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Cluster study of the neutron-scattering form factor for antiferromagnetic $KNiF_3$ and NiO

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Motivated by difficulties in understanding the magnetism of the insulating parents of high-T_c superconductors, we have studied the less covalent, and thus simpler, antiferromagnetic (AF) insulators NiO and $KNiF_3$. We also consider the apparently covalent material La_2NiO_4, which is closely related to the high-T_c superconductor parent La_2CuO_4. Despite many studies of $KNiF_3$ and NiO via cluster calculations, we found that a satisfactory *ab initio* cluster theory of the neutron form factor is lacking. We have carried out such a calculation in the unrestricted Hartree-Fock (UHF) approximation, taking the basic cluster as $(NiF_6)^{4-}$ and $(NiO_6)^{10-}$ for $KNiF_3$ and NiO, respectively, treating the remaining lattice in the point-charge model. We show that correlation effects and Pauli repulsion corrections to the point charges are negligible in these cases. After correcting for the zero-point spin fluctuations, the UHF form factor agrees well with experiment in $KNiF_3$, where the *absolute* value of the form factor is known for small scattering vectors $\mathbf{q}$. The UHF calculations agree satisfactorily with the *relative* form factor data for NiO, which cover a large range of $|\mathbf{q}|$ (the absolute experimental values are not available); the agreement in shape includes the variations with $\mathbf{q}$ due to asphericity of the spin density. We also found that the UHF results on La_2NiO_4, obtained by using similar methods, disagree sharply with experiment.

I. INTRODUCTION

We recently showed that contrary to many recent statements, the magnetism of La_2CuO_4 and $YBa_2Cu_3O_6$, insulating parents of high-T_c superconductors, is not well understood.[1,2] The ordered antiferromagnetic (AF) moment $M_{\rm ord}$ was found,[3–6] by magnetic Bragg neutron scattering, to agree with the appropriate Heisenberg model, leaving therefore no room for the large covalent reduction expected (40–50 %) in addition to the large reduction from quantum spin fluctuations in the two-dimensional spin-$\frac{1}{2}$ Heisenberg model.[1,2] We then noted an error in the interpretation[3–6] of the neutron data, and pointed out the correct procedure which involves a proper handling of the form factor $f(\mathbf{q})$.[1] We carried out that procedure[1] as far as possible on the basis of the theoretical information available.[9] This gave improvement in the resulting ordered moment, but not nearly enough, thus leaving intact the puzzle concerning the antiferromagnetic ground state of these important materials La_2CuO_4 and $YBa_2Cu_3O_6$.[1,2] Necessary to its solution is a theoretical determination of the form factor.

Since neutron data on a stochiometric sample of La_2CuO_4 are not available, we decided to focus first on the very closely related La_2NiO_4, for which there is apparently good data.[7] The first attempt at calculating the observed form factor was phenomenological, namely, an application[7] of Hubbard-Marshall (HM) theory[8] using linear combinations of Hartree-Fock ionic orbitals for Ni and O (Ni^{2+} and constrained O^{2-} orbitals). This failed when we took two different singly occupied e_g states for Ni^{2+} for the form factor calculation. This failure was confirmed by Wang *et al.*[7] even though they earlier had fit their experimental data nicely by taking two identical spherical orbitals instead of two different e_g states. (The latter procedure is of course incorrect, violating the Pauli exclusion principle.) The failure was somewhat surprising in view of the success[9] of HM theory for K_2CuF_4. We suspected that the difference might be due to the smaller degree of covalence of the fluoride, although this fluoride (which is in fact ferromagnetic) does show appreciable covalence.

To understand the problem of covalence in antiferromagnetic insulators we first studied the weakly covalent antiferromagnets $KNiF_3$ and NiO. Several *ab initio* cluster calculations have been done in $KNiF_3$ Refs. (10, 12) and NiO.[13,14] However, most of these works were interested in excitation energies rather than the ground state wave function, which is needed to obtain the neutron form factor. The only cluster calculation of the form fac-

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tor was in $KNiF_3$ Ref. (10) more than 20 years ago, and was considered by the authors to be too crude to even compare with experiment. Other attempts which had been made to get the theoretical form factor from the free ion Ni^{2+}, to compare with the experimental data, did not give good agreement.[11] This paucity of work on the theoretical form factor motivated us to carry out cluster calculations using the techniques of *ab initio* quantum chemistry which have developed rapidly during the past two decades. We followed a standard procedure, namely, the basic cluster was chosen to contain one Ni^{2+} ion and its six nearest neighbor ligands (F^- ion or O^{2-} ion respectively), and the rest of the lattice was taken into account by employing the point charge model. Corrections to the point charge model in the form of limited Pauli repulsion are also considered.

In this paper we address the methods and results of these cluster calculations of the neutron form factor for $KNiF_3$ and NiO and compare our theoretical results with experiment in both materials. We also discuss the results of form factor calculations in La_2NiO_4 obtained by applying similar methods and compare with experiment. In addition to the form factor, we address a paradox in the Mulliken charge analysis in our calculations for $KNiF_3$ and NiO.

II. CLUSTER CALCULATIONS

A. Computational procedure

Restricted Hartree-Fock (RHF) and unrestricted Hartree-Fock (UHF) calculations have been carried out on the clusters NiF_6^{4-} for $KNiF_3$ and NiO_6^{10-} for NiO. The cluster consists of one Ni ion surrounded by six ligands such as fluorine ions or oxygen ions. RHF and UHF self-consistent-field (SCF) calculations were performed with the COLUMBUS code[15] and the GAUSSIAN90 code[16] respectively using contracted Gaussian basis sets. Huzinaga[19] basis sets ($9s6p$) with an additional diffuse p function are used for F and O. The basis set for Ni is Wachters'[17] basis ($13s9p5d$). The basis set ($14s11p6d$) for Ni with additional diffuse functions suggested by Hay[18] is also used to see how sensitive the calculations are to adding the diffuse basis functions. These two basis sets, ($14s11p6d$) and ($13s9p5d$) give the same form factor and charge density (difference is less than 1.5%), and so we present the figures of the form factor with basis set ($13s9p5d$) of Ni (see Sec. III C for further discussion of this point). All the electrons of the cluster, 86 electrons, are explicitly included in these *ab initio* calculations and the rest of the system is treated as point charges to give a Madelung potential to the cluster. Formal ionic charges (for example, +2, −1, and +1 point charges for Ni^{2+}, F^-, and K^+ respectively) were assigned to the atomic positions for the rest of the system and fractional charge values on the boundary were taken to make the whole system charge neutral according to Evjen's method.[20] We took 482 point charges to obtain the Madelung potential for NiF_6^{4-} in $KNiF_3$, and 722 point charges for NiO_6^{10-} in NiO, after establishing a reasonable convergency in the value of the potential at the center of the cluster (variation within less than 0.2 %). This number of point charges in Evjen's procedure is known to give an almost constant difference from the exact Madelung sum even for the region far from the origin of the cluster for the pervoskite and fcc structures corresponding to $KNiF_3$ and NiO, respectively.[21]

For a more realistic environment in $KNiF_3$, point charges, which had originally represented the eight nearest neighboring K^+'s, were replaced by effective core potentials (ECP's).[22] This enabled us to incorporate Pauli repulsion particularly between electrons in the F^-'s of the cluster and those in neighboring K^+'s. The effect of this replacement on the form factor of $KNiF_3$ was found to be negligible, and so we did not include ECP's for our calculations in NiO.

We have also performed multiconfiguration SCF (MCSCF) calculations using the COLUMBUS code[15] to investigate correlation effects on the form factor for $KNiF_3$ and NiO. We allowed the d electrons in Ni to correlate among themselves and with p electrons in the ligands. The results of our MCSCF calculation, which included 126 configurations, indicated that mainly d-d intra-atomic correlation was important. The MCSCF form factor values however changed by less than 1% from the SCF values for both the materials. Therefore we present only the SCF form factor calculations in the figures.

B. Theoretical form factor

The spin density associated with one magnetic ion centered at the origin,

$$s(\mathbf{r}) = S_z \frac{1}{n} \sum_{j}^{\mathrm{occ}} \sigma_j |\psi_j(\mathbf{r})|^2, \tag{1}$$

is determined from the results of HF cluster calculations. In Eq. (1), $\psi_j(\mathbf{r})$ is the jth molecular orbital from the SCF results, $n = n_\uparrow - n_\downarrow$ [$n_\uparrow(n_\downarrow)$ is the number of occupied up(down) spin electrons], and σ_j is the spin state +1 or −1 for up or down spin for the jth orbital. When mean field theory (MFT) for the full antiferromagnetic crystal is assumed, S_z is 1 for Ni.

The total spin density in the AF ordered crystal is given by the sum of contributions associated with each magnetic ion,

$$S(\mathbf{r}) = \sum_{\mathbf{n}} e^{i\mathbf{q}_A\cdot\mathbf{n}} s(\mathbf{r}-\mathbf{n}). \tag{2}$$

$\mathbf{n}$ is a lattice vector associated with the chemical unit cell, and $\mathbf{q}_A$ is a particular AF wave vector: $e^{i\mathbf{q}_A\cdot\mathbf{n}}$ is $+1(-1)$ at up(down)-spin sites $\mathbf{n}$.

The experimentally measurable quantity from the neutron Bragg scattering is the Fourier transform of the magnetic moment density per unit cell, $g\mu_B S(\mathbf{r})/N$ (N is the number of unit cells),

$$\begin{aligned} m(\mathbf{q}) &= g\mu_B \frac{1}{N}\int S(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}}d\mathbf{r} \\ &= g\mu_B \frac{1}{N}\sum_n e^{i\mathbf{q}_A\cdot\mathbf{n}}\int s(\mathbf{r}-\mathbf{n})e^{-i\mathbf{q}\cdot\mathbf{r}}d\mathbf{r} \\ &= g\mu_B \frac{1}{N}\sum_n e^{-i(\mathbf{q}-\mathbf{q}_A)\cdot\mathbf{n}}\int s(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}}d\mathbf{r}. \end{aligned} \tag{3}$$

The sum $\sum_n e^{-i(\mathbf{q}-\mathbf{q}_A)\cdot\mathbf{n}}$ gives the shape of the Bragg peaks which center on the general AF wave vectors $\mathbf{q}_A$. The variation of intensity of the Bragg peaks is controlled by

$$\begin{aligned} m(\mathbf{q}_A) &= g\mu_B \int s(\mathbf{r})e^{-i\mathbf{q}_A\cdot\mathbf{r}}d\mathbf{r} \\ &= g\mu_B S_z f(\mathbf{q}_A), \end{aligned} \tag{4}$$

where $f(\mathbf{q})$ is the form factor defined by

$$f(\mathbf{q}) = \frac{1}{n}\sum_j^{\mathrm{occ}} \sigma_j \int |\psi_j(\mathbf{r})|^2 e^{i\mathbf{q}\cdot\mathbf{r}}d\mathbf{r}. \tag{5}$$

When we take account of spin fluctuations beyond the MFT, S_z is the mean value of the spin in the Heisenberg model, $\langle S_z\rangle$, instead of the MFT value 1 for Ni.[1] Thus we now have the magnetic moment density $m(\mathbf{q}_A)$ in terms of $\langle S_z\rangle$ which includes the quantum spin fluctuation effect, and $f(\mathbf{q}_A)$ which includes the covalence effect:

$$m(\mathbf{q}_A) = g\mu_B\langle S_z\rangle f(\mathbf{q}_A). \tag{6}$$

In HF molecular orbital (MO) theory, each MO is a linear combination of basis functions such as

$$\psi(\mathbf{r}) = \sum_k \chi_k^{\mathrm{Ni}}(\mathbf{r}) + \sum_j\sum_l \chi_l^{L_j}(\mathbf{r}), \tag{7}$$

where χ_k^{Ni} is a basis function centered at Ni and $\chi_l^{L_j}$ is a basis function centered at the jth ligand. The subscripts, k and l label the individual basis functions for Ni and the ligands respectively. For simplicity, we omit the label on the molecular orbitals, and the basis function χ includes its MO coefficient. The square of the MO becomes

$$\begin{aligned} |\psi(\mathbf{r})|^2 = &\sum_{k,k'} \chi_k^{\mathrm{Ni}}\chi_{k'}^{\mathrm{Ni}} + 2\sum_{k,l}\sum_j \chi_k^{\mathrm{Ni}}\chi_l^{L_j} \\ &+ \sum_{j,l}\sum_{j',l'\neq j,l} \chi_l^{L_j}\chi_{l'}^{L_{j'}} + \sum_j\sum_l \chi_l^{L_j}\chi_l^{L_j}. \end{aligned} \tag{8}$$

When the jth ligand is shared by two nearby Ni^{2+}'s with antiparallel spins, the contributions to $f(\mathbf{q})$ from the last term of Eq. (8) vanish at $\mathbf{q} = \mathbf{q}_A$. This leads to the covalent reduction in the form factor.[8] Also the Ni-ligand cross terms lead to a flattening of the form factor in the small q region.[8]

III. RESULTS

A. KNiF$_3$

The theoretical AF form factor values from RHF and UHF calculations are compared with the experimental values of Hutchings and Guggenheim[23] in Figs. 1(a),(b). The experimental values of the product $\langle S_z\rangle f(\mathbf{q}_A)$ are determined from the absolute values of $g\langle S_z\rangle f(\mathbf{q}_A)/F_{200}$ which include no unknowns and are extracted from the ratios of magnetic and nuclear Bragg scattering intensities at 4.2 K in Ref. 23. Here we took the g factor as $g = 2.29(\pm 0.02)$ and the nuclear scattering length as $F_{200} = 1.218(\pm 0.020)$ from the same Ref. 23.

The calculated form factor values are multiplied by the factor $\langle S_z\rangle$ to fit the experimental data. The UHF results, which incorporate core polarization, in Fig. 1(b) differ slightly from the RHF results in Fig. 1(a), but this small difference helped to obtain a near perfect agreement between the UHF results and the experiment. The

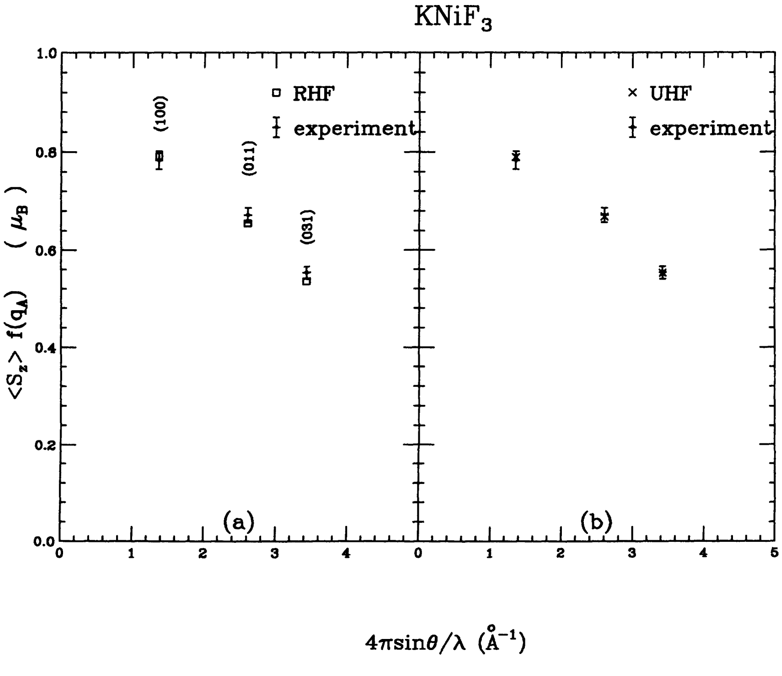

FIG. 1. Magnetic form factor in KNiF$_3$ (a) RHF, (b) UHF with scale factor $\langle S_z\rangle$ as 0.90 in the calculated values to compare with the experimental values in Ref. 23.

best fit to the experiment in Fig. 1(b) gives $\langle S_z \rangle = 0.90$ which can be directly compared with the result of spin wave theory for the simple cubic lattice $\langle S_z \rangle_{\text{spinwave}} = 0.92$.[24]

We conclude that the theoretical results for the magnetic moment density $m(\mathbf{q}_A)$ in terms of covalence and spin fluctuation effect [Eq. (6)] agree well with the experimental data in $KNiF_3$.

B. NiO

The theoretical AF form factor values from RHF and UHF calculations are compared with Alperin's experimental values[25] in Fig. 2 and Figs. 3(a),(b). The absolute values of $\langle S_z \rangle f(\mathbf{q}_A)$ are not available[26] for NiO and the experimental values were scaled by 0.93 to give the best fit to our UHF results, particularly for the small $|\mathbf{q}_A|$ region. The Bragg scattering data in NiO are extended to a larger region of $|\mathbf{q}_A|$ than those in $KNiF_3$. In Fig. 3(a), we compare our UHF results with the scaled experimental values. Apparently, the UHF results agree very well with the experiment for the first three Bragg peaks and are consistently lower than the experiment for larger $|\mathbf{q}_A|$ values. However, the bumpiness of the data is traced rather well by our theoretical calculations, which results from asphericity of the spin density around each Ni. The overall agreement between UHF results and experiment in Fig. 3(a) is reasonable.

A correction to the form factor in the larger q region comes from the orbital contribution. We took the orbital contribution for NiO from the work of Khan *et al.* who made a spherically averaged estimation of this contribution using the ionic Ni^{2+} wave function.[27] This orbital contribution is negligible in the small q region, and so we do not expect it to be important in our comparison with $KNiF_3$ experiments, where the data are available only for small q. For larger q, the orbital contribution in NiO helps to give a better fit with experiment, as shown in Fig. 3(b). The small discrepancy between the calculated and the experimental values in Fig. 3(b) might come from the error involved in the spherical averaged estimation of the orbital contribution. With the inclusion of the orbital contribution to the form factor, we conclude that the results in Fig. 3(b) are in good agreement with experiment.

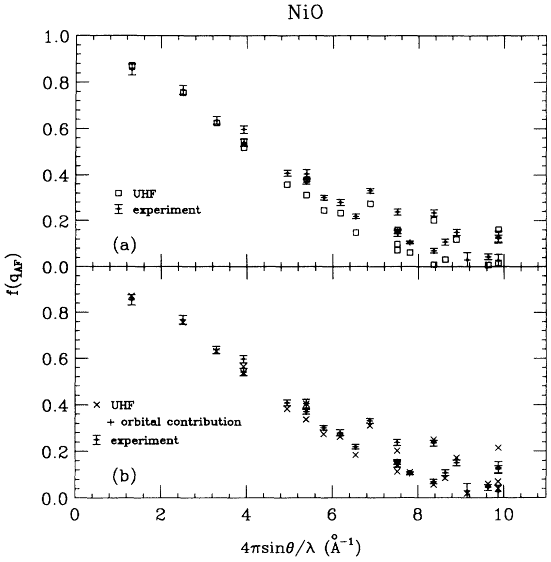

FIG. 3. Magnetic form factor in NiO (a) UHF, (b) UHF + the correction from the orbital contribution Ref. 27. The experimental values in Ref. 25 are scaled by the factor 0.93.

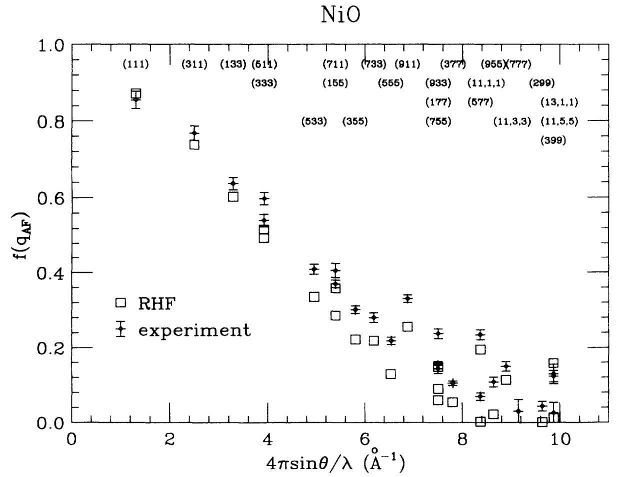

FIG. 2. Magnetic form factor in NiO. Theoretical values are from RHF calculations and the experimental values in Ref. 25 are scaled by the factor 0.93.

C. Failure of the Mulliken charge population analysis

In the UHF calculations of NiO and $KNiF_3$, we found the Mulliken charge values[28] obtained with diffuse basis functions in Ni ($14s11p6d$) to be quite different from the nominal charge values for the ionic material (see Table I). Particularly for NiO, the discrepancy is very large. These values (-0.21 for Ni and -1.63 for O) for NiO seem to contradict the assumption that NiO is highly ionic, which allows us to assign the nominal point charge values, $+2$ for Ni and -2 for O, when generating the Madelung potential. Therefore we performed the same cluster UHF calculations without diffuse basis functions in Ni ($13s9p5d$) to see how sensitive the Mulliken charge population was to the choice of basis functions. The Mulliken charge values without diffuse basis functions ($13s9p5d$) were found to be $+1.75$ for Ni and -1.95 for O, much closer to the nominal point charge values. (Similar values were obtained by Sulaiman *et al.*[29] in their cluster

TABLE I. Mulliken charge population values for different basis set for Ni.

	NiO		$KNiF_3$	
	Ni	O	Ni	F
($14s11p6d$)	-0.21	-1.63	1.76	-0.96
($13s9p5d$)	1.75	-1.96	1.86	-0.98

calculations of $YBa_2Cu_3O_6$ and La_2CuO_4.)

Even though the results of the two calculations, with different basis sets, look so different in Mulliken charge analysis, we found that physically meaningful quantities, such as the charge and the spin density, are essentially the same. Our understanding of how this is possible is the following. The diffuse functions in Ni (14*s*11*p*6*d*) are so diffuse that they spread over the neighboring oxygen sites and can mimic the diffuse function on the oxygens. We estimate that the approximately 1/3 of an electron per O assigned to the diffuse Ni orbitals are physically associated with the oxygen ions.

The Mulliken population values in $KNiF_3$ are rather stable with respect to the choice of basis sets and the calculated values are close to their ionic charges (+2 for Ni^{2+} and −1 for F^-) even when we use the diffuse basis functions in Ni (see Table I). This is due to the fact that the F^- wave function is much more compact compared with the O^{2-} wave function so that the diffuse Ni functions are simply not appreciably occupied.

In summary, these results show that the Mulliken charges assigned to different ions (such as Ni, F, O, etc.) depend not only on the choice of basis set but also on the type of ions in the cluster. (A similar problem was noted by Noell[30] and Bauschlicher and Bagus[31] for the transition metal complexes.) Therefore it sometimes may be misleading to use these charge assignments in describing physical quantities such as the electrostatic potential. As we just noted, our NiO results give an extreme example: Clearly the assignment to Ni of electrons in orbitals centered on Ni, but so diffuse that most of their weight is at the Ni-O distance, is not sensible. The Mulliken assignment is much more sensible when the orbitals are not so diffuse. The charge density was in fact found to be essentially the same with or without these diffuse Ni functions, and so it is clearly reasonable to prefer the Mulliken charges calculated without diffuse functions.

IV. DISCUSSION AND CONCLUSIONS

The good agreement between our UHF results and the experiment in $KNiF_3$ and NiO indicates that for these rather highly ionic materials, the form factor is well described by the UHF cluster calculations with a simple point charge model to describe the effect of the ions outside the basic cluster. For $KNiF_3$, where the absolute experimental values are available, we found that the experimental data support our previous theoretical studies;[1] namely, the magnetic moment density $m(\mathbf{q}_A)$ is affected by both the covalence and the quantum spin fluctuations. Furthermore, the reduction due to the spin fluctuations agrees well with the spin wave theory. The covalent reduction of the ordered moment as defined in Refs. 1,2,8 is found to be 5% and 9% for $KNiF_3$ and NiO, respectively.[32] For NiO, we conclude that the calculated values of $m(\mathbf{q}_A)$ which include an approximate evaluation of the orbital contribution are in good agreement with the experiment. For further improvement in the theoretical results, we need to use a more accurate calculation of the orbital contributions (in the larger $|\mathbf{q}|$ region).

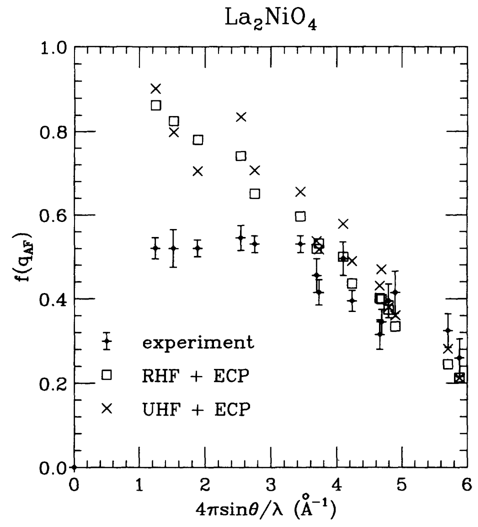

FIG. 4. Magnetic form factor in La_2NiO_4. Theoretical values are from RHF and UHF calculations. The experimental values are from Ref. 7.

We applied similar methods for La_2NiO_4, which we were originally interested in, by taking a $(NiO_6)^{-10}$ cluster with a 544 point-charge environment plus ECP for the nearest 8 La^{3+} ions.[22] (The detailed procedure and discussion for La_2NiO_4 will be published later.) Interestingly, both UHF and RHF results within our simple cluster method deviate seriously from the experimental form factor in Fig. 4. Especially, the experimentally observed plateau at small q values is not reproduced in either calculation. To incorporate the effect of the spin fluctuations, we can scale our calculated values by a constant factor, but we clearly cannot reproduce the shape of the form factor with this type of scaling. The plateau at small q in the measured form factor was seen not only in La_2NiO_4 but also in La_2CuO_4.[33] We are surprised that the present cluster model has failed so seriously for La_2NiO_4 in the view of its success in $KNiF_3$ and NiO. More extensive calculations on La_2NiO_4 are now under study and will be reported in the near future.

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[32] These values, 5% and 9%, were obtained from the UHF calculations using the basis set $(13s9p5d)$ for Ni. When we used the basis set $(14s11p6d)$ which includes diffuse basis functions for Ni, we found slightly different values, 8% and 12% for $KNiF_3$ and NiO, respectively. We understand that when the diffuse basis functions in Ni give appreciable density on the ligands, a simple subtraction of the $\chi(\mathbf{r})^2$ terms in Eq. (8) and the Appendix of Ref. 2 leads to an erroneous value of the ordered moment. Thus the calculated values without diffuse basis functions $(13s9p5d)$ are more accurate.

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