

Calculation of the electronic structure of amorphous Fe and Fe-B alloys: a simple self-consistent scheme

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 7851

(<http://iopscience.iop.org/0953-8984/1/42/007>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 10/05/2010 at 20:36

Please note that [terms and conditions apply](#).

Calculation of the electronic structure of amorphous Fe and Fe–B alloys: a simple self-consistent scheme

Š Varga† and J Krempaský‡

† Institute of Inorganic Chemistry, Chemical Research Centre, Slovak Academy of Sciences, Dúbravská cesta, 842 36 Bratislava, Czechoslovakia

‡ Department of Physics, Electrotechnical Faculty, Slovak Technical University, Mlynská dolina, 812 19 Bratislava, Czechoslovakia

Received 2 May 1989

Abstract. A simple recursion-method-based scheme within a tight-binding Hamiltonian formulation is presented. While the off-diagonal matrix elements are treated according to the Harrison parametrisation, the diagonal ones are improved so as to be consistent with the respective partial band occupations. Thus the relative positions of bands as well as the charge transfer can be easily determined. Moreover, orbital functions of the extended basis set can be conveniently incorporated. Our choice of selected random initial vector sets enables us to calculate the partial densities of states in a very fast way, keeping the occupation dispersions within 0.02 eV for each band.

The procedure is applied to the calculation of the electronic structure of amorphous Fe and Fe_{100-x}B_x ($x = 14-25$) alloy. The effect of 4p orbital inclusion on the d band density-of-states curves is examined. Comparison with an experiment as well as with other existing calculations is discussed.

1. Introduction

Considerable progress has been made in the last decade in the electronic structure calculations of amorphous solids. The progress in the development of atomic structure simulation methods, together with the advent of fast computers, made it possible to carry out large first-principles-like calculations of the electronic density of states (DOS) on realistic structural models of amorphous metals and their alloys (Fujiwara 1984). However, a complete computer simulation of a solid, a recent challenging perspective (Hafner and Jaswal 1988), requires such a calculation to be repeated many times. To achieve some progress in this field extremely fast, while sufficiently reliable, methods are necessary.

One of the most intensively studied amorphous metallic systems are the amorphous Fe and Fe–B alloys. Successful computer-simulated structural models have been generated (Boudreaux 1978, Fujiwara *et al* 1981, Krajčí and Mrafko 1988). The electronic structure has been calculated by several authors. Here the recursion method (Haydock *et al* 1972, 1975) proved to be a commonly used scheme to handle the DOS calculations. When omitting model calculations on artificial structures the main differences between the various calculations are in the electronic Hamiltonian construction. Fujiwara (1982)

employed the LMTO-ASA method and the improved screened LMTO first-principles framework (1984) with self-consistently determined potential parameters. Bose *et al* (1983) elaborated the matrix elements using the atomic potentials corrected for non-additivity. Besides these sophisticated formulations good results can be obtained within much simpler parametrised approaches (Mathur 1983, Krey *et al* 1987, Krajčí and Mrafko 1988). Here the Harrison parametrisation (Harrison 1980) has appeared to be a frequently employed scheme for electronic Hamiltonian matrix elements determination. Krajčí (1987) performed a thorough investigation of various methodological aspects of calculations within such a simple Hamiltonian, and Krajčí and Mrafko (1988) applied the parametrisation to their structural models of Fe–B alloys. However, comparison with Fujiwara (1984) suggests that higher orbitals (at least Fe 4p) should be included into the basis set. Krey *et al* (1987) obtained the diagonal elements for such a case by fitting to existing band-structure calculations.

We proceed in a different way. Obviously, the Hamiltonian elements are dependent on the occupation of respective atomic orbitals. The occupations, in turn, are determined by the electronic structure, which implicitly contains the Hamiltonian elements as input parameters. Our determination of diagonal elements of the Hamiltonian is based on a simple form of such a self-consistency requirement. The procedure is somewhat similar to that of Frota-Pessôa (1983, 1985); however, no *a priori* charge-transfer information is required.

In § 2 the philosophy of our scheme, as well as the computational aspects of the calculation, are described. The results of the calculations are presented in § 3. A brief description of the structural models used is included here. For comparison, the results of our calculations on FCC and BCC Fe are also shown. In § 4 the method and comparison of our results with other calculations and an experiment are discussed, with emphasis to the influence of 4p orbitals. Finally, § 5 contains the conclusions.

2. Method

Though the performance of present fast computers makes it possible to diagonalise even the complete Hamiltonian matrix, the partial diagonalisation procedure of Haydock (the recursion method) (Haydock *et al* 1972, 1975) still remains a sufficient tool for a wide class of electronic structure problems. This is surely also the case for our method, described below.

The electronic Hamiltonian we use has a simple LCAO form

$$\mathcal{H} = \sum_a \varepsilon_a |a\rangle\langle a| + \sum_a \sum_{b \neq a} h_{ab} |a\rangle\langle b| \quad (1)$$

where $|a\rangle = |\alpha, i\rangle$ (i, α stand for site and orbital index, respectively) are the atomic orbitals, which we assume for simplicity to be orthogonal. The matrix elements $H_{ij}^{\alpha\beta}$ are constructed as follows. The off-diagonal elements $h_{ij}^{\alpha\beta}$ are expressed through Slater–Koster parameters $V_{ll'm}(r)$. We used parametrised values of $V_{ll'm}(r)$ as tabulated by Harrison (1980), without any attempt to improve them. The diagonal elements ε_i^α we understand to be equal to the atomic orbital energies here. An initial electron configuration (usually that of a neutral atom) is chosen, from which the orbital energies follow and the Hamiltonian is constructed. Its diagonalisation and integration up to the Fermi energy results in new band occupations. Now taking them as the input electron configuration the procedure is repeated until self-consistency is achieved. Of course,

off-diagonal elements should be treated in the same way. However, as their contribution to the change of the electronic structure is expected to be of less significance, their dependence on orbital occupation is neglected. To justify this simplification we refer to the standard perturbation theory argument (e.g. only diagonal elements of the perturbation contribute to the first-order corrections of eigenvalues). Thus our scheme does not require a lot of additional effort; the dependence of orbital energies on the electron configuration is treated by the algorithm of Herman and Skillman (1963) using the Slater exchange potential. Considering the conclusions of Callaway and Wang (1977) concerning the minor importance of correlation effects on a DOS curve for BCC Fe, we did not attempt to include any correlation-potential corrections.

The scheme requires repeated partial DOS (PDOS) evaluations. The usual way of performing this within the recursion method is an averaging over sufficient number of local DOS of respective orbital type. We have adopted a different approach. It has already been realised (see for example Krajčí 1987) that choosing the initial vector $|u_0\rangle$ of the recursion in the form

$$|u_0\rangle = N^{-1/2} \sum_i \xi_i |\alpha_i\rangle \quad (2)$$

leads on average to the total DOS $g(E)$ as the off-diagonal contribution to the Green function vanishes when repeated sufficient number of times. (Here N is the total number of orbitals and ξ_i are random numbers, $\xi_i = \pm 1$.) By analogy, we employed the fact that, using

$$|u_0\rangle = N_A^{-1/2} \sum_{i \in A} \xi_i |\alpha_i\rangle \quad (3)$$

where the sum runs only over the orbitals of desired type A, results by the same argument in a PDOS $g_A(E)$ of the respective orbital type. However, as was noticed by Krajčí (1987), the DOS variance is inversely proportional to the number of orbitals N included in the sum (2) as well as to the number of initial vectors N_i used. Thus for some $g_A(E)$ calculations a large N_i should be used. To avoid this, at least partially, we introduce the following trick. Suppose we have found a single initial vector $|u_0\rangle$ that generates the PDOS $g_A(E)$ exactly. (For the case of total DOS such a vector can easily be set down explicitly (Krajčí 1987).) In this case the first recursion coefficient a_0 should be exactly ε^A , where ε^A is an average over all the diagonal elements corresponding to the orbital type A, as can be immediately verified realising that a_0 is the first moment of the respective DOS. Our scheme of the choice of $|u_0\rangle$ is now the following. We generate an initial vector of the type (3) and evaluate the a_0 . This vector is retained as a good $|u_0\rangle$ only when it approaches ε^A within a prescribed accuracy (we required 0.005 eV for the d band and 0.05 eV for other orbital types). In such a way sufficient numbers of good initial vectors can be generated easily. Though such an effort has no effect on improving the DOS variance, we have found a substantial improvement of integrated quantities dispersion.† We have found $N_i = 5$ initial vectors of this kind (we refer to them as selected initial vectors) to be sufficient to obtain the occupancy dispersion within 0.02 eV. Consequently, this value was chosen to be also the required accuracy for terminating the iteration. In such a way the occupancies can be evaluated quickly, at the same time being sufficiently accurate. Moreover, one important point deserves mention. Having

† Obviously, our trick improves in fact only the first moment of the DOS, while, contrary to what happens for integrated quantities, higher moments also contribute significantly to the DOS.

Table 1. Self-consistently determined diagonal elements of the Hamiltonian. All the values are in eV relative to the respective Fermi energy. (*a*, the a-Fe system without 4p states.)

System	3d	4s	4p	2s	2p
a-Fe ^a	-1.05	-1.75	—	—	—
a-Fe	-0.63	3.17	6.97	—	—
FCC-Fe	-0.65	3.20	7.05	—	—
BCC-Fe	-0.64	2.96	6.76	—	—
Fe ₈₀ B ₂₀	-0.63	2.90	6.63	-1.98	3.57

Table 2. Calculated orbital occupations (per atom of the respective type) and the DOS at the Fermi energy (in eV⁻¹/atom) for the Fe systems studied (*a* see table 1 caption).

System	N _{3d}	N _{4s}	N _{4p}	N _{2s}	N _{2p}	g(E _f)
a-Fe ^a	7.04	0.96	—	—	—	2.669
a-Fe	5.97	0.58	1.45	—	—	2.228
FCC-Fe	5.95	0.59	1.46	—	—	2.023
BCC-Fe	6.03	0.55	1.42	—	—	4.011
Fe ₈₀ B ₂₀	6.05	0.54	1.44	0.81	2.07	1.898

found a suitable set of initial vectors $|u_0\rangle$, it may be used with the same effect throughout the whole procedure, as for our scheme the sum $\sum_i \sum_{j \neq i} \xi_i \xi_j H_{ij}$ remains unchanged by redefinition of the Hamiltonian.

The DOS, together with the integrals over them, were evaluated by the quadrature method of Nex (Nex 1978). For a correct picture of the DOS curve the tridiagonalisation termination level $L = 25-30$, at least, would be required in our case. However, for integrated quantities we have found a considerably lower L to be sufficient. Thus, to speed up our procedure, the search for self-consistent matrix elements was carried out entirely with $L = 8$, taking $L = 25$ only for the final $g(E)$ evaluation.

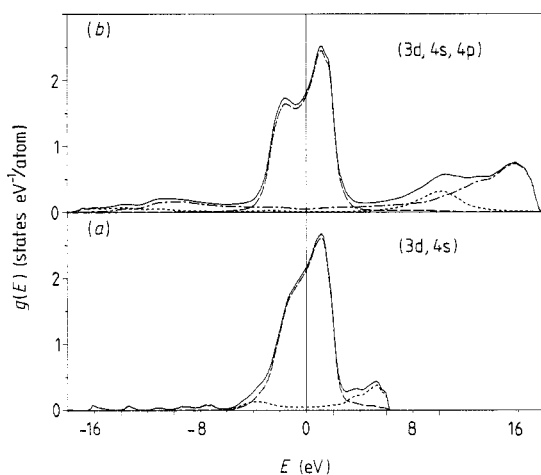
3. Results

The structure models of amorphous Fe and Fe_{100-x}B_x for $x = 14, 17, 20$ and 25 were generated by the thermodynamic simulation procedure of Krajčí and Mraňko (1984, 1986). The truncated Morse potential (Fujiwara *et al* 1981) with parameters taken from Krajčí (1987) for a-Fe and Krajčí and Mraňko (1988) for Fe-B was used for the interatomic interactions description. In the process of model generation the following steps were simulated: gradual compression of initial random distribution of low-density gaseous state to a liquid of observed density; its relaxation and equilibration; and, finally, a quenching to the amorphous state. All the models consist of $N_a = 400$ atoms enclosed in a cubic box with periodic boundary conditions, the final cube edges being determined by the mass densities according to table 3.

The basis set consists of the 3d, 4s, 4p and 2s, 2p atomic orbitals for Fe and B sites respectively. The cut-off distance for the electronic interactions we take to be $r_0 = 3.4 \times 10^{-10}$ m. The values of the Slater exchange parameter α given by the optimisation

Table 3. DOS at the Fermi energy and the calculated linear coefficient of the electronic specific heat γ for $\text{Fe}_{100-x}\text{B}_x$ systems. The mass density of structural models is also shown.

x	ρ (g cm ⁻³)	$g(E_f)$ eV ⁻¹ /atom	γ (J K ⁻² kmol ⁻¹)
0	7.86	2.228	5.251
14	7.48	2.055	4.843
17	7.45	1.946	4.586
20	7.42	1.898	4.473
25	7.37	1.711	4.032

**Figure 1.** The density of electronic states (full curve) and their respective components 3d (broken), 4s (dotted) and 4p (chained) for amorphous Fe (a) without (b) with 4p states.

of Schwarz (1972) were used. The same values $\alpha_{\text{Fe}} = 0.71151$ and $\alpha_{\text{B}} = 0.76531$ were used throughout all the calculations.

The diagonal matrix elements, as determined by our procedure, are summarised in table 1. These values are also used for the final DOS curves evaluations. As preliminary calculations for Fe–B alloys indicated only slight differences in diagonal values for different concentrations, the self-consistently determined values for $x = 20$ were also used for the other Fe–B curves. The Fermi energy was determined so as to correspond to the average number of electrons per atom of the system considering eight valence electrons of Fe and three electrons of B atom, respectively.

In figure 1 the effect of inclusion of the 4p orbital into the basis set for the case of amorphous Fe is demonstrated. As this effect evidently could not be neglected, all our subsequent calculations were carried out with 4p orbitals included. The curves of total DOS, as well as their 3d components for $\text{Fe}_{100-x}\text{B}_x$ ($x = 0, 14, 17, 20, 25$), are presented in figure 2. For comparison, our procedure was also applied to FCC and BCC Fe clusters of similar size[†]. The final DOS curves and their two d components are shown in figure 3. All the DOS curves are normalised to the average number of orbitals per atom and are shifted so as to set the Fermi energy to the zero of the energy scale.

[†] There is no need to use random initial vectors for the DOS evaluation in this case as (owing to the long-range-order preservation by the boundary conditions imposed) only four non-equivalent orbitals (4s, 4p and two 3d orbitals of symmetry e_g, t_{2g}) exist here.

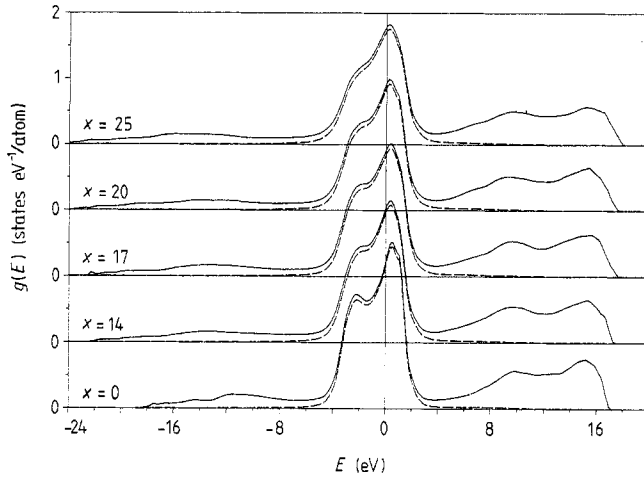


Figure 2. The density of electronic states (full curve) and their d components (broken curve) for amorphous $\text{Fe}_{100-x}\text{B}_x$ alloys. The curves for a-Fe ($x = 0$) are also shown.

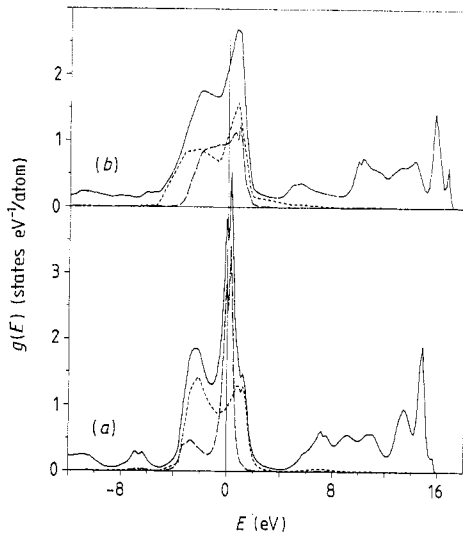


Figure 3. The density of electronic states (full curve) and its symmetry-decomposed d projections (e_g dashed, t_{2g} dotted) for (a) BCC, (b) FCC Fe.

The orbital occupancies and the DOS at the Fermi energy $g(E_f)$, as well as the calculated linear coefficients of electronic specific heat γ for all the systems studied, are summarised in tables 2 and 3. Only the $\text{Fe}_{80}\text{B}_{20}$ alloy occupancies are presented in table 2, as the differences for other boron concentrations we have found to be negligible. The charge transfer of -0.12 electrons per B or $+0.03$ electrons per Fe atom respectively was found for the $\text{Fe}_{80}\text{B}_{20}$ system.

4. Discussion

The first-principles-like methods, which treat the electronic structure fairly, are usually complex and highly computer-time consuming while still containing approximations

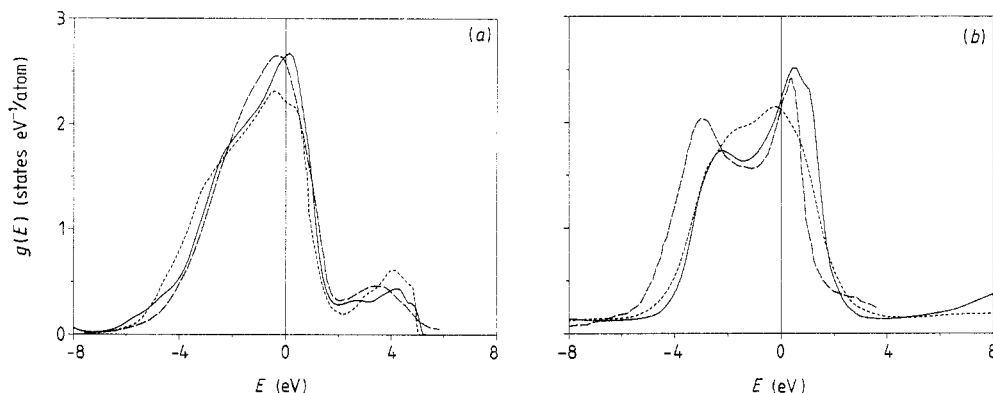


Figure 4. (a) Comparison of the results of DOS calculations for the amorphous Fe, 4p orbitals not included. Present work (full curve); Krajčič and Mraško (1988) non-self-consistent Harrison parametrisation (broken) and Fujiwara (1982) LMTO-ASA method (dotted). (b) Comparison of the results of DOS calculations for the amorphous Fe with 4p orbitals included. Present work (full curve); Fujiwara (1984) LDA-LMTO method (broken); and our calculation with Hamiltonian parameters of Krey *et al* (1987) (dotted).

their effect cannot be ever foreseen. On the other hand, simple parametrised calculations usually pay little attention to any self-consistency in determining of the Hamiltonian. The calculations of Frota-Pessôa (1983, 1985) are rare examples of a self-consistent improvement of parametrised calculations for amorphous alloys. In the quoted work the charge transfer between the alloy components is assumed to be known *a priori* and taken directly from band structure calculations. However, the charge transfer can be very sensitive to any change in the local environment. Moreover, fitting to a given charge transfer fails to work when more orbital types are explicitly included, and, of course, for a single-compound system. In this sense, our procedure is more independent of structural changes and requires no restrictions concerning the type and number of orbitals included in the basis set.

Comparison of our results for the amorphous Fe with non-self-consistent calculations of Krajčič and Mraško (1988) shows that their simple assumption $E_d = E_s$ differs only slightly from our self-consistently determined values without 4p orbitals (table 1). More generally, figure 4(a) indicates that the shape of the DOS curve, without taking the 4p orbitals into account, is not too sensitive to the way of determining of the Hamiltonian. In the result of Bose *et al* (1983) it is difficult to distinguish whether their indistinct d-band splitting is a consequence of the structure or of a finite value of broadening ϵ used in their DOS evaluation.

The situation appears to be quite different when the Fe 4p orbitals are included. In this case we have found a two-peak d-band for the amorphous Fe; the splitting vanishes with increasing concentration of boron, retaining only a hump on the high binding energy side of the d-band (figure 2). Fujiwara (1984) used the screened LMTO Hamiltonian with self-consistently determined potentials within the local density approximation and obtained a distinct two-peak d band for both amorphous Fe and $\text{Fe}_{80}\text{B}_{20}$ alloy (figures 4(b) and 5). The splitting for a-Fe can be well compared with our result (figure 4(b)). However, it was neither retained in our DOS curve for the $\text{Fe}_{80}\text{B}_{20}$ alloy nor was it found in other calculations (figure 5). Krey *et al* (1987) determined the diagonal elements of the Hamiltonian by fitting to the band-structure calculation, keeping the parametrised

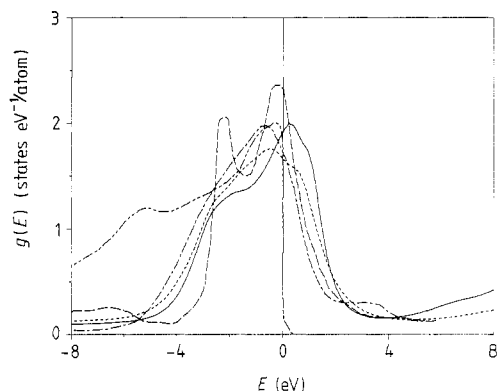


Figure 5. Comparison of the results of DOS calculations for the amorphous $\text{Fe}_{80}\text{B}_{20}$ with the experiment. Present work (full curve); Fujiwara (1984) (broken); our calculations with parameters of Krey *et al* (1987) (dotted), Krajčí and Mrafko (1988) (chained) (4p orbitals included in all cases except Krajčí and Mrafko); and UPS experiment of Paul and Neddermayer (1985) (double-dotted chain). The vertical scale for the experimental curve is arbitrary.

hopping values. As the quoted work reports only of the case of Fe–B alloy, we have also used their Hamiltonian parameters for DOS evaluation on our a-Fe model and also reproduced the calculations with their Hamiltonian parameters on our model of $\text{Fe}_{80}\text{B}_{20}$ alloy (figures 4(b) and 5). The curve for $\text{Fe}_{80}\text{B}_{20}$ is similar to our results; however, no d-band splitting was observed here for the amorphous Fe case. This supports the explanation of the amorphous Fe d-band splitting by the pd-hybridisation, since as for Krey's parameters, the 4p-energy level is too remote to significantly influence the d states.

As has been repeatedly pointed out, care must be taken to make a proper termination. For this reason values of the termination level L up to $L = 35$ were checked in order to ensure that the controversial d-band splitting is not an artifact of the method. The characteristic d-band splitting for the amorphous Fe we found to occur from $L = 25$ upwards, retaining its shape almost unchanged for larger values of L . On the other hand, no d-band splitting at all was found for the $\text{Fe}_{80}\text{B}_{20}$ alloy up to $L = 35$.

For comparison, our method was also applied to the FCC and BCC iron clusters. The position of two main peaks in the d band of BCC iron agrees well with the band structure calculations of Callaway and Wang (1977) or that of Moruzzi *et al* (1978). The missing fine structure is likely to be a consequence of the Gaussian quadrature. Our aim here, however, was not a refinement of band structure calculations; these calculations had, rather, an illustrative character. The comparison of the DOS curves (figure 3), as well as of the respective results from tables 1 and 2, with a-Fe results confirms the notion that the amorphous Fe is rather FCC- than BCC-like. Unfortunately, the paper of Fujiwara (1984) lacks the FCC-calculation to resolve the resemblance of his results. Finally, notice that the self-consistently determined energies, as well as the orbital occupancies, we found to be practically independent of the type of the structure (table 1).

We have also performed preliminary calculations on the liquid-structure models; however, as these calculations did not bring any notable difference either in the DOS curves or in the Hamiltonian parameters we do not present them here. This supports the suggestion that the main discrepancies are caused rather by different Hamiltonian construction than by faint differences in structural models. As has been demonstrated by Krey *et al* (1987) for the amorphous $\text{Fe}_{80}\text{B}_{20}$ the difference between two realistic models can be recognised only in the very fine detail of the DOS curve.

The Fermi energy was found to lie in the high DOS region in the d band, as expected from high d contribution to the total DOS; the trend in its position relative to the maximum was found to be the same as in Fujiwara (1984). However, though the trend of decreasing

value of the DOS at the Fermi energy $g(E_f)$ with increasing boron concentration is preserved (table 3, compare also with Krajčí and Mraško 1988 and Krey *et al* 1987), the absolute values are rather small to correspond to the linear coefficient of specific heat γ measurements (Matsuura *et al* 1981). We explain it rather by the non-electronic contributions to the specific heat than by not having taken into account the ferromagnetic state in the calculations. Mathur (1983) performed a spin-polarised electronic-structure calculation for the amorphous Fe, but the value of the DOS at the Fermi energy he obtained was also lower than expected from the experiment.

The closest (though far from identical) experimental quantity to compare with the DOS curves is the energy distribution of photoemitted electrons (XPS, UPS). Ample experimental results exist for the Fe–B amorphous alloy (see Oelhafen 1982 and a more recent study of Paul and Neddermayer 1985). All the experimental curves are single peaked eventually, with some structure on the high binding energy side of the d-peak, but in no case was a distinct two-peak structure observed. Unfortunately, we are not aware of any electronic structure experiment on the pure amorphous Fe to compare with the calculations. Only thin films of monometallic materials can be prepared in amorphous form and extreme experimental conditions are required for their spectroscopic investigation (Magnan *et al* 1989).

In fact, our procedure should properly take into account the local electronic structure, which for the amorphous structure differs from site to site, requiring each diagonal element to be determined separately, from the respective local DOS. This would require the local DOS calculations to be repeated many times. (The quantity of calculations would increase typically by two orders of magnitude in such a case.) However, we do not expect any significant correction to the electronic structure from an improvement of this kind.

Finally, we remark that for a reliable determination of quantities such as, e.g., the binding energy, our self-consistency condition may turn out to be rather too simple to give satisfactory results. More elaborate formulations of the electronic problem (see, e.g. the derivation of the electronic energy contributions by Sutton *et al* 1988) should probably be used in this case. Moreover, such an effort obviously requires an adequate improvement in the off-diagonal elements evaluation, too. Anyhow, for the fixing of relative band positions in a band structure calculation we believe our scheme to be a reasonable approach.

5. Conclusions

We have developed an electronic-structure calculation scheme that is a compromise between the rather complex first-principles-like methods and simple parametrised calculations. The procedure does not require any additional information; its only additional parameter is the Slater exchange parameter α . The recursion method, together with the selected random initial vector choice, appears to be an effective tool to make our computational scheme sufficiently reliable and fast.

The application of the procedure to calculations of the electronic structure of amorphous Fe and $\text{Fe}_{100-x}\text{B}_x$ ($x = 14\text{--}25$) shows that for more reliable results the inclusion of higher orbitals appears to be unavoidable. We have found a distinct d-band splitting for amorphous Fe, this effect completely missing when 4p orbitals are omitted. With increasing concentration of boron the splitting vanishes. Such a picture is in a good agreement with existing XPS/UPS data for Fe–B alloys; for pure a-Fe an experiment is

still lacking. To our knowledge first photoemission experiments on the amorphous Fe are in progress now (Hricovini 1989). The discrepancies between existing calculations we ascribe to different Hamiltonians rather than to differences in structural models.

Acknowledgment

We are grateful to Dr M Krajčí for providing us with his set of atomic structure simulation programs, for many valuable discussions and for his careful reading of the manuscript.

References

- Bose S K, Ballentine L E and Hammerberg J E 1983 *J. Phys. F: Met. Phys.* **13** 2089
 Boudreaux D S 1978 *Phys. Rev. B* **8** 4039
 Callaway J and Wang C S 1977 *Phys. Rev. B* **16** 2095
 Frota-Pessôa S 1983 *Phys. Rev. B* **28** 3753
 ——— 1985 *J. Phys. F: Met. Phys.* **15** 287
 Fujiwara T 1982 *J. Phys. F: Met. Phys.* **12** 661
 ——— 1984 *J. Non-Cryst. Solids* **61 + 62** 1039
 Fujiwara T, Chen H S and Waseda Y 1981 *J. Phys. F: Met. Phys.* **6** 1325
 Hafner J and Jaswal S S 1988 *J. Phys. F: Met. Phys.* **18** L1
 Harrison W A 1980 *Electronic Structure and the Properties of Solids* (San Francisco: Freeman)
 Haydock R, Heine V and Kelly M 1972 *J. Phys. C: Solid State Phys.* **5** 2845
 ——— 1975 *J. Phys. C: Solid State Phys.* **8** 2591
 Herman F and Skillman S 1963 *Atomic Structure Calculations* (Englewoods Cliffs, New Jersey: Prentice-Hall)
 Hricovini K 1989 private communication
 Krajčí M 1986 *Comput. Phys. Commun.* **42** 29
 ——— 1987 *J. Phys. F: Met. Phys.* **17** 2217
 Krajčí M and Mráfkó P 1984 *J. Phys. F: Met. Phys.* **14** 1325
 ——— 1988 *J. Phys. F: Met. Phys.* **18** 2137
 Krey U, Ostermeier H and Zweck J 1987 *Phys. Status Solidi b* **144** 203
 Magnan H, Chandesaris D, Rossi G, Jezequel G, Hricovini K and Lecante J 1989 to be published
 Mathur P 1983 *Z. Phys.* **B 53** 255
 Matsuura M, Mizutani U and Yazawa Y 1981 *J. Phys. F: Met. Phys.* **11** 1393
 Moruzzi V L, Janak J F and Williams A R 1978 *Calculated Electronic Properties of Metals* (New York: Pergamon)
 Nex C M M 1978 *J. Phys. A: Math. Gen.* **11** 653
 Oelhafen P 1982 *Glassy Metals II, Topics Appl. Phys.* **46** ed. H-J Güntherodt and H Beck (Berlin: Springer)
 Paul Th and Neddermeyer H 1985 *J. Phys. F: Met. Phys.* **15** 79
 Schwarz K 1972 *Phys. Rev. B* **5** 2466
 Sutton A P, Finnis M W, Pettifor D G and Ohta Y 1988 *J. Phys. C: Solid State Phys.* **21** 35