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## Covalency in NiF<sub>2</sub> from magnetisation density data and from *ab initio* theory

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**Abstract.** The polarised neutron diffraction data for NiF<sub>2</sub> have been reanalysed in terms of a covalent valence orbital population model in which the canting angles that the directions of the magnetic moment on the nickel atom, on the fluorine atom, and on the mid-bond overlap population, make with the magnetic field are all allowed to be different. A much better fit to the full data is obtained than for an earlier crystal field model,  $\chi^2 = 3.8$  versus 70. The Ni–F bonding is deduced to be surprisingly covalent; 28% of the spin appears to be delocalised onto the fluorine atoms, with much of it cancelled by the antiferromagnetism, and with large overlap populations. The canting of the moment is found to be critically dependent on the details of the Ni–F bonding, and is very different on the Ni and on the F sites. An *ab initio* calculation on a [NiF<sub>6</sub>]<sup>4-</sup> unit to simulate the crystal environment, using the DV-X<sub>α</sub> local density method, confirms the high covalence in the Ni–F bonding and gives insight into the relative sizes of the ferro- and antiferromagnetic components of the magnetic moments.

### 1. Introduction

The background to the present study has been set out in the previous paper, which deals with the related, but distinctly separate, case of FeF<sub>2</sub>.

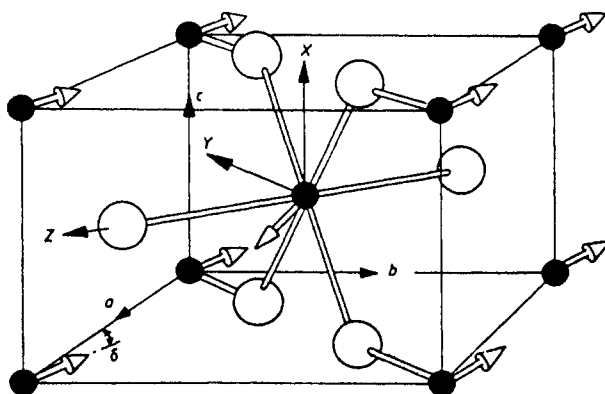
### 2. Previous work on NiF<sub>2</sub>

#### 2.1. Crystal and magnetic structures

Like FeF<sub>2</sub>, NiF<sub>2</sub> at room temperature has the tetragonal rutile structure, space group P4<sub>2</sub>/mnm [1], and further details have been set out in the previous paper.

NiF<sub>2</sub> orders magnetically at 73.2 K, forming a slightly canted antiferromagnetic structure. This is monoclinic, but the departure of the nuclear structure from tetragonal is small enough to be neglected in analysis of the polarised neutron experiment [2]. The magnetic behaviour has been thoroughly investigated [3–8]. The moment at 0, 0, 0 is almost aligned along the crystal *a* axis and that at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$  is almost along  $-a$ , forming an antiferromagnetic arrangement. On both sites, however, the moment is tilted in the *ab* plane along *b* by  $\approx 0.9^\circ$ . Although this angle is so small, it gives a net ferromagnetic moment, to which both sites along *b* contribute equally. This is illustrated schematically

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**Figure 1.** The tetragonal unit cell of  $\text{NiF}_2$ , which has the rutile structure. The directions of the magnetic moments on the nickel atoms at  $(0, 0, 0)$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  are indicated by open arrows; they lie in the basal plane and are inclined to the  $a$  axis by the angle  $\delta$ . Each nickel atom is octahedrally coordinated by fluorine atoms and the quantization axes  $X$ ,  $Y$  and  $Z$  are shown for the atom at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ .

in figure 1. In the absence of a magnetic field there is the domain that has been described and in addition three others related by symmetry. With a sufficiently strong magnetic field along  $b$  the further domains are swept away leaving only the one described, and the crystal is then suitable for polarised neutron diffraction experiments. As the field is increased from zero there is a linear increase in the net ferromagnetic moment and thus the canting angle.

The nuclear structure of  $\text{NiF}_2$  has been investigated by unpolarised neutron diffraction [9]. The agreement factors were satisfactory  $R(F) = 0.045$ , but extinction was severe enough to markedly affect the polarised neutron diffraction (PND) results [9].

## 2.2. Other experiments and wavefunctions

The ground state wavefunctions of the  $\text{Ni}^{2+}$  ion have been estimated in the form of a crystal field approximation. A detailed exposition is given elsewhere [9] and we repeat only enough to understand the interpretation of the previous PND experiment. Joenk and Bozorth [6] derived a crystal field ground state compatible with magnetic, infra-red, and magnetic resonance data. As for  $\text{FeF}_2$ , the ground state consists mainly of a simple configuration, now holes in the  $3d_{z^2}$  and  $3d_{xy}$  orbitals, with small spin-orbit-induced contributions from higher terms. We note that it is only these contributions that introduce the non-collinearity of the magnetic moment with the magnetic field direction.

The  $^{19}\text{F}$  NMR experiments on  $\text{NiF}_2$  again show covalence to be present, with a substantial spin population in both  $2s$  and  $2p$  fluorine orbitals. While there have been many calculations performed on an octahedral  $[\text{NiF}_6]^{4-}$  unit, there appear to be none on the tetragonally distorted clusters such as exist in  $\text{NiF}_2$ .

## 2.3. Previous polarised neutron diffraction experiments

We refer to the material set out in section 2.3 of the preceding paper for  $\text{FeF}_2$ . In  $\text{NiF}_2$  we consider the antiferromagnetic moment along  $a$  and  $-a$ , and separately the ferromagnetic moment along  $b$ . The antiferromagnetic moment behaves similarly to that for  $\text{FeF}_2$ , except that its direction is along  $a$  rather than  $c$ . The scattering from the ferromagnetic moment behaves in the opposite way. For reflections with  $h + k + l$  odd

we see the spherical component of the antiferromagnetic moment, while with  $h + k + l$  even it is the spherical component of the ferromagnetic moment. All reflections contain some contribution from aspherical terms in the magnetisation. This has an important consequence in that the reflections with  $h + k + l$  even may be significantly affected by the small ferromagnetic moment and are not swamped there, as for the reflections with  $h + k + l$  odd, by the much larger antiferromagnetic term in the magnetisation.

For NiF<sub>2</sub> Brown and Forsyth [9] measured 26 unique reflections with  $h + k + l$  even at 1.4 and 4.2 K. Without an assumption as to the directional properties of  $M(\mathbf{r})$  we cannot extract the magnetic structure factors,  $F_M(\mathbf{k})$ , from the data. However we can extract a quantity  $F_{M,Z}(\text{eff})(\mathbf{k})$  [10], as a more convenient representation of the flipping ratio, via solution of the equation

$$R(\mathbf{k}) = (F_N(\mathbf{k})^2 + 2F_N(\mathbf{k})F_{M,Z}(\text{eff})(\mathbf{k}) + F_{M,Z}(\text{eff})(\mathbf{k})^2) \\ \times (F_N(\mathbf{k})^2 - 2F_N(\mathbf{k})F_{M,Z}(\text{eff})(\mathbf{k}) + F_{M,Z}(\text{eff})(\mathbf{k})^2)^{-1}. \quad (1)$$

The quantities  $\gamma(\mathbf{k})$ , which are essentially the observed values of the ratios  $F_{M,Z}(\text{eff})(\mathbf{k})/F_N(\mathbf{k})$ , were listed [9]. Again, after extensive correction for extinction, the data were averaged over the symmetry-related equivalent reflections to yield finally 26 unique values.

### 3. Previous analysis of PND data

24 of the 26 observed reflections were fitted to the parameters of a crystal field wavefunction [9]. This gave  $\chi^2 = 20$  (70 on all reflections). The refined values of the coefficients are similar to, although significantly different from, those derived from resonance measurements. This indicates that the canted antiferromagnetic model of the magnetic structure is correct, that canting arises through a spin-orbit coupling mechanism, that the orbital magnetic moment is significant, and that the spin in 3d<sub>z<sup>2</sup></sub> and 3d<sub>xy</sub> orbitals is the dominant feature of the ground term. Finally it was concluded [9] that, while the crystal field wavefunction is a good first approximation, covalence effects are so large that they make more quantitative statements uncertain on the basis of the wavefunction assumed.

### 4. Valence orbital analysis of PND data

The reasons for preferring a valence orbital population to a conventional multipole model for the investigation of better fitting the available magnetic scattering data have been set out in the preceding paper. We employ essentially the same set of atomic orbitals here as for FeF<sub>2</sub>. The NiF<sub>2</sub> and FeF<sub>2</sub> paramagnets differ slightly, and that will be detailed later. The relationship of the magnetisation to the spin density has also been treated in the previous paper, and is the same here as for FeF<sub>2</sub>. Again, we emphasise that here we use all the data simultaneously, rather than using stepwise methods neglecting certain reflections expected to be poorly modelled.

The application of a valence orbital population model, as of a multipole model, must be made with care for this NiF<sub>2</sub> case, since only even- $h + k + l$  reflections have been measured. Given the site symmetry, the assumption of a mirror plane in the magnetisation in the  $ab$  plane of the crystal, the twofold screw axis along  $b$ , the inversion symmetry, and using the multipolar functions up to order four necessary for the 3d

**Table 1.** NiF<sub>2</sub> refinement results. Units are spins/atom unless otherwise stated. *r* indicates the radial contraction/expansion factor.  $\varphi$  is the canting angle, in degrees. (a) Multipole results. (b) Constrained valence results.

(a)			
Ni	Antiferromagnetic component		
	(22) = 0.06(4)	(42) = -1.6(2)	(4 -4) = 0.18(2)
	<i>r</i> = 0.65(8)		
	Ferromagnetic component		
	(00) = 0.05(1)	(20) = -0.06(1)	(40) = -0.03(2)
	(2 -2) = 0.07(4)	(4 -2) = -0.02(4)	(44) = 0.02(8)
F	$\varphi$ = 24(5)	(sp <sup>2</sup> ) <sub>1</sub> = 0.042(7)	(sp <sup>2</sup> ) <sub>2</sub> = 0.019(7)      2p <sub>π</sub> = -0.042(12)
Mid-bond	$\varphi$ as on fluorine		
Short	0.02(1)		
Long	0.09(3)		
(b)			
(i) Fluorine and overlap canting angles equal			
Ni	$\mu_{\text{ferro}}$ (3d e <sub>g</sub> )		= 0.039(5)
	$\mu_{\text{antiferro}}$ (3d <sub>z<sup>2</sup></sub> -3d <sub>xy</sub> )		= 0.15(4)
F	$\varphi$ = 23(5)	0.064(25) ((sp <sup>2</sup> ) plane)	2p <sub>π</sub> = -0.021(16)
Mid-bond	0.06(2)		
(ii) Nickel and overlap canting angles equal			
	$\mu_{\text{ferro}}$ (3d e <sub>g</sub> )		= 0.034(6)
	$\mu_{\text{antiferro}}$ (3d <sub>z<sup>2</sup></sub> -3d <sub>xy</sub> )		= 0.10(4)
F	$\varphi$ = 167(54)	-0.010(10) ((sp <sup>2</sup> ) plane)	2p <sub>π</sub> = 0.003(4)
Mid-bond	0.02(2)		

orbitals, only nine functions centred on the nickel atom site remain. For the anti-ferromagnetic part of the moment the multipoles (2, 2), (4, 2) and (4, -4) are determined by the data. For the ferromagnetic component (0, 0), (2, 0), (4, 0), (2, -2), (4, -2) and (4, 4) are determined. On the fluorine atoms we continue to restrict the parameters to the three independent populations. We retain the two mid-bond populations. Since the canting of the moment may not be constant through the cell we allow the angle of cant on F and on the mid-bond populations to vary separately from that of the Ni centre, using a single common parameter. Refinement of this model gave  $\chi^2 = 6.6$ ,  $R(\text{F}) = 0.12$ , and showed a very large antiferromagnetic effect on the scattering. We then introduced a Ni 3d radial expansion/contraction parameter and obtained  $\chi^2 = 3.8$ ,  $R(\text{F}) = 0.076$ , a significant improvement to the fit. The results are listed in table 1.

The improvement of these refinements over the earlier four parameter model [9] with  $\chi^2 = 70$  is very great, but so is the increase in the number parameters, now 16 for only 26 reflections: the data-to-variable ratio is unacceptably low. We can reduce the number of variables considerably if we assume that spin on the nickel atom resides only in the 3d e<sub>g</sub> orbitals, that there is cylindrical symmetry of the distribution on the fluorine atoms, and that the mid-bond populations are equal. On refining this model we found that the sum of the 3d<sub>z<sup>2</sup></sub> and 3d<sub>x<sup>2</sup>-y<sup>2</sup></sub> populations was ill defined, and only the 3d e<sub>g</sub> ferromagnetic moment and the difference of the 3d<sub>z<sup>2</sup></sub> and 3d<sub>x<sup>2</sup>-y<sup>2</sup></sub> populations were

**Table 2.** Theoretical charge and spin population changes in overlap matrix from free ions in [NiF<sub>6</sub>]<sup>4-</sup> cluster.

	Spin			Charge		
	Ni	F (short)	F (long)	Ni	F (short)	F (long)
Ni	-0.236	-0.064	-0.229	0.538	0.020	-0.117
F (short)		0.222	-0.059		-0.062	-0.387
F (long)			0.370			0.004

significant. Arbitrarily then, we fixed the 3d<sub>z<sup>2</sup></sub> population at 1.0 spins. The data/variable ratio is now acceptable at 26/7, and the refinement yielded  $\chi^2 = 20$ ,  $R(F) = 0.26$ , and the results are listed in table 1. We then investigated the assumption that the nickel atom and the mid-bond populations have a common canting angle, and fluorine atom a separate one. The refinement gave  $\chi^2 = 36$  and  $R(F) = 0.28$ ; it is reported as the third set of results in table 1. Removal of the (110) and (220) reflections from consideration, to follow the procedure of the earlier treatment [9], changed the results very little; these reflections then do seem by inference to be reasonably free of experimental systematic error.

### 5. *Ab initio* DV-X<sub>α</sub> calculations

The calculations performed were essentially the same as those for FeF<sub>2</sub> detailed in the preceding paper. However, comparison of the DV-X<sub>α</sub> results with the spectra has not been attempted here since it is well known that a 'strong field' approximation is very poor for ionic Ni<sup>2+</sup> complexes. Our calculations would require further incorporation of electron correlation to reach an appropriate 'weak field' result, with appropriate non-integral orbital occupancies. This difficulty did not arise in the FeF<sub>2</sub> case involving the Fe<sup>2+</sup> ion since for the d<sup>1</sup>, d<sup>4</sup>, d<sup>6</sup> and d<sup>9</sup> systems the weak and strong field electron configurations are both the same and the orbital populations are integral. The calculated Fermi level of -2.05 eV is again, as for the [FeF<sub>6</sub>]<sup>4-</sup> case, about 2 eV higher than the experimental value of  $\approx -4$  eV [11], and the effect of the external electric field is again vital to produce a reasonable agreement.

As in the case of FeF<sub>2</sub>, the charge and spin populations are not obviously related. This is shown in table 2 for the overlap populations and table 3 for the Mulliken populations. 90% of the spin arises from the molecular orbitals containing formally unpaired electrons (3d<sub>z<sup>2</sup></sub> and 3d<sub>xy</sub>) and spin polarisation of formally paired orbitals of the same A<sub>1g</sub> and B<sub>3g</sub> symmetries. Again, the calculations show the cores are essentially non-bonded.

## 6. Discussion

### 6.1. DV-X<sub>α</sub> calculations and expectations for [NiF<sub>6</sub>]<sup>4-</sup>

The general comments about the DV-X<sub>α</sub> calculations as applied to a [FeF<sub>6</sub>]<sup>4-</sup> cluster in the preceding paper should be consulted. Again, spin is transferred from the nickel atom to fluorine atoms, and charge vice versa, as expected from simple molecular orbital

**Table 3.** Mulliken populations for spin and charge in the  $[\text{NiF}_6]^{4-}$  unit.

		Spin	Charge	
Ni	3d <sub>z<sup>2</sup></sub>	0.771	1.224	
	3d <sub>xy</sub>	0.832	1.168	
	3d <sub>xz</sub>	0.003	1.988	
	3d <sub>yz</sub>	0.002	1.997	
	3d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	0.031	1.935	
	Total 3d	1.639	8.312	
	4s	-0.002	0.098	
	4d	-0.024	0.087	
Total spin/charge		1.615	1.508	
F (short)	Bond {	2s	0.001	1.998
		2p	0.078	5.894
		3d	0.000	-0.014
	Total spin/charge	0.080	-0.878	
F (long)	Bond {	2s	0.002	1.997
		2p	0.056	5.859
		3d	-0.002	0.082
	Total spin/charge	0.056	-0.938	

theories of covalent bonding. The main participants are the nickel 3d and the fluorine 2p orbitals, with F 2s orbitals contributing. The significant nickel 4s and 4d and fluorine 3d populations reflect their role as polarisation functions, improving nickel-fluorine overlap and transferring charge into the mid-bond region. The low fluorine 3d spin population reflects the fact that the spin resides in antibonding orbitals with a node along the metal-fluorine bond. Overlap populations are again very significant in this still rather ionic complex. Spin polarisation and covalence effects in the  $\pi$ -system are small compared with the  $\sigma$ -bonded 3d<sub>z<sup>2</sup></sub> and 3d<sub>xy</sub> populations.

As for  $[\text{FeF}_6]^{4-}$ , the short Ni-F bond donates more than does the long one, although the difference is much less marked. We also note that transfers for Ni II are larger than for Fe II, reflecting the expected increase in covalence as we cross the transition series to the right. Again the spin transfer calculated to the ligands is large; here 19% of the spin is calculated to be lost from the nickel atom and the fluorine atoms and the Ni-F bonding region.

### 6.2. The wavefunction of the $[\text{NiF}_6]^{4-}$ cluster and the $\text{NiF}_2$ crystal

For  $\text{NiF}_2$  it is necessary to consider the antiferromagnetic and the ferromagnetic contributions to the magnetisation density separately. As for  $\text{FeF}_2$ , the antiferromagnetic contribution on the fluorine atoms from the long and from the short bonded nickel neighbours cancel, giving an estimate from table 2 of a fluorine population of  $-0.075 \sigma$ , negligible  $\pi$ -spins, and with an antiferromagnetic spin component reduction from 2 to 1.256. In contrast the ferromagnetic contributions at the fluorine atom all add. Thus, for a canting angle on Ni of  $1.1^\circ$  (table 1) we obtain a ferromagnetic moment of  $0.006 \sigma$  and negligible  $\pi$ -spins. As a consequence, the canting angle on the fluorine atom changes dramatically from  $\approx 1.1^\circ$  to  $\tan^{-1}(0.006/-0.075) = 175^\circ$ . The moment has actually changed direction because of the over-complete cancellation of the moment transferred from the nickel atom at 0, 0, 0. If the cancellation were complete then the canting angle on F would be  $90^\circ$ . Thus the antiferromagnetic cancellation of the moment can produce dramatic changes in canting angle on the fluorine atom.

### 6.3. The PND results and the ab initio predictions

The NiF<sub>2</sub> data are limited, particularly as they contain only  $h + k + l$  even reflections, so our conclusions must be less complete than for FeF<sub>2</sub>. The general multipole fit set out in table 1 is a great improvement on the earlier analysis [9]. The improvement arises, in equal importance, from three sources. Firstly, the inclusion of covalence and secondly, allowing different angles of canting away from that of the nickel 3d orbitals, and thirdly, allowing the nickel 3d radius to contract.

When we examine the spin distribution on the fluorine atoms we see that the canting angle is much greater than on the nickel atom for the constrained refinements. This has been explained earlier as a result of covalence. This canting angle is a physical property and as such must change continuously in space. The best type of two-canting-angle parameter model should be determined theoretically. We have presented here two obvious ones. Since the ferromagnetic component is now the more important if not the dominant one, the positive (sp<sup>2</sup>)<sub>1</sub> population on F along the long Ni–F bond makes sense, and contrasts, as it should, with the FeF<sub>2</sub> case. It is also less than the feature along the short Ni–F bond, again as expected. The lack of spin in the  $\pi$ -system is evident in the 2p <sub>$\pi$</sub>  population. The negative value there may arise through spin polarisation. The ratio of the ferromagnetic moment on the fluorine atom to that on the nickel is 0.34(11), which indicates that a very large degree of covalence is present. In terms of bond parameters this corresponds to a transfer of 0.11(4) spins per bond, a number very similar to that given by theory, as listed in table 2. The spin transfer number also agrees well with the magnetic resonance measurement value [5] of  $\approx 0.1$  spins per bond. This indicates that covalence in NiF<sub>2</sub> is greater than in FeF<sub>2</sub>, as expected. The small size of the antiferromagnetic component on the fluorine atom means that the actual canting angle depends critically on the balance of cancelling antiferromagnetic contributions. We can only say it is small, as our two models give different signs. The indications of covalence deduced above are in excellent agreement with the DV-X <sub>$\alpha$</sub>  calculation predictions.

Of the other parameters of the model, the mid-bond population is, although small and only just significant, of the wrong sign to that expected for antibonding overlap. The 3d radius is highly contracted, as expected if the system is as highly covalent as it appears on other grounds. The model with spin in the 3d e<sub>g</sub> orbitals is satisfactory, but it is surprising that the 3d<sub>z<sup>2</sup></sub> population is observed to be greater than that of 3d<sub>xy</sub>, since we expect the former to lose more spin through greater covalence along the short Ni–F bond. The model total ferromagnetic moment is too large at  $\approx 0.2\mu_B$  per nickel atom, compared with the value of 0.05 found from the bulk magnetisation studies.

A more complete data set including reflections with  $h + k + l$  odd, would illuminate some of these problems, especially the canting details. However, the larger number of parameters necessary to take such things into account makes NiF<sub>2</sub> inherently a more difficult case than FeF<sub>2</sub>. It is, none the less, clear that covalence is very important in NiF<sub>2</sub>, and that its behaviour is consistent with that expected from a simple  $\sigma$ -bonding model.

## 7. Conclusions

As with FeF<sub>2</sub>, it is clear that for crystals such as NiF<sub>2</sub>, in which the orbital contribution to the magnetisation is not large, it is important to consider covalence as the major feature, after scaling and the use of the dipole approximation correction for orbital magnetisation, in determining the magnetisation density in the crystal.



A simple localised chemical bond model in which 3d, 4s and 4p orbitals on the nickel atom interact with 2p and 3d orbitals on the fluorine atoms via large  $\sigma$ - and small  $\pi$ -bonding overlaps appears adequate to describe both the experiments and the theoretical DV- $X_\alpha$  calculations.

A surprising feature of both theory and experiment is the very large amount of covalence, with about 28% of the nickel ion spin delocalised on to the fluorine atoms, with correspondingly large overlap populations, in what is traditionally thought to be an 'ionic' compound.

A last, qualitative, point is that in NiF<sub>2</sub> it has been necessary to employ a truly vector model of the magnetisation density. Our results indicate that the direction of that density is different, in different regions of the crystal.

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### References

- [1] Ferrari A 1926 *Rend. Accad. Lincei* III 6 224
- [2] Haefner K, Stout J W and Barrett C S 1966 *J. Appl. Phys.* **37** 449
- [3] Matarrese L M and Stout J W 1954 *Phys. Rev.* **94** 1792
- [4] Moriya T 1960 *Phys. Rev.* **117** 635
- [5] Shulman R G 1961 *Phys. Rev.* **121** 125
- [6] Joenk R J and Bozorth R M 1965 *Proc. Int. Conf. on Magnetism (Nottingham, 1964)* (London: Institute of Physics and Physical Society) p 493
- [7] Cooke A H, Gehring K A and Lazenby R 1965 *Proc. Phys. Soc.* **85** 967
- [8] Borovik-Romanov A S, Bazhan A N and Kreines N M 1973 *Sov. Phys.-JETP* **3** 695
- [9] Brown P J and Forsyth J B 1981 *J. Phys. C: Solid State Phys.* **14** 5171
- [10] Figgis B N, Forsyth J B, Kucharski E S, Reynolds P A and Tasset F 1990 *Proc. R. Soc.* at press
- [11] Kowalczyk S P, Ley L, McFeely F R and Shirley D A 1977 *Phys. Rev. B* **15** 4997