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Accurate densities of states for metallic compounds from parametrized tight-binding calculations?

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Abstract. The local density of states is calculated for an Fe atom in various 4d transition-metal hosts on the one hand by the linear-muffin-tin-orbital method in the atomic-sphere approximation, and on the other hand by a two-centre orthogonal Slater–Koster tight-binding method supplemented by the demand for local charge neutrality. The comparison demonstrates that the latter method is able to yield accurate densities of states for metallic compounds.

In the conventional tight-binding (TB) schemes there is no self-consistency between the elements of the TB Hamiltonian matrix and the output charge density obtained from the TB calculation: they may be derived from the Harris–Foulkes approximation (see, for instance, [1] and references therein) and thus yield an expression for the binding energy that is correct to first order in the charge density. In spite of the many successful applications of these schemes, there are also limitations. For instance, it is well known [1] that for the calculation of second-order quantities such as force constants or heats of formation some form of approximate self-consistency has to be included. The simplest form of self-consistency is to assume that due to the excellent screening properties of a metal each atom remains charge neutral. In a TB calculation, local charge neutrality (LCN) can be achieved by varying the on-site matrix elements of the TB Hamiltonian for each atom α in an appropriate way, thereby fixing the splittings between different orbitals on the same atom. (Alternatively, a Hubbard-like term may be added [2] to the TB Hamiltonian and LCN may be achieved by using an infinitely large Hubbard U .) This procedure leads to a consistent picture of the heats of formation of transition-metal alloys [3]. Because the binding energy is mainly determined by lower moments of the electronic densities of states, $Z_\alpha(E)$, this means that these lower moments are reasonably well obtained by a TB method with LCN. Furthermore, the TB scheme with LCN has been also used for the treatment of surfaces and interfaces [2].

In the present paper we want to demonstrate that the TB method with LCN is even able to yield highly accurate local electronic densities of states, i.e., to determine also the higher moments. Accurate information on the density of states is required, for example, in the theory of magnetism, because the paramagnetic state of atom α becomes unstable if the Stoner criterion [4], $Z_\alpha(E_F)I > 1$, is fulfilled, where I is the Stoner exchange integral and E_F denotes the Fermi energy. An accurate determination of $Z_\alpha(E_F)$ is highly critical when E_F is located in an energy regime with strong variations of the electronic density of states, which is, for instance, the case for Fe atoms in various hosts (see below). For systems with constituents of different electronegativities the conventional TB calculations would

yield considerable and unphysical charge transfers between the various atoms which could seriously affect the local densities of states. Nevertheless, most of the TB investigations of magnetism in alloys and compounds (see, for instance, [5–7]) did not introduce LCN but used for the on-site matrix elements of the constituents the values obtained for the respective perfect elementary crystals. Lorenz and Hafner [8] emphasized the importance of local self-consistency for the influence of the local atomic structure on the local electronic and magnetic properties. In their treatment of noncollinear spin systems they therefore used the self-consistent spin-averaged matrix elements obtained from a TB–LMTO calculation [9] for the ferromagnetic state of the considered atomic arrangement to represent the paramagnetic part of the TB Hamiltonian. Thereby, self-consistency holds both for the on-site and for the off-site matrix elements.

In the present paper we want to demonstrate that the most important effect is the self-consistency of the on-site matrix elements and that this is indeed approximately achieved by imposing LCN. The calculations are performed for an Fe atom in various 4d transition-metal (T) hosts in a bcc configuration, for the following reasons:

- (i) There is high interest in these systems, because it was found experimentally [10] that the magnetic moment on the Fe atom disappears for Nb, but is rather large for Mo. This experimental result raised the question of under what circumstances a magnetic moment on a transition metal impurity exists. *Ab initio* calculations [11–13] based on the local-spin-density approximation elucidated the important role of crystal symmetry for this problem.
- (ii) There is already much information available on the local density of states from the above-mentioned *ab initio* calculations.
- (iii) In most of these systems E_F is located in a regime of strong variation of the local density of states. Predictions on magnetism based on the Stoner criterion thus indeed require highly accurate determinations of the density of states.

The calculations were performed for an eight-atom supercell FeT_7 and are based on a two-centre orthogonal Slater–Koster TB method [14], taking into account off-site matrix elements up to third-nearest neighbours. For the lattice constants we insert the values obtained by a LMTO–ASA calculation [9] for the pure bcc T host. The matrix elements for the constituents were obtained by fitting the TB eigenvalue spectrum of the elementary bcc crystals to the *ab initio* eigenvalue spectrum from the LMTO–ASA calculation for the respective lattice constants. (Crystal field splittings of the on-site matrix elements thereby were neglected.) It thereby turned out that it was not sufficient to determine the matrix elements once for Fe for the equilibrium lattice constant of bcc Fe and to scale the off-site matrix elements according to Harrison [14], for instance, in order to obtain the respective parameters for the equilibrium lattice constants of the T hosts. For lattice constants which differ considerably from the equilibrium lattice constant of bcc Fe the thus-obtained bandstructure of Fe deviated strongly from the corresponding *ab initio* band structure. There is some systematics concerning the signs and the relative magnitudes of the off-site matrix elements. Most the the $ss\sigma$, $dd\sigma$, $sd\sigma$ and $pd\sigma$ elements are negative, the $dd\delta$ elements are sometimes positive, sometimes negative, and the other matrix elements are mainly positive. The $pp\sigma$ elements are the largest ones; the $dd\delta$ elements are smallest. Most matrix elements decay monotonically with distance. Exceptions, for instance, are the $pp\sigma$ matrix elements of Y, Zr, Nb and Mo, which are largest for the next-nearest neighbours. The mixed off-site matrix elements between Fe and T were calculated from the corresponding matrix elements of the elementary crystals by geometrical averaging for the case of equal signs. For different signs the mixed matrix elements were set equal to zero. (This concerns mainly the $dd\delta$ matrix elements which are often the smallest dd matrix elements.) The

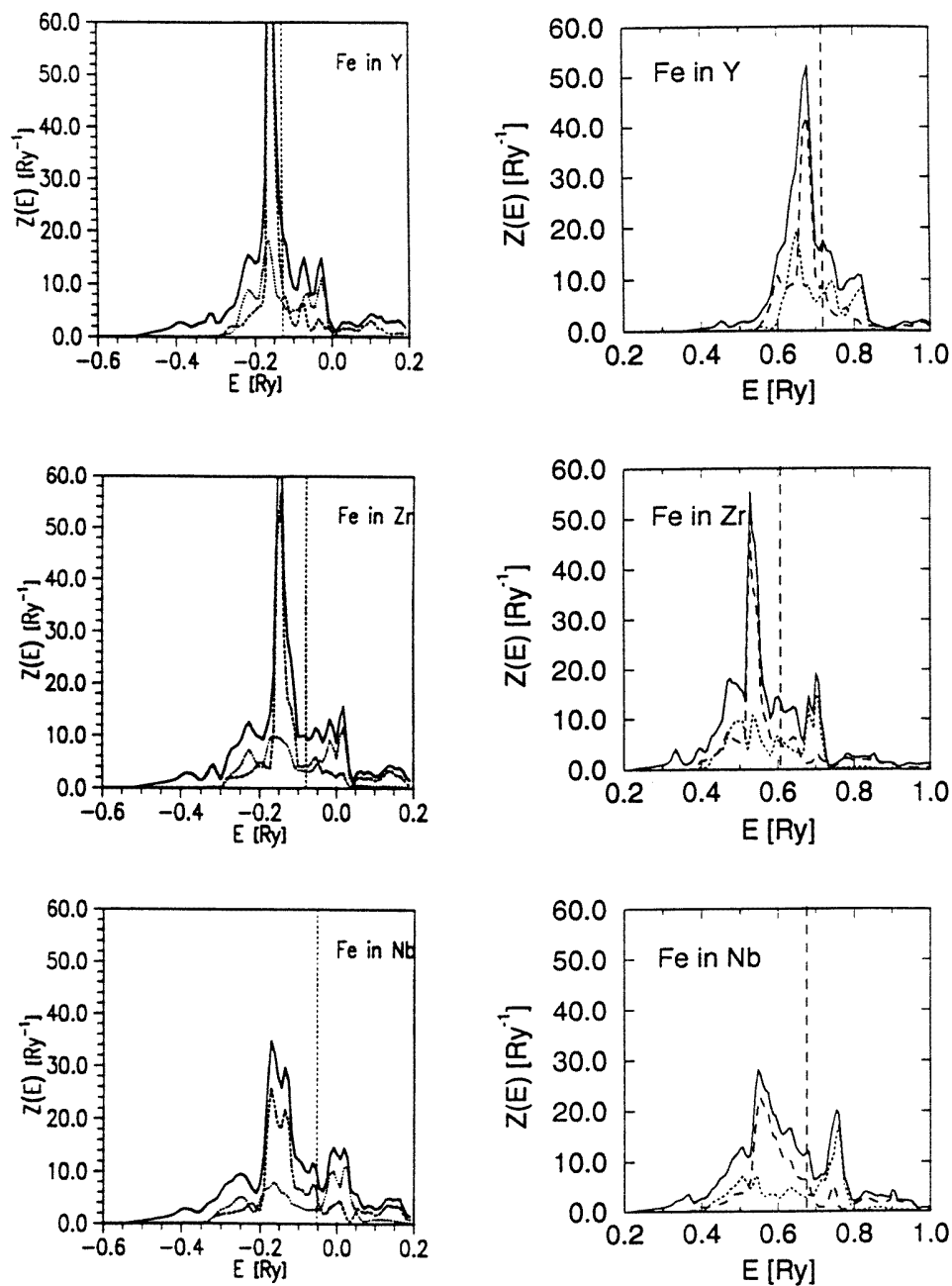


Figure 1. Local density of states per spin, $Z_{\text{Fe}}(E)$, for the Fe atom in FeT_7 . Left: LMTO, right: TB; dashed line: contribution of $d\text{-}T_{2g}$ states, dotted line: $d\text{-}E_g$ states, full line: total density of states; dashed vertical line: E_F .

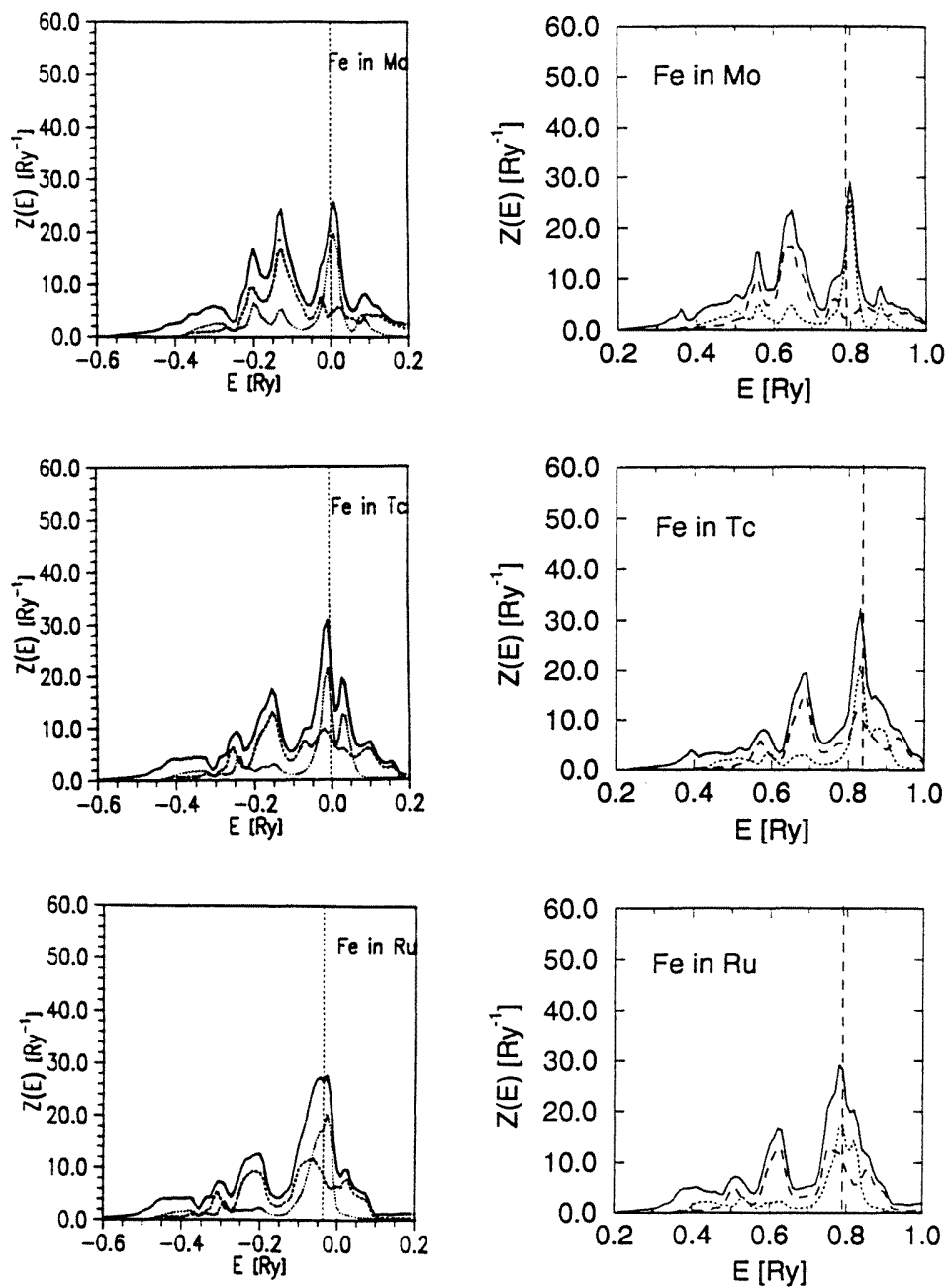


Figure 1. Continued.

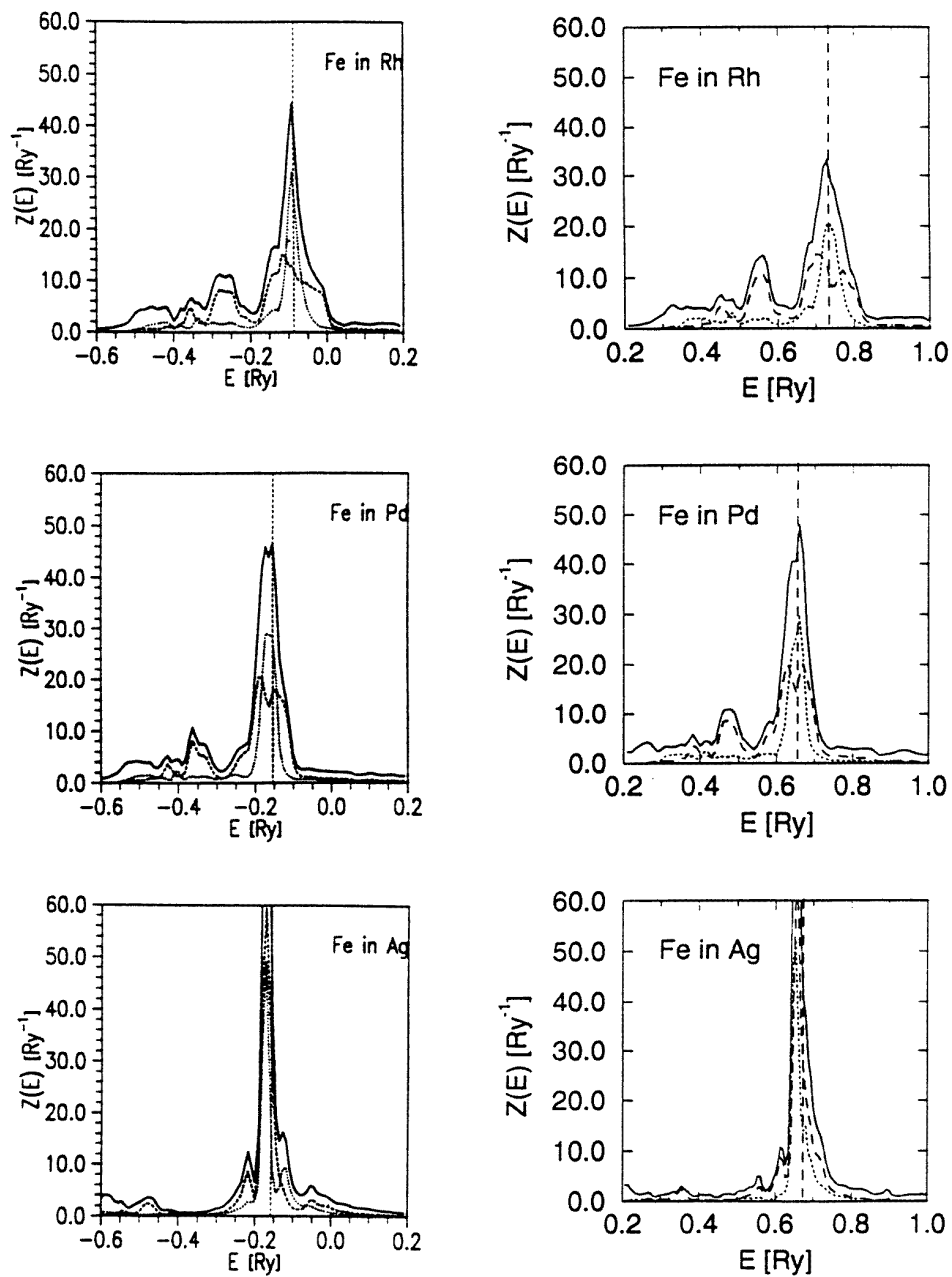


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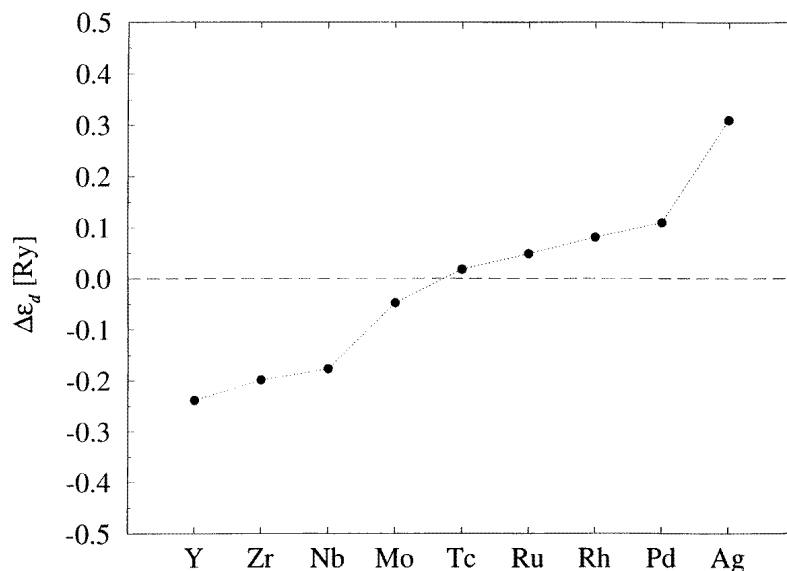


Figure 2. $\Delta\epsilon_d = \epsilon_d(\text{Fe}) - \epsilon_d(\text{T})$ for FeT_7 .

on-site matrix elements for the Fe atom then were shifted until LCN for the Fe atom was achieved. (This does not necessarily guarantee LCN for all the T atoms in the supercell, but even for the system with the largest difference in electronegativities (FeY_7) the charge transfer between crystallographically different Y atoms was less than 0.15 electrons per atom.)

Figure 1 shows a comparison of the density of states for FeT_7 obtained by LMTO–ASA calculations [11] and by the present TB calculations. In both calculations, 47 k points in the irreducible part of the Brillouin zone of the supercell were used and the density of states was constructed by use of the tetrahedron method [15]. There is a very good agreement for the whole transition-metal series, although the shape of the density of states curves changes drastically across the series. With the calculated density of states at the Fermi energy, $Z_{\text{Fe}}(E_F)$, and the intraatomic exchange integral $I_{\text{Fe}} = 0.068$ Ryd, the Stoner criterion predicts that the Fe atom should be magnetic for all T except for T = Zr, Nb, in agreement with the predictions of the *ab initio* calculations [11–13]. Altogether, this demonstrates that a TB calculation supplemented by the demand for LCN is indeed able to yield accurate densities of states for compounds.

It should be noted that Shore and Papaconstantopoulos [16] used a different idea and obtained a TB model for compounds from the TB parameters of the constituents and an alignment of the E_F by shifting the on-site parameters for one constituent. This does not necessarily guarantee LCN, especially when there are strong modifications of the hybridization by the formation of the compound as in the system FeT_7 : for T = Ag the density of states curve at the Fe atom is very narrow, it broadens when going to the middle of the 4d series and it is again narrow at the left-hand side of the d series. The degree of hybridization thereby is mainly determined by the interatomic distance and by the difference $\Delta\epsilon_d = \epsilon_d(\text{Fe}) - \epsilon_d(\text{T})$. An analysis of the *ab initio* data [11, 12] and the present TB results demonstrates that the small bandwidth at the left-hand side originates mainly from the strong increase of the lattice constant when going from Mo to Y, whereas it is

caused on the right-hand side by the increase in $\Delta\varepsilon_d$ when going from Tc to Ag (figure 2), where the lattice constant varies only slightly [17].

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