where ligand-to-metal and metal-to-metal local excitations are possible. Hereafter, this model will be referred to as Ni_2F . The second cluster is as Ni_2F , but it explicitly includes the remaining nearest neighbor of each metal cation; the final model may be represented as Ni_2F_{11} . To avoid any artificial polarizations, we consider a third model in which each F^- anion is surrounded by four K pseudopotentials and also with a finite-size representation of the F^- nearest-neighbor Ni^{2+} cation not explicitly included in the cluster model. This finite-size ion representation is achieved by simply including a suitable pseudopotential at the corresponding ion sites. The use of pseudopotentials permits us to account for the finite size of the second-neighbor ions and will prevent the polarization of the electronic charge density towards the positive point charges that surround the most external F^- anions of the Ni_2F_{11} cluster.¹³⁻¹⁵ This cluster will be denoted as $\text{Ni}_2\text{F}_{11}\text{PP}$.

III. CLUSTER-MODEL WAVE FUNCTIONS

Different *ab initio* wave functions were used to investigate different aspects of the electronic structure of KNiF_3 . All these *ab initio* wave functions correspond to different levels of theory, which go from the purely (*ab initio*) ionic model to the configuration interaction ap-

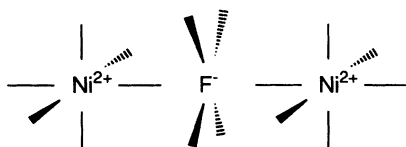


FIG. 1. Schematic representation of the Ni_2F cluster model of KNiF_3 .

proach. In all cases we consider explicitly valence electrons and use nonempirical pseudopotentials^{16,17} to represent the effect of the inner cores in the valence electronic distribution. For each Ni^{2+} cations in the Ni_2F , Ni_2F_{11} , or $\text{Ni}_2\text{F}_{11}\text{PP}$ clusters we consider explicitly the $3d^8$ electrons, whereas for F^- we explicitly consider the $2s^2 2p^6$ ones. Notice that the number of electrons explicitly considered corresponds to the ionic situation. However, this does not necessarily mean that the system will be ionic; the final distribution will depend on the final electronic wave function. This wave function has enough variational flexibility so that charge-transfer flow between the cluster model atoms is permitted and the final physical situation will be that leading to minimum cluster energy. The study of this electronic distribution is precisely one of the goals of the present work.

To obtain the *ab initio* cluster wave functions commented upon above we use a valence basis set of contracted Gaussian-type orbitals (CGTO's). For Ni^{2+} we use a basis set of $3s$, $3p$, and $6d$ primitive GTO's contracted to $2s$, $2p$, and $3d$ CGTO's and for F^- we use $5s$, $5p$, and $1p$ primitives contracted to $3s$, $3p$, $1d$. These basis sets will be referred to as $(3s, 3p, 6d/2s, 2p, 3d)$ and $(5s, 5p, 1d/3s, 3p, 1d)$, respectively. The primitive sets were initially optimized for the neutral Ni and F and supplemented with additional primitives optimized for the gas phase ions; in the case of F^- the two outermost GTO's are diffuse functions.

First, we consider the ground-state electronic structure. In this case we use *ab initio* self-consistent-field (SCF) Hartree-Fock wave functions. In the bulk crystal each Ni^{2+} cations exhibits a $t_{2g}^6 e_g^2$ electronic configuration with the two open shells coupled as $^3A_{2g}$ (in D_{2h} symmetry). In a cluster model with two Ni^{2+} cations, the two $^3A_{2g}$ can be coupled to either $^5A_{1g}$, $^3A_{1u}$, or $^1A_{1g}$. These different spin couplings are responsible for the magnetic behavior of KNiF_3 and have already been discussed in our previous works.⁸⁻¹⁰ To study the ground-state electronic structure we have chosen the high spin coupling of the two Ni^{2+} cations. This choice is justified because of the very small energy difference between the high and low spin states. To understand the nature of the chemical bond in KNiF_3 we have obtained the SCF wave function using the constrained space orbital variation (CSOV) method.¹⁸⁻²⁰ In this technique the SCF wave function is obtained following well-defined steps, each associated with a physical effect.

The second aspect of the electronic structure included in this work concerns the electronic excited states, which correspond to local excitations from the ligand to the metal or from the metal to the metal. Also, these are the electronic states considered in the model Hamiltonian approaches.^{1,6} The open-shell character of the cation's d shell originates a fairly large number of electronic states and to choose the "right" one is not that simple. This fact will be illustrated through the simplest Ni_2F cluster model. In this case it is important to use an electronic wave function, which preserves the local character of the orbitals. Hence, we start from orthogonal atomic orbitals (OAO's) (see Ref. 4), and construct an orthogonal

valence-bond (OVB) wave function which involves all the resonant VB structures (or Slater determinants written in the basis of the OAO's) that can be constructed by moving electrons in the valence space. This space involves the five $3d$ orbitals of each Ni^{2+} cation, the $2s2p$ of the central F^- anion bridge, and includes 24 active electrons. The complete active space configuration interaction (CASCI) wave function for 24 electrons in 14 orbitals (28 spin orbitals) contains too many determinants to be used as a reference function for a subsequent improved calculation involving excitations out of the valence space. Therefore, we have used a different selection criteria to include the relevant VB determinants in our OVB wave function. This selection starts with a zero-order wave function, which includes all the "logic" VB determinants and uses the perturbation theory as a guide for the determinant selection. The important determinants are included in the reference space, and external correlation is included by allowing single and double excitations out of each reference determinant. The resulting multireference configuration interaction (MRCI) problem is solved using a variation plus perturbation technique as in the CIPSI algorithm.²¹⁻²³

All the electronic wave functions described above were obtained using a locally modified version of the HONDO-size - 2CIPSI package of programs.²⁴

IV. NATURE OF THE ELECTRONIC GROUND STATE

The purpose of this section is to analyze the nature of the chemical bond in the KNiF_3 perovskite-type compound. We will be particularly concerned with the importance of different physical contributions to the total energy of the cluster-model representations of KNiF_3 . To this end we will use the CSOV technique to obtain the SCF wave functions for the Ni_2F_{11} and $\text{Ni}_2\text{F}_{11}\text{PP}$ cluster models. We start our calculation by computing the SCF wave functions for the separated $[\text{Ni}_2]^{4+}$ and $[\text{F}_{11}]^{11-}$ units. The cluster for each unit contains the appropriate background of point charges and pseudopotentials. Thus, the $[\text{F}_{11}]^{11-}$ unit for Ni_2F_{11} is calculated by substituting the real Ni^{2+} cations for Ni pseudopotentials, while maintaining the rest of the point charges as in the cluster model for Ni_2F_{11} . This strategy avoids the artificial polarizations of the anionic unit due to the point charges.^{13,25}

Once the SCF wave functions for the separated units are computed, we construct our first wave function by simply superimposing the two electronic densities without allowing any other variation. At this step we have an *ab initio* representation of the ionic model.⁵ We note that this frozen orbital (FO) initial wave function accounts for electrostatic effects due to the Madelung potential and, also, for the Pauli repulsion (or Born-repulsion terms) between the two electronic clouds. Moreover, this FO wave function is invariant with respect to similarity and unitary transformations; a localized form may be suitable for the study of the excited states, but, at this step, either a localized or delocalized description leads to the same FO wave function.

Once the FO is constructed, it is possible to study sepa-

rately the different contributions to the chemical bond in going from the FO to the full SCF cluster-model wave function. The first physical effect we include is the polarization of the cationic $[\text{Ni}_2]^{4+}$ unit. This effect is obtained by allowing the $[\text{Ni}_2]^{4+}$ occupied orbitals to vary in its own orbital space; $\text{V}(\text{Ni};\text{Ni})$. Next, we allow the Ni^{2+} cations to donate charge to the anionic $[\text{F}_{11}]^{11-}$ unit; $\text{V}(\text{Ni};\text{all})$. Clearly, this contribution cannot represent a physical effect and can only be attributed to the basis-set superposition error (BSSE). In a third step we allow the variation of the occupied orbitals of the $[\text{F}_{11}]^{11-}$ unit in its virtual space; $\text{V}(\text{F};\text{F})$. This variation accounts for the polarization of the $[\text{F}_{11}]^{11-}$ unit in response to the presence of the cations. Covalent bonding can occur in the two next variations. In the first one, $\text{V}(\text{F};\text{all})$, we allow the occupied orbitals of the $[\text{F}_{11}]^{11-}$ unit to donate charge to the $[\text{Ni}_2]^{4+}$ one, while maintaining the open shell fixed as in $[\text{Ni}_2]^{4+}$. In the second variation we allow the $[\text{Ni}_2]^{4+}$ open-shell orbitals to mix with closed-shell ones of the $[\text{F}_{11}]^{11-}$ unit; $\text{V}(\text{open};\text{closed})$. If the starting point has been properly chosen and the different contributions are not coupled, the above decomposition has to be correct. In this case, the energy at the last $\text{V}(\text{open};\text{closed})$ step will be very close to that of the unconstrained SCF wave function. Contrary to what might be initially thought, not all starting points are equally good. To illustrate this fact we have carried out a CSOV decomposition of the SCF energy for the NiF_2 cluster model, which permits us to start from either the ionic ansatz, $[\text{Ni}]^{2+}$ and $[\text{F}_2]^{2-}$, or from the neutral, one $[\text{Ni}]^0$ and $[\text{F}_2]^0$. In each case the starting orbitals for each unit have been computed separately in the remaining of the crystal as indicated above. In the first case, the expectation value for the energy corresponding to the FO ionic starting wave function is only 0.465 eV higher than the unconstrained SCF energy. However, in the second case, where the FO is constructed by superimposing the electron densities of the neutral atoms, the energy difference commented on above is 40.109 eV. After a CSOV cycle, i.e., at the $\text{V}(\text{open};\text{closed})$ step, the energy is 38.724 eV higher than the SCF one. Therefore, if the starting point corresponds to the neutral limit, the different CSOV steps are highly coupled and many CSOV cycles will be required to reach the unconstrained Hartree-Fock SCF solution. The physical origin of the difference obtained from the two FO wave functions is a first indication of the highly ionic character of KNiF_3 (*vide infra*). Moreover, the above discussion tells us that the largest contribution to the bond comes precisely from the Madelung potential.

The different contributions to the final energy obtained when going from the ionic FO wave function to the SCF one may be expressed as the difference between the energy at a given step and the FO energy,

$$\Delta_1 = E_{\text{step } "i"} - E_{\text{FO}} , \quad (1)$$

and the energy gain at each step of the CSOV procedure,

$$\Delta_2 = E_{\text{step } "i"} - E_{\text{step } "i-1"} . \quad (2)$$

In Table I we report numerical results for the importance

TABLE I. CSOV energy decomposition of the Ni_2F_{11} (first column) and $\text{Ni}_2\text{F}_{11}\text{PP}$ (second column) cluster models of KNiF_3 starting from the ionic, FO, situation. The different contributions to the bond (in eV) are expressed as Δ_1 and Δ_2 defined as in Eqs. (2) and (3), respectively. Results in the third column correspond to a calculation for $\text{Ni}_2\text{F}_{11}\text{PP}$ in which the $4s$ and $4p$ basis functions of each Ni^{2+} cation have been deleted.

Orbital variation	Physical contribution	Cluster model		
		Ni_2F_{11}	$\text{Ni}_2\text{F}_{11}\text{PP}$	$\text{Ni}_2\text{F}_{11}\text{PP}$ (no $4sp$ basis)
Step "i"		Δ_1/Δ_2	Δ_1/Δ_2	Δ_1/Δ_2
V(Ni;Ni)	Cation polarization	0.072/0.072	0.069/0.069	0.063/0.063
V(Ni;all)	Cation donation (BSSE)	0.173/0.102	0.138/0.069	0.134/0.071
V(F;F)	Anion polarization	0.726/0.553	0.605/0.467	0.601/0.466
V(F;all)	Anion donation	1.865/1.139	1.576/0.971	0.700/0.099
V(open;closed)	Open-shell delocation	2.491/0.625	2.245/0.669	1.390/0.690
Full SCF	Remaining terms	2.524/0.033	2.283/0.038	1.418/0.028

of each of the contributions commented on above in the Ni_2F_{11} and $\text{Ni}_2\text{F}_{11}\text{PP}$ cluster models.

With respect to the numerical values corresponding to the Ni_2F_{11} and $\text{Ni}_2\text{F}_{11}\text{PP}$ clusters, first and second columns of Table I, we first notice that, as expected, the sum of all contributions is only of ≈ 2.5 eV; compared to the crystal binding energy per atom or the effect of the Madelung contribution, this is only a small contribution, which shows that KNiF_3 can in fact be regarded as a highly ionic material. Now let us analyze the different contributions to the final SCF wave functions. As expected, polarization of the cationic part is very small. The covalent donation from each Ni^{2+} cation to the $[\text{F}_{11}]^{11-}$ unit has no physical meaning because the valence shell of each F^- anion is already filled, and it can only be due to the BSSE. The energy contributions of this variation provides a measure of the uncertainties of our analysis of the interaction; this uncertainty is of only ≈ 0.1 eV. Next we have the contribution of polarization of the $[\text{F}_{11}]^{11-}$ unit, which allows for a 0.5-eV stabilization. The rest of the terms are due to covalent contributions to the chemical bond. Charge donation from $[\text{F}_{11}]^{11-}$ to the cation appears to be the most important contribution, ≈ 1 eV. This contribution is smaller in the $\text{Ni}_2\text{F}_{11}\text{PP}$ cluster model and shows the importance of the finite size of the cations, which surround the $[\text{F}_{11}]^{11-}$ unit. The delocalization of the Ni^{2+} magnetic open-shell orbitals in the anion "p band" is also of importance; it is similar to the $[\text{F}_{11}]^{11-}$ polarization. At the last V(open;closed) step the energy of our cluster model is only ≈ 0.04 eV higher than the SCF solution, showing the goodness of the above decomposition.

The previous analysis points out the importance of different physical contributions to the bonding in KNiF_3 . While the $[\text{F}_{11}]^{11-}$ polarization and V(open;closed) contributions are rather modest, the V(F;all) seems to be the more important bonding mechanism after the purely electrostatic Madelung term. This seems to indicate that covalency can play a role in the bonding in KNiF_3 . To further analyze the origin of this contribution, we have again carried out the CSOV analysis but deleting the basis-set functions, which represent the $4s$ and $4p$ Ni atomic orbitals. As it appears in the third column of

Table I, all the CSOV steps except one are identical to the results obtained with the full basis set. The contribution of the V(F;all) step is ten times smaller. The interpretation of this fact is straightforward: charge donation from the $[\text{F}_{11}]^{11-}$ unit does not go to the empty e_g orbitals of each Ni^{2+} cation but rather to the $4sp$ shell. This result may indicate a certain d -to- sp hybridization in KNiF_3 or may reveal an artifact of the previous analysis. At this point we must recall that the electronic ground state of the gas phase Ni^{2+} is ^3F arising from a d^8 electronic configuration, whereas the lowest term of the d^7s^1 configuration lies 6.8 eV higher. In the case of Ni^+ , the electronic ground state is ^2D from a d^9 configuration, and the ^4F from d^8s^1 lies at 0.89 eV in energy.²⁶ However, at the Hartree-Fock level the order of multiplets is not well reproduced and the ^4F from d^8s^1 lies 0.63 eV below the ^2D state which arises from the d^9 configuration.²⁷ Hence, the Hartree-Fock approach will incorrectly favor a d^8s^1 occupation and the charge-transfer donation at the V(F;all) CSOV step will be an artifact. The use of a basis set without the $4sp$ functions avoids this possibility. While d -to- sp hybridization cannot be completely excluded the atomic data above reported suggest to interpret the V(F;all) donation as an artifact. Given the quality of the basis sets we use it is also unlikely that this effect is simply due to BSSE. Our interpretation is that the $[\text{F}_{11}]^{11-}$ unit gains an additional stabilization by allowing the electronic distribution to be polarized using the rather diffuse $4s$ and $4p$ functions. Below we present a different analysis, which further clarifies this point.

The above CSOV analysis exclusively based in energy contributions makes it difficult to establish the relationship between an energy stabilization due to charge donation and the extent to which charge donation occurs. To have a definitive answer, an analysis of the wave function seems unavoidable. The main idea of this analysis is simply to compare the changes introduced in the wave function at each step of the CSOV procedure. To this end, we have computed the overlap Ω between the FO wave function and that obtained at a given step of the CSOV procedure.

$$\Omega = \langle \Psi_{\text{FO}} | \Psi_{\text{step "i"}} \rangle . \quad (3)$$

This is the overlap integral between two Slater determinants each written in a different set of molecular orbitals. Obviously, these two sets of molecular orbitals are nonorthogonal, and the computation of Ω requires us to compute the determinant of the overlap integrals between the two sets of molecular orbitals [see Eq. (39) in Ref. 28]. Since FO is a representation of the ionic model, any deviation of Ω from unity will indicate a deviation from the ionic model. This analysis can be thought as a valence-bond decomposition of the SCF wave function. In fact, the square of Ω represents, in percent, the contribution of the ionic VB resonating forms to the total SCF wave function (see Refs. 25, 29, and 30).

The analysis of the Ω values has been carried out for the Ni₂F₁₁PP cluster with and without including a basis-set representation of the 4s and 4p orbitals of Ni. A summary of results for Ω is reported in Table II. Of particular interest is the value of Ω after the donation from the anionic unit to the cationic part, $\langle \Psi_{FO} | \Psi_{V(F;all)} \rangle$. For the cluster with the full basis $\langle \Psi_{FO} | \Psi_{V(F;all)} \rangle = 0.9749$, whereas this value is 0.9899 if the 4sp basis of the Ni²⁺ cations is deleted. This means that after the V(F;all) step 95% of the wave function can be represented by the ionic model if the 4sp basis set are explicitly introduced and 98% if these functions are deleted. This is a clear indication that the energy stabilization due to charge donation from [F₁₁]¹¹⁻ to [Ni₂]⁴⁺ that can be attributed to covalency does not introduce significant changes in the description of the bonding in KNiF₃. Even accepting that V(F;all) represents a covalent effect due to orbital hybridization, the final SCF wave function does not deviate largely from the FO ionic one. In the less covalent scenario, the FO wave function accounts for 92% of the SCF wave function; a 95% if the Ni 4sp basis is omitted.

Our analysis has been based in *ab initio* Hartree-Fock wave functions, which do not include electronic correlation. Also, we have considered only the high spin coupling of the two open-shell cations. For alkaline-earth oxides it has been recently shown that correlation effects are mainly of atomic nature;⁵ the main effect is the radial and angular correlation of the O²⁻ electronic distribution. It is very likely that correlation effects will play the same role in KNiF₃. Likewise, the effect of magnetic coupling has not been included in our SCF cluster-model wave function. However, a complete active space configuration interaction (CASCI) calculation, which

only involves the open-shell magnetic orbitals, is enough to predict the correct antiferromagnetic behavior.⁸ Hence, this CASCI does not introduce additional covalent effects, but it is enough to properly describe the magnetic behavior of KNiF₃.

We conclude this section by pointing out that both analyses, the CSOV and the Ω results, are consistent. Both approaches indicate that KNiF₃ can be largely described as an ionic system. Moreover, the deviation from the ionic model only permits a modest stabilization, ≈ 2.5 eV, compared to the magnitude of the electrostatic contribution arising from the Madelung potential. Moreover, 50% of this effect is due to the polarization of the anionic electronic cloud, the other moiety being a purely covalent effect. The analysis of the wave function indicates that covalent contributions to the SCF wave function are less than 10%. This contribution is probably overestimated because of the cluster stoichiometry; in our cluster there are eleven anions for two cations, whereas the proper stoichiometry will contain six anions (see Ref. 13).

Finally, we note that it may be properly argued that the present clusters provide only a small representation of the bulk crystal. While this limited representation may affect some of the crystal properties, there is a large body of evidence indicating that these limited models are suitable to study local properties and especially well suited to study ionic systems.³¹ We would like to point out that the importance of the covalent effects in KNiF₃ was analyzed much earlier by Wachters and Nieuwpoort.³² Based on different cluster models and, also, on the study of rather different properties, Wachters and Nieuwpoort concluded that for KNiF₃ the classical ionic model provides a good physical approach to explain the major part of the crystal-field splitting. These conclusions are in perfect agreement with those described above.

V. EXCITED STATES OF KNiF₃ AND THE ORIGIN OF THE OPTICAL GAP

In this section we will investigate the physical nature of some excited states of KNiF₃. We will be particularly concerned with the electronic states originating from local charge-transfer excitations and not with those states arising from the crystal-field splitting. The former are those to which the ionic model of Torrance *et al.*^{2,3} refers, while the latter have been extensively studied in the past; see for instance the work by Wachters and Nieuwpoort.³²

The basic idea behind this work is that the electronic wave function corresponding to each electronic state can be written as a configuration interaction of some resonant structures as in the valence-bond theory of Hubbard, Rimmer, and Hopgood,³³ but following a purely *ab initio* approach as in the recent work of Lorda *et al.*⁴ Associated to each resonant structure there are many Slater determinants that can be constructed from the set of valence orthogonal atomic orbitals. The use of atomic orbitals as one electron functions is strictly necessary if one wants to ascribe the Slater determinants to a given valence-bond structure. Unfortunately there is no

TABLE II. Overlap integral between the frozen orbital (FO) wave function and that obtained at each step of the CSOV procedure (see Sec. IV).

Overlap integral	Cluster model	
	Ni ₂ F ₁₁ PP (full basis)	Ni ₂ F ₁₁ PP (no 4sp basis)
$\langle \Psi_{FO} \Psi_{V(Ni;Ni)} \rangle$	0.9993	0.9994
$\langle \Psi_{FO} \Psi_{V(Ni;all)} \rangle$	0.9988	0.9988
$\langle \Psi_{FO} \Psi_{V(F;F)} \rangle$	0.9905	0.9906
$\langle \Psi_{FO} \Psi_{V(F;all)} \rangle$	0.9749	0.9899
$\langle \Psi_{FO} \Psi_{V(open;closed)} \rangle$	0.9607	0.9748
$\langle \Psi_{FO} \Psi_{SCF} \rangle$	0.9583	0.9728

guarantee that the orthogonal atomic orbitals preserve their atomic character (see Ref. 30). In some cases the physical nature of a given state is delocalized and cannot be properly described through a local picture.⁷ However, the analysis of the ground state reported in the preceding section permits us to use such a local description of the charge-transfer states of KNiF_3 , i.e., there is no doubt about the local nature of the partially filled cation d orbitals. The OAO's used to construct the Slater determinants are obtained by previous SCF calculations for ions in the Madelung field, and, in a second step, they are orthogonalized following the procedure described by Loda *et al.*⁴ For F^- the AO's are essentially $2s$, $2p_x$, $2p_y$, and $2p_z$, and this character is not changed by the orthogonalization procedure. For the Ni^{2+} cations the d atomic orbitals split in t_{2g} and e_g because of the Madelung field. However, because of the use of a finite-cluster model centered in the anion, these cations no longer have the full octahedral symmetry as in bulk KNiF_3 . However, they can still be identified as "nearly" t_{2g} (d_{xy} , d_{xz} , and d_{yz}) and e_g ($d_{x^2-y^2}$, d_{z^2}) when orthogonalized. We will use this notation when constructing the orthogonal valence-bond determinants from the set of OAO's. We must recall that these valence-bond determinants are not symmetry adapted because they are constructed from almost purely atomic one-electron functions and not from molecular orbitals. With the Ni_2F cluster model it is possible to work with C_s symmetry, while still preserving the atomic character of the orbitals; this is the point group we used in our orthogonal valence-bond calculations. The final electronic wave function is, of course, symmetry adapted (for the Ni_2F cluster model the proper symmetry group is D_{2h}). For simplicity we will, however, make use of the irreducible representations of the C_s point group when necessary.

As in the case of alkaline-earth oxides,^{4,5} there are three main resonant structures in KNiF_3 , which correspond to the ground state, the ligand-to-metal charge transfer, and the metal-to-metal charge transfer. The ground-state resonant valence-bond form may be viewed as a structure in which each cation has a $2+$ charge and each anion a -1 one (see Fig. 1). In a finite-cluster model representation this resonant form will be written in terms of Slater determinants having eight electrons per atom. However, because of the unfilled nature of the cation d shells, there are many possible configurations and each configuration generates many Slater determinants cause of the different spin combinations. Many of these spin combinations correspond to the different magnetic coupling states discussed in Refs. 8–10. The energy difference between these magnetic states is fairly small, it is smaller by several orders of magnitude than the energy difference between the ground and charge transfer states. Therefore, we have decided to include only those states where the four open-shell electrons are coupled to give $S_z=2$. With this spin restriction there is only one Slater determinant corresponding to the ground-state resonating structure and with all the atoms in their electronic ground state. If A , B , and F label the cations and the anion, this state can be written as

$$|\Psi_G\rangle = |(t_{2g}^6 e_g^2)_A (2s^2 2p^6)_F (t_{2g}^6 e_g^2)_B\rangle. \quad (4)$$

Even with the spin restriction described above, there are 52 Slater determinants (of A' symmetry), where the full ionicity is preserved; these are the different spin combinations associated with intra-atomic crystal-field excitations in each one of the cations or in both of them. Hence, we may have

$$\begin{aligned} |\Psi_2\rangle &= |(t_{2g}^5 e_g^3)_A (2s^2 2p^6)_F (t_{2g}^6 e_g^2)_B\rangle, \\ |\Psi_3\rangle &= |(t_{2g}^6 e_g^2)_A (2s^2 2p^6)_F (t_{2g}^5 e_g^3)_B\rangle, \\ |\Psi_4\rangle &= |(t_{2g}^5 e_g^3)_A (2s^2 2p^6)_F (t_{2g}^5 e_g^3)_B\rangle, \\ |\Psi_5\rangle &= |(t_{2g}^4 e_g^4)_A (2s^2 2p^6)_F (t_{2g}^6 e_g^2)_B\rangle, \end{aligned} \quad (5)$$

which, for interpretative purposes, will be designated as $|\Psi_{10Dq}\rangle$.

Ligand-to-metal charge-transfer valence-bond states can be obtained by single excitations from one electron in the $2s$, $2p_x$, $2p_y$, or $2p_z$ (the z axis along the three cluster atoms) orbitals of F^- to the unfilled orbitals of either A or B and from any one of the Slater determinants corresponding to the full ionic resonant form. All the resulting determinants correspond to the same generic valence bond structure, where an electron has been transferred from F^- to the cation on the right or to the cation on the left. With the $S_z=2$ spin restriction there is a total of 148 determinants belonging to the A' irreducible representation. These 148 Slater determinants associated to the ligand-to-cation charge transfer will be schematically represented as $|\Psi_\Delta\rangle$. To describe the electronic structure of the ligand to metal charge-transfer states, some of these determinants are more important than others. In particular, we define

$$\begin{aligned} |\Psi_{\Delta(z)}\rangle &= |(t_{2g}^6 e_g^2)_A (2s^2 2p_x^2 2p_y^2 2p_z^1)_F (t_{2g}^6 e_g^3)_B\rangle, \\ |\Psi_{\Delta(y)}\rangle &= |(t_{2g}^6 e_g^2)_A (2s^2 2p_x^2 2p_y^1 2p_z^2)_F (t_{2g}^6 e_g^3)_B\rangle, \\ |\Psi_{\Delta(x)}\rangle &= |(t_{2g}^6 e_g^2)_A (2s^1 2p_x^2 2p_y^2 2p_z^2)_F (t_{2g}^6 e_g^3)_B\rangle, \\ |\Psi_{\Delta(z)} + 10Dq\rangle &= |(t_{2g}^5 e_g^3)_A (2s^2 2p_x^2 2p_y^2 2p_z^1)_F (t_{2g}^6 e_g^3)_B\rangle. \end{aligned} \quad (6)$$

Finally, we consider the states where the charge transfer is from metal to metal. In this case there are 48 Slater determinants with $S_z=2$ and of A' symmetry. A representative example of this determinants will be

$$|\Psi_U\rangle = |(t_{2g}^6 e_g^1)_A (2s^2 2p^6)_F (t_{2g}^6 e_g^3)_B\rangle, \quad (7)$$

where an electron has been transferred from the cation on the left, in our Ni_2F cluster model, to the one in the right. Of course, there are symmetric structures, where the charge transfer is right to left.

The model space involving simultaneously the three valence-bond resonating forms contains 248 orthogonal valence-bond determinants. The diagonal elements H_{ii} of the matrix representation of the full *ab initio* Hamiltonian in this model space can be taken as a crude approximation of the energy corresponding to each state. Notice that there are many states corresponding to the same resonant structure and that contrarily to what happens in

alkaline-earth oxides these are not necessarily degenerated. The states corresponding to each resonant structure may be viewed as a "band," and the lowest H_{ii} element may be taken as the *ab initio* ionic model energies (4), which will correspond to those of the empirical ionic model of Torrance *et al.*^{2,3} The relevant energies are

$$\begin{aligned} E_G^{\text{IM}} &= \langle \Psi_G | \hat{H} | \Psi_G \rangle, \\ E_{\Delta(Z)}^{\text{IM}} &= \langle \Psi_{\Delta(Z)} | \hat{H} | \Psi_{\Delta(Z)} \rangle, \\ E_{\Delta(Y)}^{\text{IM}} &= \langle \Psi_{\Delta(Y)} | \hat{H} | \Psi_{\Delta(Y)} \rangle, \end{aligned} \quad (8)$$

where the IM superscript stands for *ab initio* ionic model. According to the ionic model, the optical gap can be thought as a local excitation from the full ionic structure to either ligand-to-metal or metal-to-metal resonant forms. In KNiF₃ the lowest excitation is ligand-to-metal charge transfer or, using the *ab initio* ionic model, from $|\Psi_G\rangle$ to $|\Psi_{\Delta}\rangle$ (either $|\Psi_{\Delta(y)}\rangle$ or $|\Psi_{\Delta(z)}\rangle$). In this model we are implicitly assuming that the optical gap is of excitonic nature or that the lower excitons are very close to the optical gap. We then define the two following excitation energies:

$$\begin{aligned} \Delta_Y^{\text{IM}} &= E_{\Delta(Y)}^{\text{IM}} - E_G^{\text{IM}}, \\ \Delta_Z^{\text{IM}} &= E_{\Delta(Z)}^{\text{IM}} - E_G^{\text{IM}}. \end{aligned} \quad (9)$$

The calculated value for Δ_Y^{IM} and Δ_Z^{IM} is of 20.1 and 20.5 eV, respectively; both values being considerably larger than the experimental optical gap which is of ≈ 12.5 eV.³⁴

Now we will explicitly consider the configuration interaction mixing of the different valence bond determinants corresponding to the above described resonant forms. This is done by solving the secular equations for the valence configuration interaction problem. In this case we have to analyze different roots of the Hamiltonian matrix. The relevant roots are those dominated by the resonant structures above described. In Table III we report an analysis of those electronic states, which are dominated by the $|\Psi_G\rangle$, $|\Psi_{\Delta(z)}\rangle$, and $|\Psi_{\Delta(y)}\rangle$ deter-

TABLE III. Major contributions of different Slater determinants to the valence configuration interaction wave functions corresponding to the ground state and the lowest charge-transfer excited states. Electronic states (in columns) are denoted by the Slater determinant with largest contribution. The contributions of different determinants (in files) are given in percent.

	$ \Psi_G\rangle$	$ \Psi_{\Delta(z)}\rangle$	$ \Psi_{\Delta(y)}\rangle$
$ \Psi_G\rangle$	96.7		
$ \Psi_{10Dq}\rangle$			0.9
$ \Psi_{\Delta(z)}\rangle$	2.6	99.5	6.0
$ \Psi_{\Delta(y)}\rangle$			81.8
$ \Psi_{\Delta(s)}\rangle$	0.6	0.3	
$ \Psi_{\Delta(z)+10Dq}\rangle$		0.1	2.5
$ \Psi_{\Delta(y)+\Delta(z)}\rangle$			1.8
$ \Psi_U\rangle$			7.0
Others	0.1	0.1	

minants. We will use the same notation to indicate a given electronic state and its leading determinant and comment on the differences when necessary. The energy expectation value for each of these electronic states permits to define the valence configuration interaction (VCI) excitation energies corresponding to Eq. (9). Thus, we have

$$\begin{aligned} \Delta_Y^{\text{VCI}} &= E_{\Delta(Y)}^{\text{VCI}} - E_G^{\text{VCI}}, \\ \Delta_Z^{\text{VCI}} &= E_{\Delta(Z)}^{\text{VCI}} - E_G^{\text{VCI}}. \end{aligned} \quad (10)$$

The calculated values for Δ_Y^{VCI} and Δ_Z^{VCI} are now 20.3 and 21.2 eV, respectively. Therefore, inclusion of valence correlation does not largely affect the calculated excitation energies. The effect in Δ_z is almost negligible because, at the VCI level, $|\Psi_{\Delta(z)}\rangle$ does not mix appreciably with any other state (see Table III). Hence, the 0.7-eV increase from the IM to the VCI value in Δ_z arises from the energy decrease on $|\Psi_G\rangle$ due to the configurational mixing. Notice that even after configurational mixing the electronic ground state can be represented by the $|\Psi_G\rangle$ determinant up to 96%. The ionic nature of the electronic ground state found arising from the explicitly correlated VCI wave function is in perfect agreement with the analysis of the chemical bond presented in Sec. IV. The effect of valence correlation is rather large for $|\Psi_{\Delta(y)}\rangle$; the leading determinant only contributes to the VCI wave function by $\approx 82\%$ and the Δ_Y^{IM} and Δ_Y^{VCI} values appear to be very close.

There are two important conclusions arising from the above analysis. The first one is that configuration interaction, in the valence space, does not largely affect the charge-transfer excitation energies. The second conclusion is that an important effect appears in the corresponding wave functions. As commented on above, the valence CI wave function for $|\Psi_{\Delta(y)}\rangle$ is essentially a mixture of 82% of the $|\Psi_{\Delta(y)}\rangle$ determinant, 6% of $|\Psi_{\Delta(z)}\rangle$, and 7% of $|\Psi_U\rangle$. We must point out that $|\Psi_{\Delta(y)}\rangle$ and $|\Psi_{\Delta(z)}\rangle$ belong to the same ligand-to-metal resonant form, whereas $|\Psi_U\rangle$ corresponds to a metal-to-metal resonating structure. Therefore, there seems to exist a real effect of valence-bond resonance, or valence correlation, in some excited states. This effect largely increases when considering higher roots of the valence configuration interaction matrix and makes it almost impossible to find excited states, where $|\Psi_U\rangle$ is the dominant configuration. The reason for this large configuration mixing can be understood by looking at the distribution of the diagonal elements of the valence configuration interaction matrix. In Fig. 2 we present such a distribution in the form of a density of states $D(E)$ obtained by smoothing the discrete spectral distribution by a Lorentzian with a 0.5 constant width.

The $D(E)$ curve in Fig. 2 exhibits three clear peaks; each one is associated to a resonant structure. Hence, the lower peak corresponds to all the determinants associated with the full ionic form (Fig. 1), while the other two correspond to ligand-to-metal and metal-to-metal charge-transfer excitations, respectively. These two peaks present a considerable overlap and are responsible for the

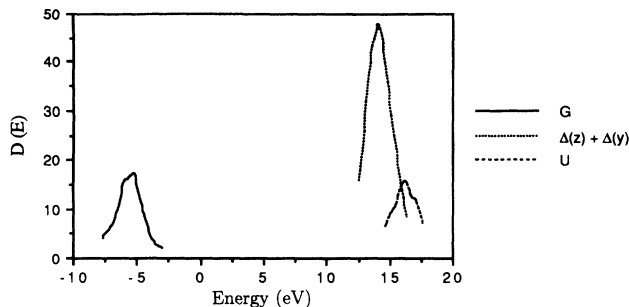


FIG. 2. Representation of the density of states, $D(E)$, corresponding to the Ni_2F cluster model of KNiF_3 , as obtained from the diagonal elements of the valence configuration interaction matrix, i.e., from the *ab initio* ionic model. A 0.5 constant width Lorentzian has been used to fit the energy discrete values to $D(E)$.

configuration mixing in the excited states.

To end this section we discuss the effect of external correlation in the charge-transfer excitation energies. We have used the valence configuration interaction wave functions as references for a multireference configuration interaction (MRCI) treatment involving single and double excitations out of each reference determinant. The reference spaces thus constructed contain between 10 and 30 determinants and generate about 500 000 determinants. The resulting MRCI problem is solved by including the variational contribution of those determinants contributing to the first-order wave function by more than 0.00008, whereas the energy contribution of the rest of generated determinants is taken up to second order using the CIPSI algorithm and the Epstein-Nesbet partition of the total Hamiltonian.^{21–24} The calculated MRCI excitation energies, Δ_Y^{MRCI} and Δ_Z^{MRCI} , defined as in Eq. (10), are rather different from the VCI or IM values. For Δ_Z^{MRCI} the calculated value is 14.7 eV, whereas for Δ_Y^{MRCI} , for which there is an important valence configuration mixing in the reference $|\Psi_{\Delta(y)}\rangle$ wave function, the calculated value is of 13.6 eV. Both calculated MRCI values are quite close to the experimental excitation energy corresponding to the optical gap, which is 12.5 eV.³⁴ Considering the simplicity of our cluster model, the agreement is quite satisfactory. The large effect of external correlation was also found in the previous study of Lorda *et al.*⁴ and attributed to the instantaneous adaptation of the atomic orbitals to each resonant form. We strongly believe that the same explanation holds here.

Finally, let us close this section by pointing out that, even if the agreement with calculated and experimental optical excitation is reasonable, the importance of the present model lies in the analysis of the physical nature of the different electronic states. The present study shows that the ligand-to-metal charge transfer are largely the excitations leading to the optical gap and indicate that KNiF_3 is well described as a ligand-to-metal charge-transfer insulator in good agreement with the experimental evidence. However, these excitations are mixed to the local metal-to-metal charge-transfer excitations, although

to a modest 7% contribution. Therefore, the model permits not only a reliable estimate of the optical gap but it also allows an estimate of the physical nature of the relevant excited states. In particular, the strong configuration interaction mixing in the excited electronic states may be of importance to understand the electronic structure of the high- T_c superconductor mother compounds such as La_2CuO_4 .

VI. IMPLICATIONS TO THE FORMULATION OF MODEL HAMILTONIANS

In this work we have shown that a careful analysis of the electronic structure of the electronic states involved in the excitations leading to the optical gap is of importance to understand its physical nature. Work along the same lines has been recently reported by Martin and Hay³⁵ and by Wang, Newton, and Davenport,³⁶ although both studies were concerned with La_2CuO_4 . Based on the *ab initio* calculations, Martin was able to derive an effective Pariser-Parr-Pople (PPP) Hamiltonian³⁷ for La_2CuO_4 . A very important conclusion of the work of Martin³⁷ was to show that one should not expect to reproduce both the optical gap and the magnetic coupling constant J in a PPP or Hubbard model.

Based on our results, we would like to point out the difficulty in the proper choice of the relevant orbitals that one must consider in the effective Hamiltonian. In KNiF_3 a first guess would be to consider charge-transfer excitations from the anion p orbital following the Ni-F-Ni axis. However, the *ab initio* calculation shows that it is better to consider an excitation from a p orbital perpendicular to this axis because it permits a more efficient configurational mixing. A second point concerns the number of resonant structures that one should include in the effective Hamiltonian and how many determinants associated to each resonant structure are necessary. The analysis in Table III provides useful information to any researcher interested in developing a model Hamiltonian for KNiF_3 . A similar study for La_2CuO_4 is currently being carried out in our laboratory.³⁸

Finally, it is necessary to point out that our approach is very close to the theory developed by Zaanen, Sawatzky, and Allen¹ but, while these authors consider metal-metal and ligand-metal charge transfer for ions, which are infinitely far away, our work explicitly considers the hole-particle interaction. Even if we ignore the hole-particle interaction and use a cluster model with the ions at very large distance of each other, there still will be a large number of important determinants associated to each “distant” valence-bond structure. An important point is that many diagonal elements will appear. In a model Hamiltonian approach these elements are reduced to a single Δ and/or a single U parameter. Therefore, a preliminary *ab initio* study will be able to show whether a model Hamiltonian is suitable or not and which are the relevant parameters. In some cases it might be found that a single-band-model Hamiltonian can be formulated, as in La_2CuO_4 , while in other cases it might not be possible to use such a simplified model or its use will lead to less reliable results. Use of model Hamiltonians is very

attractive because some of them can be exactly solved in the case of an extended system (in the one, two, or three-dimensional case). However, the parameters entering into the model Hamiltonian are usually extracted from experiments. Therefore, it may well be possible to make good predictions from a model Hamiltonian that does not have the proper physical basis. In this sense, *ab initio* and model Hamiltonian approaches have to be regarded as complementary, and work along the lines presented by Martin³⁷ seems to be in the right direction.

VII. CONCLUSIONS

Using a finite-cluster model representation of bulk KNiF₃ and several theoretical techniques, we have shown that KNiF₃ can be described as an ionic system and the covalent contributions quantified to the bond from two different points of view; these are the contributions to the energy and to the total SCF wave function. Both techniques are consistent with a small participation of covalent effects. The contribution of covalent effects to the SCF energy of our cluster models is less than 2 eV and is due to two different physical effects. The first effect is the charge donation from the anions to the unfilled *d* orbitals of each cation. The contribution of this charge donation covalent effect is rather small, as shown by the calculations, which do not include the cation 4*s* and 4*p* orbitals in the variational space, and we suggest that this covalent effect may be an artifact of the incorrect order of the electronic states of Ni⁺ at the Hartree-Fock level of theory. The second effect is the delocalization of the magnetic orbitals in the closed-shell orbitals of the anionic unit, and its contribution to the stabilization energy is more important than the charge donation effect discussed above. The last effect is responsible for an important contribution to the antiferromagnetism of KNiF₃.⁸⁻¹⁰ Cluster-model calculations using an explicitly correlated wave function indicate that the physical nature of the ground state does not change upon introduction of valence correlation effects.

The low-lying excited states involving local charge transfer have been found to be mainly of ligand-to-metal charge-transfer character. However, a strong configuration interaction mixing appears in these excited states making it very difficult to study the excited states dominated by metal-to-metal charge donation. The origin of this configuration mixing can be understood at the very simple *ab initio* ionic model, to which our model reduces if no configurational mixing is allowed. The *ab*

initio ionic model values for ligand-to-metal and metal-to-metal charge transfer are very close thus mixing strongly to each other. The lowest ligand-to-metal charge-transfer state involves the transference of one electron from the ligand orbitals, which are perpendicular to the Ni-F-Ni axis, contrarily to chemical intuition. The calculated optical gap, defined as the energy difference between ground state and lowest-charge-transfer excited state with the restriction of preserving the spin multiplicity, is 13.6 eV. This value is very close to the experimental gap (12.5 eV). This provides additional support to the goodness of the *ab initio* cluster model approach to the study of ionic solids. The analysis of the wave functions corresponding to the low-lying charge-transfer excited states permits us to extract the leading configurations and the important orbitals. The implications to the formulation of model Hamiltonians is clear; the *ab initio* approach provides a useful guide to decide which orbitals one has to include in the Hamiltonian.

Finally, we would like to point out that although the present results are based on the use of finite, and rather small, cluster models for a bulk crystal, it is unlikely that the physical nature of the different electronic states described above will change if the cluster-model size is largely increased. This is because of the high ionic character of the electronic states of KNiF₃ studied here; in these states the electron density is highly localized around the crystal ions and delocalization plays only a modest role. In conclusion, we have presented a unified *ab initio* cluster-model vision of the electronic structure of bulk KNiF₃. The present work has permitted us to understand the nature of the chemical bond in the electronic ground state and, also, of the optical gap.

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