Transferability and scaling of Slater-Koster parameters in transition metals

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We present a study of the following aspects of the Slater-Koster method in transition metals: (a) A quantitative analysis of the band structures resulting from Harrison's solid-state table. (b) An evaluation of the Andersen-Harrison scaling laws for obtaining tight-binding parameters at different lattice constants. (c) An examination of the transferability of Slater-Koster parameters from elements to compounds.

I. INTRODUCTION

The results of first-principles band-structure calculations can be recast in a linear combination of atomic orbitals (LCAO) basis using the Slater-Koster (SK) method.[1] We have recently presented[2] SK parameters for 53 elements in the periodic table derived by a least-squares fit to augmented plane wave (APW) calculations.

In his recent book Harrison[3] has developed an elegant theory by which one can determine the SK parameters with little computational effort. In the present work, we assess the quantitative validity of Harrison's theory and present studies of two different ways in which the range of applicability of the SK parameters can be broadened. The first study is a test of the transferability of the SK parameters from transition elements to a compound. That is, we explore the possibility of using the parameters of two different elements to derive a set of parameters for an ordered compound formed from these two elements. The second study is to check the accuracy of the scaling laws proposed by Andersen *et al.*[4] and Harrison,[3] which allow one to scale the SK parameters for a change in the lattice constant of a material.

In this communication we indeed demonstrate the potential transferability of the SK parameters of the transition elements in obtaining the band structure of compounds. We believe that the SK parameters can be exceedingly useful in calculations of the band structure of complicated materials with many atoms per unit cell and low crystallographic symmetry. Such calculations, involving for example, a system with 50 atoms per unit cell are not possible to perform with the present state of the art of first-principles band theory.

II. HARRISON'S THEORY

In this section we present a comparison between the band structure obtained by our SK fit to the APW calculations and that found by applying Harrison's LCAO theory.[3] Harrison has made the simplification of considering a 6×6 secular equation that includes the s and d orbitals, omitting the p orbitals, which by contrast are part of our 9×9 Hamiltonian. The basis of this simplification

is the observation that the p-like states at the symmetry points Γ and H lie approximately 2 and 1 Ry, respectively, above the Fermi level E_F for typical transition metals. However, at the point N one finds that, in the transition metals, the state $N_{1'}$, which has pure p-like symmetry, lies very near E_F. Therefore, neglecting the p orbitals in the SK scheme, although it appears to be a reasonable approximation for the Δ direction, is a serious error in other directions in the Brillouin zone. In view of this problem we propose an improved way of applying the Harrison theory. We use a 9×9 Hamiltonian for which we determine all hopping integrals for first and second neighbors using the formulas given by Harrison in his solid-state table.[3] However, the on-site parameters ϵ_s, ϵ_p, $\epsilon_{t_{2g}}$, and ϵ_{e_g}, we determine by fitting to the APW results at the points Γ_1, $N_{1'}$, $\Gamma_{25'}$, and Γ_{12} respectively. We have applied the Harrison theory using both a 6×6 and 9×9 Hamiltonian for Nb and Fe. The resulting energy bands of Nb are shown in Fig. 1 in three panels. The lower panel shows the results of the very accurate fit that we performed on the APW results. The middle and top panels correspond to the results from the 9×9 and 6×6 Hamiltonian, respectively. It is clear that there exist substantial differences between our elaborate fit and the two calculations based on the Harrison theory. The most serious deficiency of the Harrison calculations is the location of E_F, particularly in relation to $\Gamma_{25'}$. Also, the higher energy bands tend to be placed at too high energies in the Harrison theory. There are also several less-pronounced qualitative differences in mainly the shape of the bands. This is particularly true for the Harrison calculation, which omits the p states. Figure 2 shows the density of states (DOS) of Nb for the three calculations discussed above. It is very important to note that the three-peak structure of the DOS below E_F (shown in the right panel) characteristic of the bcc transition metals, is lost in the simple Harrison theory (shown in the two left side panels). We thus conclude that the Harrison theory is improved significantly by incorporating the p states, but that even then, the band structures (and DOS) produced suffer from some rather serious deficiencies that would limit their usefulness. The need to include p states for the pure metals
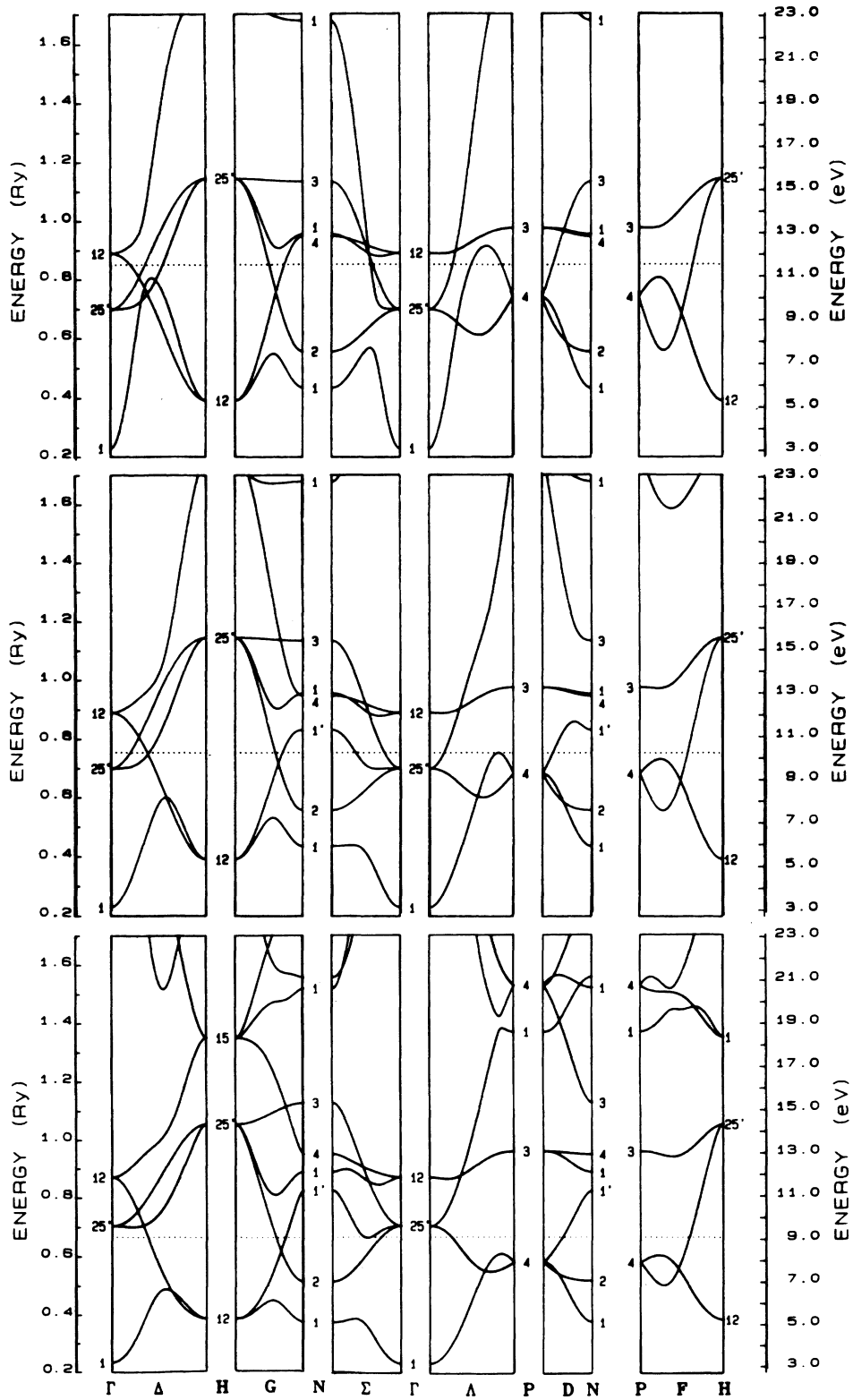
FIG. 1. Top and middle panels show the energy bands of Nb calculated using Harrison parameters from 6×6 and 9×9 Hamiltonians, respectively. Bottom panel shows the energy bands of Nb calculated using our SK parameters fitted to the APW results. Note the position of E_F.
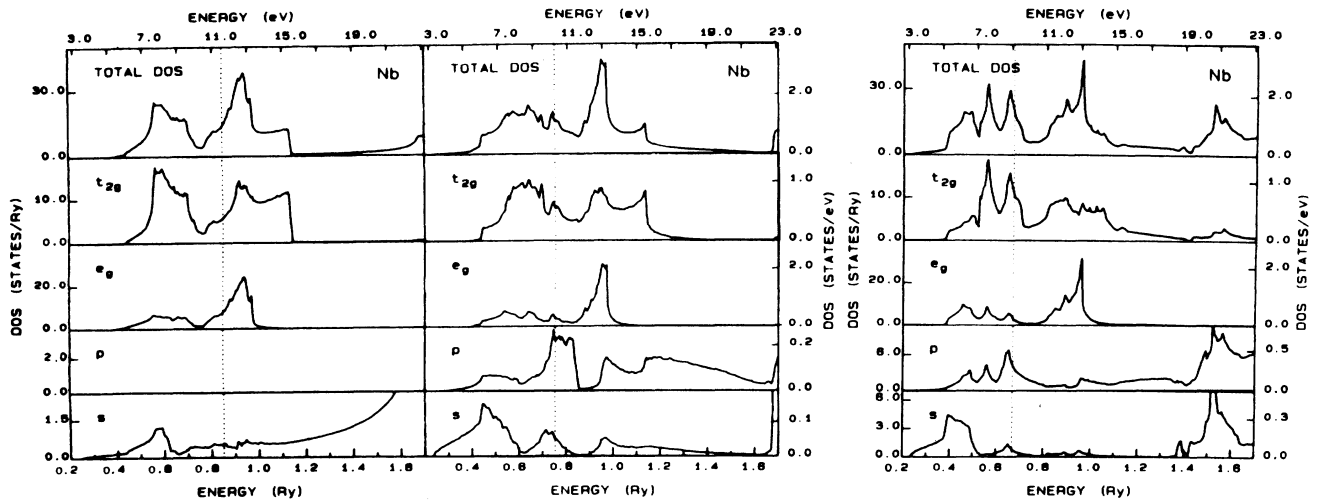
FIG. 2. The left side panels show the DOS of Nb for the 6×6 and 9×9 Hamiltonians, respectively, derived by the Harrison theory. The right side shows the DOS generated from our SK parameter calculations.

seems analogous to finding that it is necessary to add d states to get the conduction bands correct in semiconductors.

III. TRANSFERABILITY

In order to test the transferability of SK parameters from the elements to a compound, we chose to study the compound TiFe whose energy bands in the CsCl structure are known.[5] First, self-consistent APW calculations were performed, in the bcc structure, for both Ti and Fe at the TiFe lattice constant of 5.624 a.u. Energy-band values were calculated at 55 k points in the irreducible Brillouin zone in the final APW iteration. We then applied the SK method, fitting the bands to our LCAO Hamiltonian at these 55 k points. We used an orthogonal basis set and considered first- and second-neighbor interactions. The resulting Hamiltonian contained 27 three-center SK parameters. rms errors for both fits averaged 7—8 mRy in the first 6 bands.

Next, we used the resulting parameters to calculate energy bands at 285 k points and then applied the tetrahedron method[6] in order to calculate the DOS and the E_F of Ti and Fe. Neglecting any possible charge transfer we aligned the E_F of Ti to that of Fe by adding the appropriate uniform shift to the Ti on-site SK parameters.

Finally, we combined the Ti and Fe parameters to form 48 TiFe parameters. The on-site and second-nearest-neighbor parameters were taken directly from the bcc Ti and Fe parameters (since, in the CsCl lattice, the second-nearest-neighbors of an atom are atoms of the same type). However, the nearest-neighbor parameters in TiFe involve interactions between Ti and Fe atoms, so in this case, we performed an arithmetic averaging of the corresponding Ti and Fe parameters, and used these for both the Ti-Fe and Fe-Ti interaction parameters. It should be mentioned that, due to phase differences in the definition of SK parameters it was necessary[7] to reverse the signs of four of

the Fe-Ti parameters: $E_{s,x}(111)$, $E_{x,xy}(111)$, $E_{x,yz}(111)$, $E_{x,d1}(111)$.

Figure 3 on the left shows the total and decomposed DOS calculated using these parameters, while Fig. 3 on the right shows the DOS calculated using a direct fit to the APW calculations of TiFe in the CsCl structure[5] (with rms errors of only 2—3 mRy in the first 10 bands). Both figures were produced by calculating energy bands at 165 k points and applying the tetrahedron method. While the figures show differences in their details, we can see that we have accurately reproduced the qualitative features of the DOS. For example, the DOS at E_F and the width of the valley between the bonding and antibonding bands are fairly accurately reproduced. The decomposed DOS, particularly in the d-like states, also shows reasonable agreement. However, there are some important differences in the decomposition, as reflected by the differences in the DOS and integrated DOS at the Fermi level, shown in Table I. In particular the direct fit calculation shows a charge transfer from Fe to Ti, while the calculation that originates from the elements shows charge transfer in the opposite direction.

We conclude that such a method for producing a set of SK parameters for a compound from those of the constituent elements yields results in semiquantitative agreement with those obtained from the direct calculations. Therefore, provided that the constitutent atoms do not have very different electronegativity, this approach appears promising for performing band-structure calculations in systems with many atoms per unit cell for which first-principles calculations are not feasible with presently available computers.

Recently, Allen et al.[8] presented an interesting study of transferability of nonorthogonal tight-binding parameters for Si. They found that an approximate transferability exists at constant volume between simple cubic, fcc, and bcc structures.
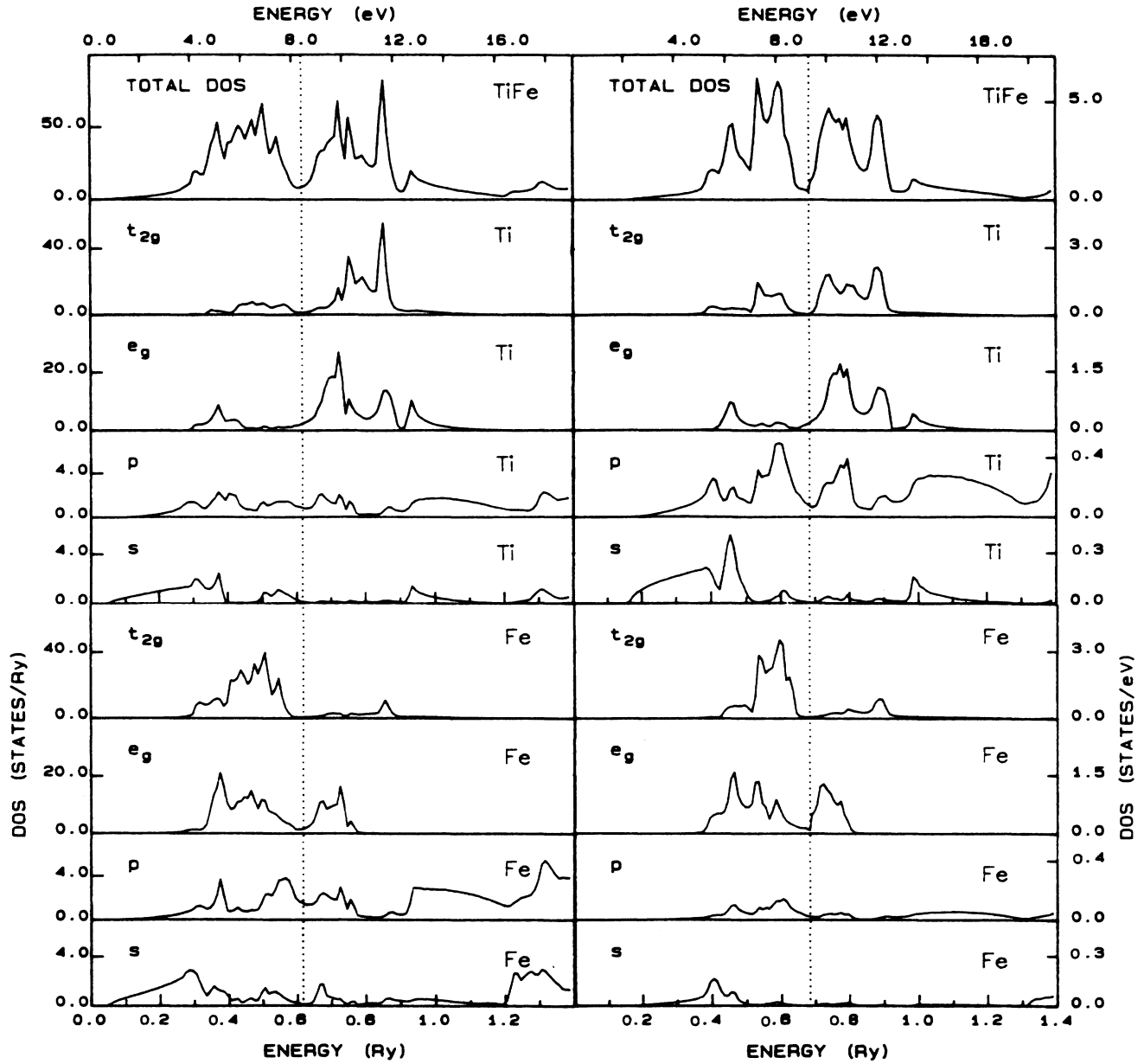
FIG. 3. The panels on the left show the DOS of TiFe generated with the SK parameters determined by fits to APW calculations of the elements. The panels on the right side show the DOS of TiFe using the SK parameters of the direct fit to the APW calculations of TiFe in the CsCl structure.

TABLE I. DOS and integrated DOS at E_F for TiFe. Calculations A are from parameters determined by fit to the APW calculations of TiFe compound; calculation B are from parameters determined by fit to the elements Ti and Fe at the TiFe lattice constant.

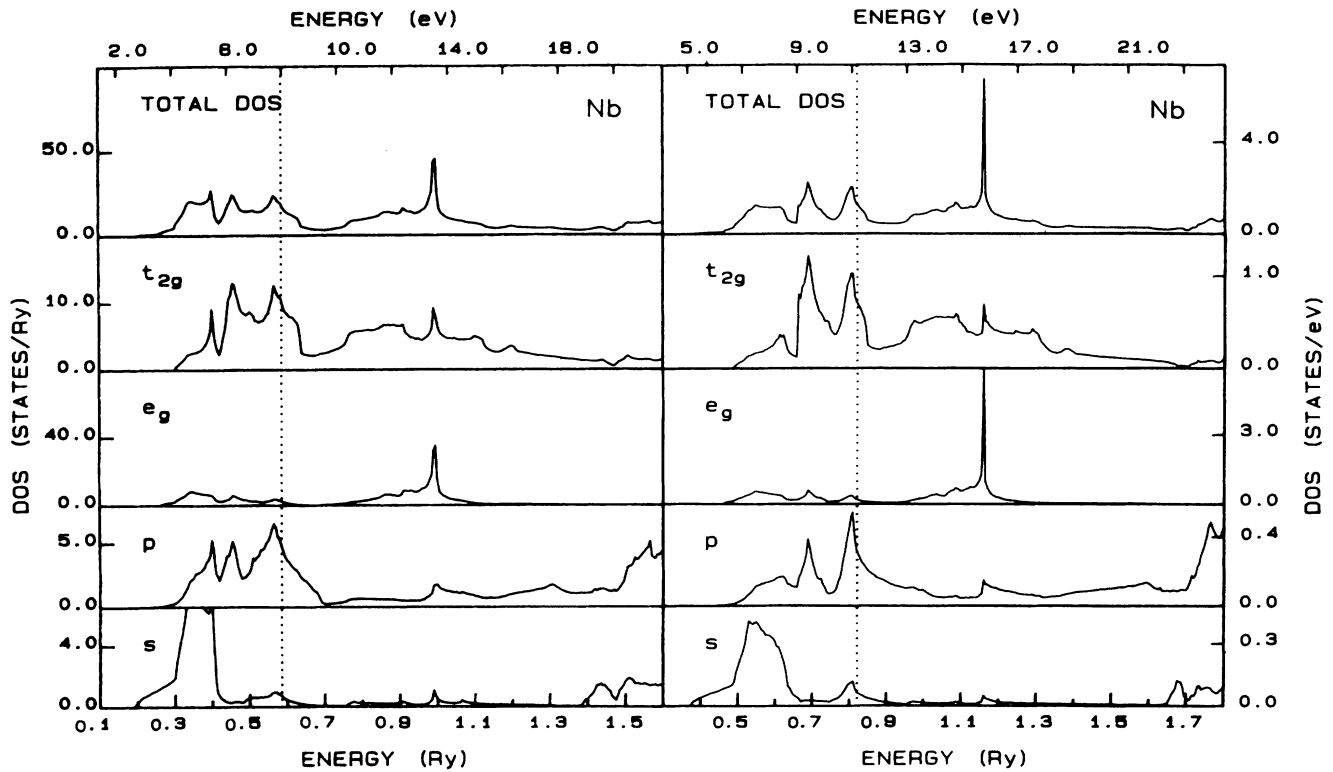| Calculation		DOS (states/Ry)					Integrated DOS (electrons)				
		s	p	t_{2g}	e_g	Total	s	p	t_{2g}	e_g	Total
A	Ti	0.06	1.03	0.45	2.60	6.29	0.81	1.05	1.89	0.81	4.57
	Fe	0.01	0.29	0.81	1.03		0.22	0.29	4.36	2.55	7.43
B	Ti	0.14	0.86	1.57	2.38	8.65	0.45	0.50	1.25	0.76	2.96
	Fe	0.13	1.47	0.58	1.52		0.62	0.63	5.15	2.64	9.04

FIG. 4. Total and decomposed DOS of Nb. On the left panel is the calculation that used the scaled SK parameters. On the right panel is the calculation resulting from fitting directly to the APW calculation at the reduced lattice constant.
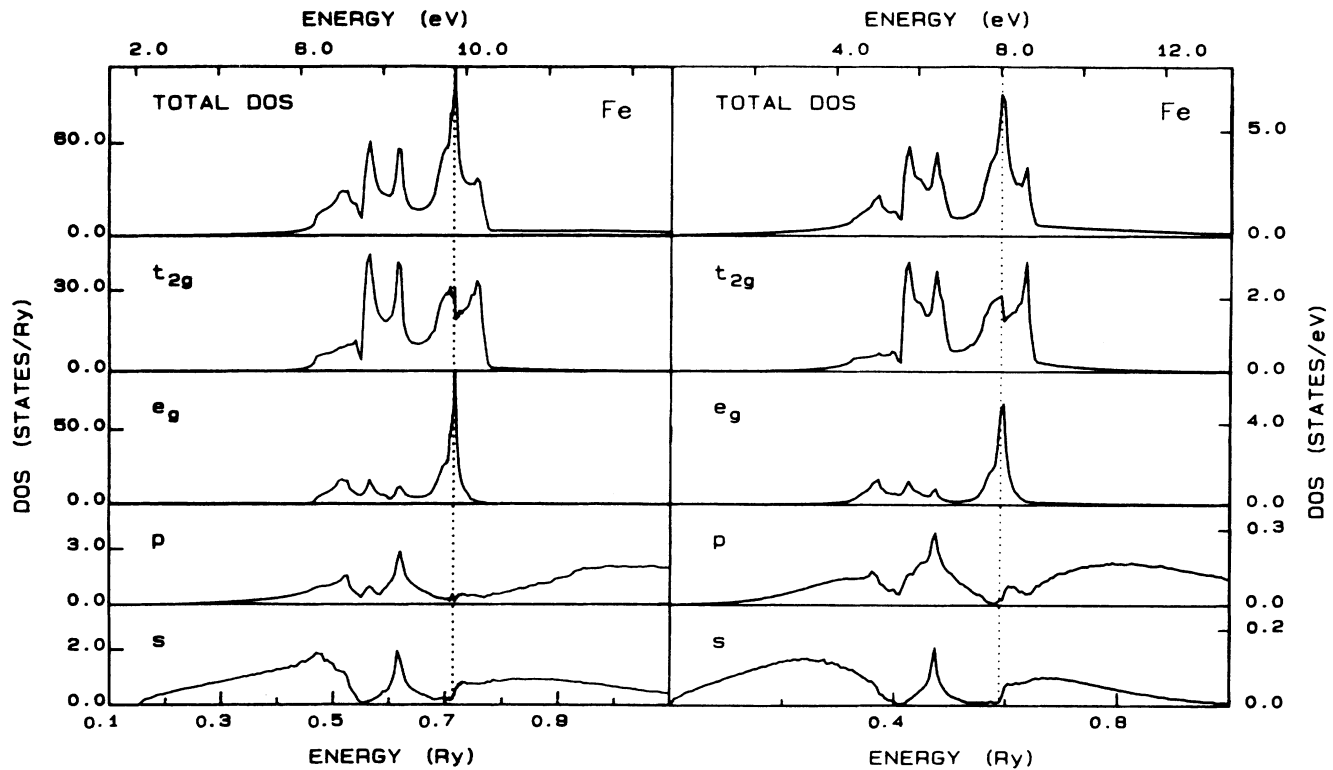
FIG. 5. Total and decomposed DOS of Fe. On the left panel we have the DOS found from the scaled SK parameters. On the right panel we have the DOS found from the fit to the direct calculation at the expanded lattice constant.

TABLE II. Selected bandwidths in Ry.

	Fit at normal lattice constant	Fit at new lattice constant	Scaled to new lattice constant (Andersen scaling)
Fe			
E_F-Γ_1	0.653	0.591	0.564
$N_{1'}$-E_F	0.026	0.016	0.220
E_F-H_{12}	0.331	0.262	0.247
$N_{1'}$-Γ_1	0.679	0.607	0.784
$\Gamma_{25'}$-Γ_1	0.534	0.499	0.475
$H_{25'}$-Γ_1	0.715	0.638	0.610
$H_{25'}$-H_{12}	0.393	0.308	0.293
Γ_{12}-$\Gamma_{25'}$	0.111	0.086	0.081
Nb			
E_F-Γ_1	0.433	0.451	0.395
$N_{1'}$-E_F	0.156	0.219	0.114
E_F-H_{12}	0.286	0.362	0.327
$N_{1'}$-Γ_1	0.589	0.670	0.509
$\Gamma_{25'}$-Γ_1	0.464	0.475	0.447
$H_{25'}$-Γ_1	0.840	0.939	0.934
$H_{25'}$-H_{12}	0.694	0.850	0.866
Γ_{12}-$\Gamma_{25'}$	0.185	0.216	0.270

IV. SCALING

To test the applicability of scaling the SK parameters for a change in lattice constant, we applied the Andersen et al.[4] scaling law $H_{l,l'} \sim (a_0/a)^{l+l'+1}$ to all but the on-site parameters, where l and l' are angular momentum quantum numbers, a_0 is the original lattice constant, and a is the new lattice constant. This law was tested on the bcc metals, Fe and Nb, performing changes in the lattice constant of $+6.1\%$ and -5%, respectively. The shift in the lattice constants of Fe was chosen such that it was scaled to the lattice constant of TiFe. Thus, we could compare results to our SK fit performed on the self-consistent APW calculations made at this lattice constant. For Nb, we also performed a self-consistent APW calculation and SK fit at the new lattice constant. For Nb, the SK fit and scaling were done out to third-nearest-neighbor interactions, using 44 SK parameters, while for Fe, we considered only first- and second-nearest-neighbor interactions, using 27 parameters.

Figures 4 and 5 show total and decomposed DOS for Nb and Fe, comparing the results of scaling (on the left) to the results of direct calculation (on the right) at the new lattice constant. One can see the good agreement between the two calculations. However, since the change in lattice constant itself causes only small changes in the features of the DOS, this evidence does not show conclusively that the scaling has worked well. To do this, we must look more closely at the results by comparing bandwidths.

Table II shows selected bandwidths for Nb and Fe, comparing the results of scaling to the results of the direct calculations at both the new and the original lattice constant. Features such as narrowing of the d-band widths for Fe, and broadening of the d-band widths for Nb, have been successfully reproduced by the scaling. However, there has been an artificial drop in Nb, and rise in Fe, of the p-like states, such as $N_{1'}$, relative to E_F and the other

bands. When one looks at the absolute energy shifts produced by the scaling, one finds that the problem is that the p bands have shifted too much relative to the other bands. This led us to do a calculation for Fe using the scaling law suggested by Harrison,[3] since this law shifts the p parameters less. Harrison's bond-length dependences are d^{-2} for s-s, s-p, and p-p interactions, $d^{-7/2}$ for s-d and p-d interactions, and d^{-5} for d-d interactions. This did improve the p bands somewhat, but they were still too high. However, it worsened s-like states, in particular, the s-like Γ_1, which increased in energy. This is due to the fact that the Harrison scheme shifts the s-interaction parameters more than the Andersen scheme does. Thus, neither scheme seems totally satisfactory in its treatment of parameters involving s and p interactions.

At any rate, we conclude that starting with our very accurate SK parameters and using either the Andersen or Harrison scaling laws, we can reproduce the basic features in the band structure and DOS, for changes as large as $5-6\%$ in the lattice constant. We expect that for smaller changes in the lattice constant, of the order of a $1-2\%$, the results of scaling should be significantly better than those for the $5-6\%$ changes which we have studied here.

V. CONCLUSIONS

We generated the energy bands and DOS of Fe and Nb using the solid-state table of Harrison[3] and compared them with our band structure found by an elaborate fit to APW calculations. We conclude that Harrison's theory can only give a qualitative description of the band structure of the transition metals and should be used with caution. Regarding the scaling laws of Andersen et al.[4] and of Harrison[3] we found that they are fairly reliable for moderate (up to 5%) changes of the lattice constant. In the case of the TiFe intermetallic compound, we have shown that the SK parameters of the elements Ti and Fe

are capable of reproducing a semiquantitatively accurate picture of the TiFe band structure. This property of transferability of the SK parameters coupled with the reliability of the scaling laws provides interesting possibilities for calculating the band structure of polyatomic systems where first principles calculations are not feasible.

In such cases where the electronegativities of the constituent atoms are very different, intermediate first-principles calculations for diatomic compounds can be used in order to determine the hopping integrals between dissimilar atoms. Finally, we wish to point out that SK parametrizations of the type discussed here may be particularly useful in the study of crystal stability of transition-metal compounds in a way that parallels the recent work of Majewski and Vogl[9] for sp-bonded solids.

ACKNOWLEDGMENT

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