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First-principles calculations for vacancy formation energies in Cu and Al; non-local effect beyond the LSDA and lattice distortion

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Abstract

We show ab initio calculations for vacancy formation energies in Cu and Al. The calculations are based on density-functional theory and the full-potential Korringa–Kohn–Rostoker Green's function method for impurities. The non-local effect beyond the local-spin-density approximation (LSDA) for density-functional theory is taken into account within the generalized-gradient approximation (GGA) of Perdew and Wang. The lattice relaxation around a vacancy is also investigated using calculated Hellmann–Feynman forces exerted on atoms in the vicinity of a vacancy. We show that the GGA calculations reproduce very well the experimental values of vacancy formation energies and bulk properties of Cu and Al, as they correct the deficiency of LSDA results (underestimation of equilibrium lattice parameters, overestimation of bulk moduli, and vacancy formation energies). It is also shown that the GGA calculations reduce the LSDA results for the lattice relaxation energy for a vacancy in Cu.

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Keywords: Vacancy formation energy; Al; Cu; LSDA; GGA; Lattice distortion; KKR Green's function method

Knowledge of the energetics of point defects in solids is indispensable for the understanding of many physical processes, such as diffusion, short-range order, segregation, ordering, etc. We have recently shown that the local-spin-density approximation (LSDA) for density-functional theory, combined with the Korringa–Kohn–Rostoker (KKR) Green's function method for impurities, reproduces very well the experimental values of defects energies such as interactions of the impurities with vacancies or with probe atoms in metals [1]. On the other hand, it has been shown that the non-local effect (NLE) beyond the LSDA, as given by the generalized-gradient approximation (GGA) [2], corrects certain deficiencies of the LSDA in magnetic 3d systems where the space-variation of electron density is fairly large [3]. Following these works, we have also shown that the NLE is important quantitatively for interactions of 3d and 4sp impurities with a vacancy in Al and Cu [4].

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Thus, it may be easily anticipated that the NLE becomes important for vacancy formation energies in metals.

In the present paper we study the NLE for vacancy formation energies in Cu and Al. The calculations are based on the full-potential KKR Green's function method for impurities [5] and use the GGA functional proposed by Perdew and Wang [2]. The lattice relaxation effects around a vacancy can also be investigated by the present method [6]. However, the self-consistent GGA calculations for complex systems such as a vacancy system with lattice relaxation are very time-consuming because a high-quality representation of the electron density must be used and a perturbed region enlarges due to the lattice relaxation around defects. In order to circumvent the self-consistent procedure for GGA calculations, we propose a non-self-consistent(non-SC)-GGA calculations where the self-consistent LSDA electron-density is used for the GGA functional [7]. The lattice relaxation effects are studied by the non-SC-GGA calculations. A detailed desription of our method is reported elsewhere [5–7]. Here we only mention that a cutoff $l_{\max} = 4$ is used to truncate the angular momentum expansions of the Green function and wave functions.

Before showing the calculated results for vacancy formation energies, we discuss the NLE for bulk properties. Fig. 1 shows the lattice-parameter dependence of total energies for Al, Cu, Ni, and Fe. Table 1 lists the calculated and experimental results for the equilibrium lattice parameters and bulk moduli. The LSDA and GGA results, together with the non-SC-GGA results, are shown in Fig. 1, where the experimental values are shown by vertical lines [8]. It is obvious that the GGA calculations reproduce the experimental results almost completely, while the LSDA calculations always underestimate the equilibrium lattice parameters by 1.3% for Al, 2.8% for Cu, 2.7% for Ni, and 3.7% for Fe, as seen in Table 1. The bulk moduli are also reproduced very well by the GGA calculations, while the LSDA calculations overestimate the bulk moduli by 15% for Al, 38% for Cu, 37% for Ni and 48% for Fe (see Table 1). Thus the GGA improves the quantitative deficiency of LSDA, in particular for 3d metals. Here we discuss the accuracy of non-SC-GGA calculations. The self-consistent electron density obtained by the

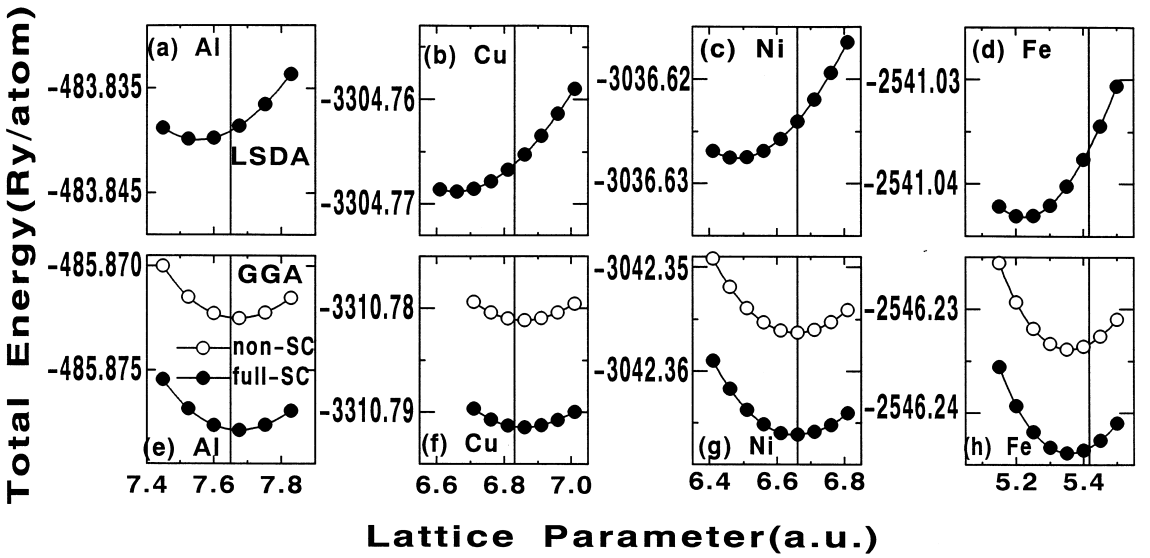

Fig. 1. Lattice parameter dependence for total energies for Al, Cu, Ni, and Fe. The LSDA (● in (a)–(d)) and GGA (● in (e)–(h)) results are shown. The vertical lines indicate the experimental equilibrium lattice parameters. The non-SC-GGA results (○) are also shown in (e)–(h). See the text for details.

Table 1
Equilibrium lattice parameters a and bulk moduli B for Al, Cu, Ni, and Fe, obtained by GGA–FP–KKR and non-SC-GGA–FP–KKR Calculations. The results of LSDA–FP–KKR calculations (in parentheses) as well as experimental values [8] are also shown

Element	a (a.u.)			B (Mbar)		
	GGA(LSDA)	Non-SC-GGA	Experimental	GGA(LSDA)	Non-SC-GGA	Experimental
Al	7.67(7.55)	7.67	7.65	0.73(0.83)	0.73	0.72
Cu	6.86(6.65)	6.86	6.84	1.42(1.89)	1.42	1.37
Ni	6.66(6.48)	6.66	6.66	1.98(2.53)	1.99	1.86
Fe	5.37(5.22)	5.36	5.42	1.84(2.41)	1.90	1.68

GGA calculations may be very similar to that obtained by the LSDA because the gradient correction is considered as a small perturbation; as seen in Fig. 1, the LSDA total energies are ~ -484, ~ -3305, ~ -3037 and ~ -2541 Ry for Al, Cu, Ni, and Fe, respectively, while the total-energy changes due to the gradient-corrections are as small as ~ -2,~ -6, ~ -6 and ~ -5 Ry. Thus we may easily anticipate that the non-SC-GGA calculations with the LSDA electron density reproduce the full-SC-GGA results, as also seen in Fig. 1 The numerical values of equilibrium lattice parameters and bulk moduli, obtained from the non-SC-GGA calculations, are listed in Table 1. It is noted that differences between the full-SC-GGA and non-SC-GGA results are very small (<1%). These results suggest that the non-SC-GGA calculations are useful for the study of the complex systems which involve lattice relaxation around a vacancy, as discussed later.

We now discuss the vacancy formation energies in Al and Cu. Firstly, we show the calculated results for vacancy systems without lattice relaxation. The potentials up to the nearest neighbors to a vacancy are calculated self-consistently. Fig. 2 shows the lattice parameter dependence for vacancy formation energies. Table 2 lists the calculated values at the calculated equilibrium lattice parameters, together with the experimental values [9]. It is seen in Fig. 2 that for the same lattice constant the GGA calculations reduce the LSDA values strongly ($\sim$0.2 eV for Al and $\sim$0.5 eV for Cu) and lead to a nice agreement with the experimental values; the overestimation of LSDA for vacancy formation energies may correspond to the overestimation of LSDA for the cohesive energies [2]. However, it is also seen in Fig. 2 and Table 2 that if the equlibrium lattice parameters of LSDA (0.1–0.2 a.u. smaller than the experimental values) are used, the LSDA results tend to agree with the

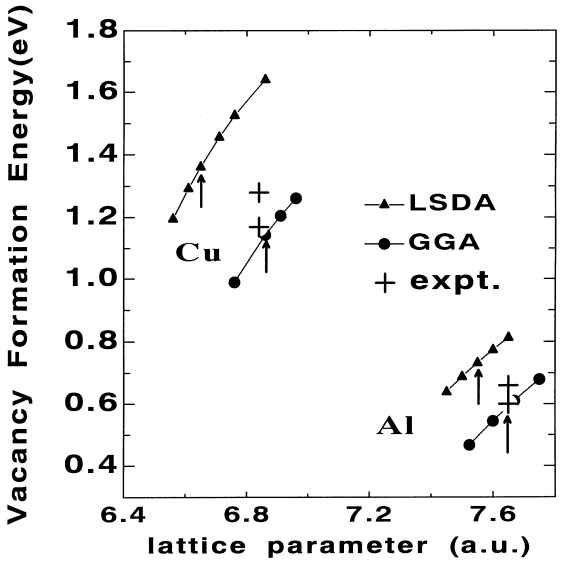

Fig. 2. Lattice parameter dependence for vacancy formation energies in Cu and Al. The LSDA (●) and GGA (▲) results, together with the experimental values (+) are shown, the vacancy formation energies at the calculated equilibrium lattice parameters are also shown by arrows. The lattice relaxation effects are neglected.

Table 2
Vacancy formation energies (in eV) in Al and Cu, obtained by the GGA–FP–KKR and non-SC-GGA–FP–KKR calculations. The results of LSDA–FP–KKR (in parentheses) as well as experimental values [9] are also shown

Element	GGA(LSDA)	Non-SC-GGA	Experimental
Al	0.59(0.73)	0.60	0.60–0.66
Cu	1.14(1.36)	1.13	1.17–1.28

experimental values since the vacancy formation energy decreases strongly with the decrease of the lattice parameter; ~0.14 eV (Cu) and ~0.09 eV (Al) per 0.1 a.u. The values at the calculated equilibrium lattice parameters are also shown by arrows in Fig. 2. The non-SC-GGA results are also given in Table 2. The agreement between the full-SC-GGA and non-SC-GGA results are very nice. The discrepancies are smaller than 2% of calculated values.

We next study the relaxation effects around a vacancy by use of the non-SC-GGA calculations. As a first step we neglect distortion of distant neighbors and consider only the relaxation of the first nearest neighbors(NN's) of a vacancy. It is noted that in the first step the relaxation effects are underestimated, as shown later. For symmetric reasons the NN atoms relax only radially, i.e., along the ⟨1 1 0⟩ directions. The perturbation induced by a vacancy and relaxation of NN atoms is calculated self-consistently for a cluster consisting of five shells around a vacancy (78 atoms + a vacancy), while potentials of the outer host atoms are assumed to be unperturbed. Their equilibrium positions can be found either from the minimum of the total energy or from the zero-force condition. Fig. 3 shows the LSDA and non-SC-GGA results for the relaxation energies of a vacancy in Cu. In order to study the lattice parameter dependence we show the results for two lattice parameters, (1) the lattice parameter of LSDA (6.65 a.u.) in Fig. 3(a) and (2) the lattice parameter of GGA (6.86 a.u.) in Fig. 3(b). It is seen from a comparison of Fig. 3(a) with Fig. 3(b) that the lattice relaxation strongly depends on the lattice parameter. Both the LSDA and GGA calculations with the lattice parameter of LSDA ($a = 6.65$ a.u.) predict a compression of the NN atoms (inward relaxation); ~0.7% (LSDA) and ~1.2% (GGA), corresponding to the relaxation energies of −0.016 and −0.054 eV. It is understood that the inward relaxation becomes larger in the GGA calculations because the NLE tends to lengthen the interatomic distance of LSDA. On the other hand, for the lattice parameter of GGA (6.86 a.u.), the LSDA calculations predict an expansion of the NN atoms by ~0.2% (relaxation energy of almost zero), while the GGA calculations indicate a compression of

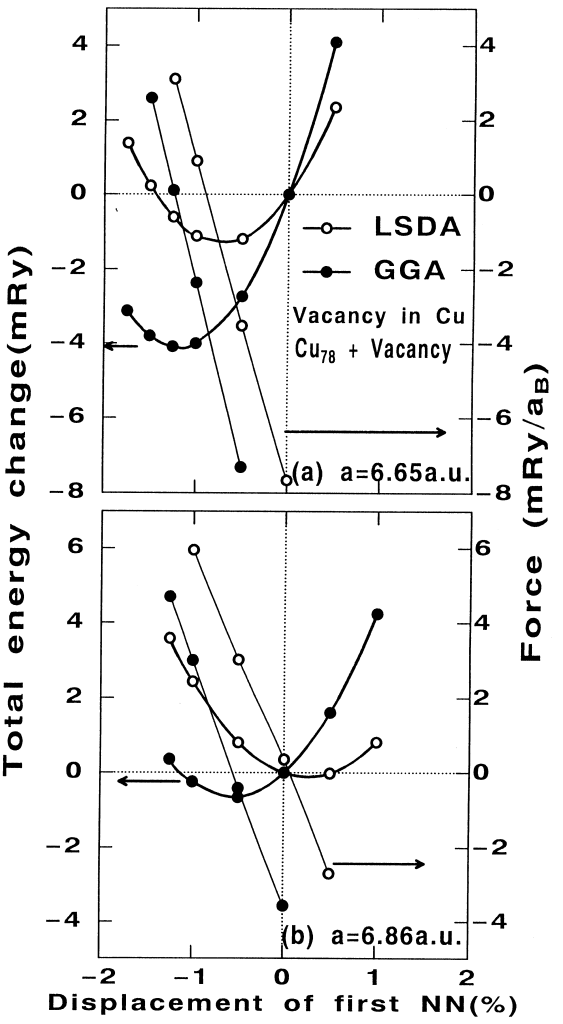

Fig. 3. Total-energy change and radial force on a first NN atom as a function of the first NN distance, for a vacancy in Cu. The LSDA and GGA results are shown for two equilibrium lattice parameters, 6.65 a.u. (a) and 6.86 a.u. (b), obtained from LSDA and GGA calculations, respectively.

the NN atoms by ~0.5% (relaxation energy of −0.009 eV). These results may also be easily understood by considering that the NLE tends to lengthen the equilibrium interatomic distance of LSDA; this means that the LSDA calculations tend to shorten the interatomic distance of GGA. Judging from the accuracy of GGA calculations, we may conclude that the lattice relaxation effects become very small for a vacancy in Cu, as seen in Fig. 3(b); this is not the case for a vacancy in Al, as

shown later. Fig. 3 also shows the Hellmann–Feynman (HF) forces exerted on the first NN for different radial shifts [6]. The forces vary linearly with the displacement and the equilibrium positions obtained from the zero-force condition agree with those obtained from the total-energy minimization. This fact confirms the accuracy of the present first-principles calculations for HF forces [6].

Here we can proceed to the 2nd step where the lattice relaxation of distant neighbors is estimated with the help of lattice-statics simulations based on the Kanzaki model. Accuracy of the Kanzaki model based on the present first-principles HF forces has already been discussed in Ref. [6]. Fig. 4 shows the calculated HF forces and the resulting atomic displacements in the neighborhood of a vacancy (the unit of displacement is one half of a lattice parameter). It is found that the inward first NN shifts are enhanced by allowing relaxation of the distant neighbors; the inward first NN shifts change from ~0.7% (LSDA), ~0.5% (GGA) to ~1.33% (LSDA), ~0.75%(GGA). The relaxation energies become −0.057 eV (LSDA) and −0.017 eV (GGA), corresponding to −0.016 eV and −0.009 eV for the case of restricted first NN relaxation, respectively. Including lattice relaxation energy, the GGA result for a vacancy formation energy in Cu becomes ~1.13 eV.

Lastly we briefly discuss the calculated results for a vacancy in Al, shown in Figs. 5 and 6.

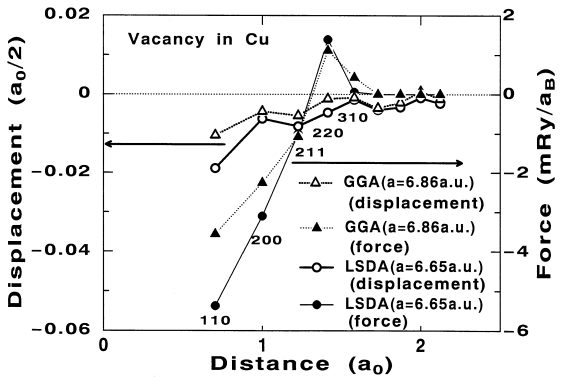

Fig. 4. HF forces (▲, ●) and resulting atomic displacements (△, ○) in the neighborhood of a vacancy in Cu. The LSDA (a = 6.65 a.u.) and GGA (a = 6.86 a.u.) results are shown.

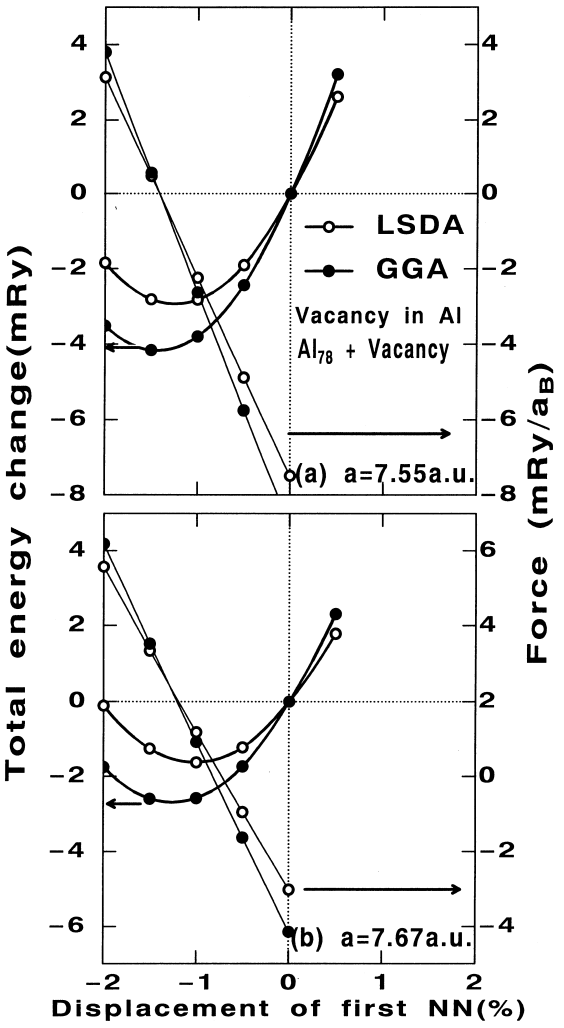

Fig. 5. Same as Fig. 3, but for a vacancy in Cu. The LSDA and GGA results are shown for two lattice parameters, 7.55 a.u. (a) and 7.67 a.u. (b).

Compared with a vacancy in Cu, the lattice relaxation is large and does not depend much on the lattice parameter. For the lattice parameter of LSDA (7.55 a.u., Fig. 5(a)), the inward relaxation for LSDA and GGA is almost same (~1.5%); the relaxation energy is −0.038 eV (−0.057 eV) for LSDA (GGA), while for the lattice parameter of GGA (7.67 a.u., Fig. 5(b)), the inward relaxation for LSDA and GGA is almost the same (~1.25%). The relaxation energy is −0.022 eV (−0.035 eV) for LSDA (GGA). Thus the NLE does not depend

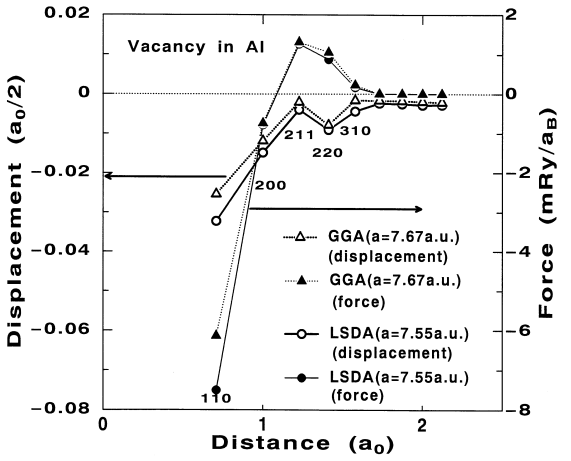

Fig. 6. Same as Fig. 4, but for a vacancy in Al. The LSDA ($a = 7.55$ a.u.) and GGA ($a = 7.67$ a.u.) results are shown.

very much on the lattice parameter. Fig. 6 shows the lattice relaxation of distant neighbors obtained from the calculations based on the Kanzaki model; the inward relaxation is ~2.28% (relaxation energy of ~−0.11 eV) for LSDA [10], while ~1.80% is (relaxation energy of ~−0.07 eV) for GGA. As a result, the relaxation energy is still large (~−0.07 eV) for the experimental lattice parameter. Including the lattice relaxation energy, the GGA result for a vacancy formation energy in Al becomes ~0.53 eV.

We showed that the GGA calculations correct the overestimation of LSDA for vacancy formation energies, together with the deficiencies of LSDA for bulk properties (lattice parameters and bulk moduli). The lattice relaxation energy for a vacancy in Cu is reduced very much by the GGA calculations. Similar results may be expected for a vacancy in the other 3d metals.

References

[1] U. Klemradt, B. Drittler, T. Hoshino, R. Zeller, P.H. Dederichs, N. Stefanou, Phys. Rev. B 43 (1991) 9487; P.H. Dederichs, T. Hoshino, B. Drittler, K. Abraham, R. Zeller, Physica B 172 (1991) 203; T. Hoshino, R. Zeller, P.H. Dederichs, T. Asada, in: H. Takayama et al. (Eds.), Computational Physics as a New Frontier, Japanese Physical Society, 1995, p. 105.

[2] J.P. Perdew, in: P. Zieshe, H. Eschrig (Eds.), Electronic Structure of Solid'91, Academic Verlag, Berlin, 1991; J.P. Perdew, Physica. B 172 (1991) 1.

[3] P. Bagno, O. Jepsen, O. Gunnarsson, Phys. Rev. B 40 (1989) 1997; T. Asada, K. Terakura, Phys. Rev. B 46 (1992) 13599, ibid. 47(1993) 15992; Ozolinš, M. Körling, Phys. Rev. B 48 (1993) 18304.

[4] T. Hoshino, R. Zeller, P.H. Dederichs, T. Asada, Physica B 237–238 (1997) 361.

[5] P.H. Dederichs, B. Drittler, R. Zeller, in: W.H. Buttler et al., (Eds.), Application of Multiple Scattering Theory to Materials Science, MRS Symposia Proceedings No. 253, Material Research Society, Pittsburgh, 1992, p. 185; R. Zeller, Int. J. Mod. Phys. C4 (1993) 1109.

[6] N. Papanikolaou, R. Zeller, P.H. Dederichs, N. Stefanou, Phys. Rev. B 55 (1997) 4157.

[7] T. Hoshino, M. Asato, T. Asada, R. Zeller, P.H. Dederichs, J. Magn. Magn. Mater. 177–181 (1998) 1403.

[8] C. Kittel, Introduction to Solid State Physics, 7th ed., Wiley, New York, 1996.

[9] M.J. Fluss, L.C. Smedskjaer, M.K. Chason, D.G. Legnini, R.W. Siegel, Phys. Rev. B 17 (1978) 3444; W. Triftshäuser, J.D. McGervey, Appl. Phys. 6 (1975) 177; R.O. Simmons, R.W. Ballufi, Phys. Rev. 129 (1963) 1533.

[10] N. Chetty, M. Weinert, T.S. Rahman, J.W. Davenport, Phys. Rev. B 52 (1995) 6373.