



Volume effect and electron band modification in α -Fe by substitutional impurities

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ABSTRACT

Systematic investigation of the various impurities influence on the electron and electron spin density on the iron nucleus has been undertaken for impurities dissolved randomly on the regular iron sites in the ferromagnetic BCC iron. The average electron and spin density on the iron nucleus is affected by the volume effect caused by solution of the impurity and by the conduction band modification due to the same impurity. It was attempted to correct data for the volume effect by using information obtained by *ab initio* calculations of the hyperfine field B and electron density ρ in pure iron versus varying lattice constant a . It was found that $\partial B/\partial a = 33(3) \text{ T Å}^{-1}$ and $\partial \rho/\partial a = -5.2(1) \text{ el. a.u.}^{-3} \text{ Å}^{-1}$. Mössbauer data were used to evaluate hyperfine parameters versus particular impurity concentration c , while the corresponding lattice constant evolution was obtained from the X-ray diffraction data. Hence, it was possible to make volume correction by using above slopes obtained in calculations. It was found that for all d impurities one has the linear correlation between volume corrected hyperfine field variation $(dB/dc)_b$ and corresponding electron density variation $(d\rho/dc)_b$. The slope for the above correlation amounts to $(\partial \rho/\partial B)_b = -0.031(3) \text{ el. a.u.}^{-3} \text{ T}^{-1}$. A linear correlation between the out of the core electrons N_e of the impurity and electron density on the iron nucleus was found with the slope $-0.0038(7) \text{ a.u.}^{-3} \text{ at.}\%^{-1}$ for all d impurities and $-0.0072(3) \text{ a.u.}^{-3} \text{ at.}\%^{-1}$ for the s–p impurities of the fourth period.

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1. Introduction

Iron crystallizes close to the ground state of the system and under ambient pressure in the BCC structure with the ferromagnetic order. Magnetic anisotropy is very small with the easy axes of magnetization being aligned with the main directions of the chemical unit cell. The major contribution to the magnetic hyperfine field on the iron nucleus is due to the Fermi contact field, the latter field having significant contribution caused by the spin polarization of the conduction band. Hence, the magnetic hyperfine field on the iron nucleus is proportional to the total (isotropic) electron spin density on the iron nucleus. The electron density on the iron nucleus has significant contribution due to the conduction electrons as well. One can dissolve randomly many impurities on the regular lattice sites of iron. The solubility limit depends on the impurity and the cooling rate from the liquid state [1]. Such impurities modify hyperfine field and electron density on the iron nuclei. On the other hand, they are practically unable to generate measurable electric field gradient (EFG) on the iron nuclei [2]. The latter

effect is due to the effective shielding of the higher order charge perturbations by conduction electrons. One can study the variation dB/dc of the average magnetic hyperfine field B on iron nucleus versus particular impurity concentration c in the null external field. Similar variation $d\rho/dc$ of the average electron density ρ on the iron nucleus could be conveniently observed via the isomer shift variation dS/dc , where the symbol S denotes a total shift versus total shift in pure α -Fe staying at room temperature and under ambient pressure [2–5]. Hence, one can study impurity effect on the electron spin and charge density on the iron nucleus. The Vegard law is satisfied for impurities randomly distributed on the regular iron sites [6–8]. Therefore one can attempt to separate volume and conduction band (chemical bonds) modification effects due to addition of impurity provided the volume effect is calculated by using *ab initio* methods for the pure iron. In order to do so one has to calculate the magnetic hyperfine field and electron density on the iron nucleus for pure α -Fe staying in the ground state of the system, albeit varying the lattice constant around the value occurring at the ambient (null) pressure. One can expect linear variation of the above hyperfine parameters for small variation of the lattice constant. The phonon density of states projected on the average iron atom (PDOS) weakly depends on the particular impurity and impurity concentration. Hence, the variation in the second order Doppler shift

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(SOD) could be neglected provided spectra are recorded at similar temperatures [9].

The main aim of this contribution is to study the band effect for various impurities in iron upon having removed the volume effect introduced by the impurity. The paper is organized as follows. Section 2 deals with the *ab initio* calculations, Section 3 discusses available experimental data, while the last Section 4 is devoted to the discussion of results and conclusions.

2. Calculation of the electron density and hyperfine field

Calculations have been performed within density functional theory (DFT) using the full-potential linearized augmented plane wave (FLAPW) and augmented plane wave plus local orbitals (APW+lo) methods as implemented in the WIEN2k code [10–12]. Fully relativistic spin dependent approach was applied, albeit without taking into account spin–orbit (SO) coupling, as the latter is irrelevant for the system investigated [9]. The APW+lo extension was used for the valence electrons as it assures faster convergence at the same high level of accuracy as the LAPW+lo method. Wave functions are expanded into spherical harmonics inside the non-overlapping atomic spheres (muffin-tins) centered on the atomic sites and of the radius R_{MT} in the FLAPW and APW+lo methods. Plane waves are used as the basal functions in the remaining space of the unit cell. We have used almost touching muffin-tin spheres with the radius 2.27–2.35 a.u. depending on the lattice constant chosen. The maximum angular momentum used in the expansion of the wave function within muffin-tin spheres was set to $l_{max} = 10$. The wave functions between muffin-tin spheres were expanded into plane waves with a cutoff set to $K_{max} = 8/R_{MT}$, and the magnitude of the largest wave vector in the Fourier expansion of the charge density was applied as $G_{max} = 16 \text{ Ry}^{1/2}$. The APW+lo basis for $l=0, 1, 2$ and the standard LAPW expansion for higher angular momenta l were used. States lying more than 7 Ry below Fermi level were treated as the core states. The number of irreducible k points was set to 286 per Brillouin zone. The convergence of the quantities of interest with respect to the number of k points and the basis size, the latter determined by the $R_{MT}K_{max}$ criterion was checked. The integrated difference between the input and output charge densities was less than $5 \times 10^{-5} \text{ e/a.u.}^3$ at convergence. The number of radial mesh points was kept at constant value 781. The correlation and exchange potentials were treated within the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) [13]. The iron nucleus has been approximated by the homogeneously charged sphere, the latter having radius $R_0 = 4.897 \text{ fm}$. Further details on the calculations could be found in Ref. [9].

Fig. 1 shows electron density difference $\rho - \rho_0$ versus difference in the lattice constant $a - a_0$ and similar difference of the hyperfine field $B - B_0$. Symbols with index denote respective values for the unperturbed iron. For unperturbed iron one obtains $\rho_0 = 15322.046 \text{ el. a.u.}^{-3}$, $a_0 = 2.8311 \text{ Å}$ and $B_0 = 30.94 \text{ T}$ (pure contact term). A standard linear regression fit was used to obtain respective slopes $\partial \rho / \partial a = -5.2(1) \text{ el. a.u.}^{-3} \text{ Å}^{-1}$ and $\partial B / \partial a = 33(3) \text{ T Å}^{-1}$. Variation shown in Fig. 1 is due to the pure volume (pressure) effect, and parameters obtained could be used to correct for the volume effect in alloys provided the lattice constant is measured for each alloy.

3. Analysis of the Mössbauer data

Mössbauer data for the 14.41-keV resonant transition in ^{57}Fe are usually obtained by using resonantly thin single line (unpolarized) source kept at room temperature and random absorber kept at ambient pressure and temperature as well. Ambient temper-

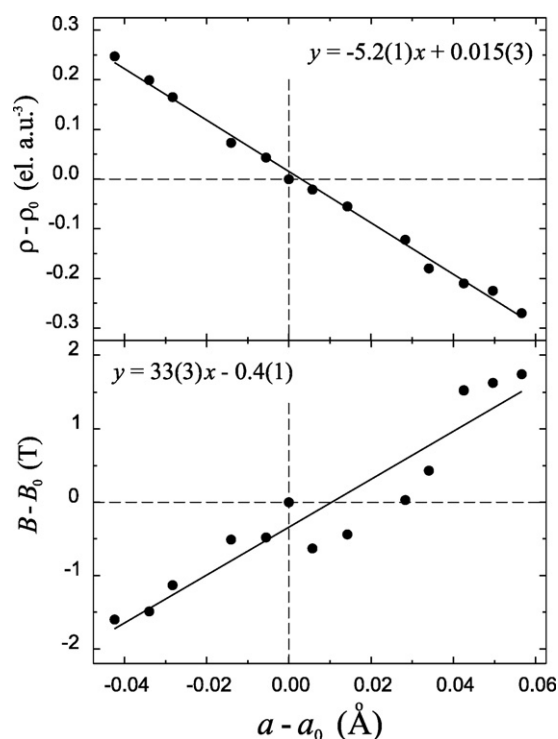


Fig. 1. Variation of the electron density and iron hyperfine field (contact field) versus lattice constant. Linear regression results are shown in the form $y = \alpha_0 x + \beta_0$.

ature is sufficiently low to approximate magnetic and electronic ground state, and on the other hand sufficiently high to make SOD contribution negligible while comparing various alloys [2,9]. It is desirable to process spectra within the transmission integral approximation. A series of spectra for various impurity concentrations is required to obtain the average isomer shift S and average hyperfine field B versus concentration c . Typical spectra are shown in Fig. 2. For the majority of cases the average hyperfine field and average spectral (isomer) shift vary linearly versus impurity concentration within the solubility range. Fig. 3 illustrates such situation for the same impurities as for Fig. 2. Such linear variation is obtained experimentally provided data are collected for various impurity concentrations within the solubility range.

The isomer shift could be readily transformed into the electron density on the iron nucleus applying the expression $\rho - \rho_0 = \alpha^{-1} S$. The calibration constant for the resonant transition considered here amounts to $\alpha = -0.291(14) \text{ a.u.}^3 \text{ mm s}^{-1}$ [9]. Hence, one can calculate the following slopes for each impurity dB/dc , dS/dc and $d\rho/dc$. Quantities dB/dc and dS/dc are shown for various impurities in Table 1 together with the slope of the lattice constant da/dc , the latter following from the Vegard law [6–8].

4. Discussion and conclusions

Correlation between dB/dc and dS/dc and/or $d\rho/dc$ is shown in Fig. 4a for various impurities. One can see that impurities 3d, 4d and 5d are described by almost parallel straight lines with the positive slope. Addition of subsequent d electron on the impurity leads to the reduction of the total electron spin density on the iron nucleus followed by the proportional reduction of the electron density on the same nucleus. A reduction of the total spin density means that transferred spin density has increased as for iron the core and transferred electron spin densities (hyperfine field components) have opposite sign due to the fact that iron atom has localized electronic magnetic moment in the alloys considered here. The core spin density is almost unperturbed by the solid state environment as the

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