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Ab initio study of the effect of pressure on the hyperfine parameters of ^{57}Fe in bcc phase

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Abstract In this paper the results of studies on the effect of pressure on hyperfine magnetic field (B_f) and isomer shift (IS) for Fe-bcc are presented. Two calculation methods were used: TB-LMTO (Tight Binding Linear Muffin-Tin) and FP-LAPW (Full Potential Linearized Augmented Plane Wave) and the obtained results have been compared. Both methods lead to comparable results. In the study a particular emphasis has been laid on investigations of the atomic core electrons (1*s*, 2*s*, 3*s*) and of the conduction electrons 4*s* on the B_f and IS values. The calculated values of the dIS/$d\ln V$ and $d\ln B$ /$d\ln V$ parameters give evidence of good conformity with those derived from experimental data.

Key words TB-LMTO • FP-LAPW • Fe-bcc • pressure • hyperfine magnetic field • isomer shift

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Introduction

The hyperfine interaction parameters for the ^{57}Fe nuclide such as: IS and B_f, determined by means of Mössbauer spectroscopy, constitute a source of information concerning the immediate neighbourhood of the Fe nuclides. The IS is related to the *s*-type electron charge density at the Fe nucleus, whereas B_f is related to the electronic spin density. Both values are sensitive to change of the interatomic distances. Therefore, theoretical calculations of these parameters necessitate precise determination of the effect of the lattice constant modifications on the electronic charge and spin densities.

Pressure and volume coefficients for Fe-bcc

Starting from the electronic structure calculations, one can estimate values of macroscopic quantities for varying lattice parameters and, as a result, get their volume dependence [6]. To get their pressure dependence, one have to know the explicit form of $P(V)$ function. One of the most important results of *ab initio* investigations is the total energy including all interactions taken into account. Its volume dependence can be described with the use of formula [8]

$$E(V) = a + bV^{-1/3} + cV^{-2/3} + dV^{-1} \tag{1}$$

where a, b, c and d are the matching factors. Having the $E(V)$ function (1), the corresponding $P(V)$ dependence can be determined from the equation $P(V) = -dE(V)/dV$ and then the bulk modulus from $B = (dP/dV)\cdot V$. Another relation between variations of the elementary cell volume and pressure can be determined basing on the experimental Bridgmann's equation [4]

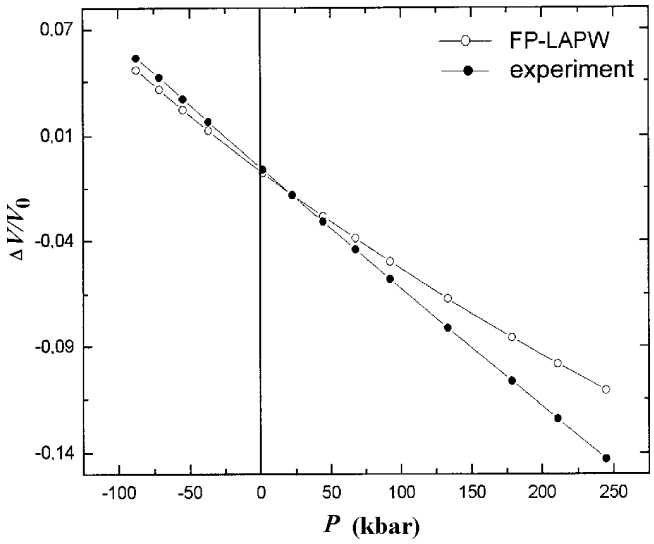

Fig. 1. Compressibility ($\Delta V/V$) *vs.* pressure (P) graph for Fe-bcc.

$$\Delta V/V = AP + BP^2 \quad (2)$$

where A and B are typical for the definite element parameters. In case of iron (Fe) the parameters A and B in equation (2) amount successively to $A = -5.826\ 10^{-4}$ 1/kbar, $B = 0.798^{-7}$ 1/kbar^2 [9]. Figure 1 presents the $\Delta V/V$ *vs.* pressure dependence. The open circles present the results of the FP-LAPW calculations. The points represented by solid circles were obtained from the relation (2). For small pressures (up to 50 kbar) both curves fits very well. Table 1 puts together the calculated values of the $\partial\ln\mu/\partial P$, $\partial\ln B_f/\partial P$, $\partial IS/\partial\ln V$ and $\partial\ln B_f/\partial\ln V$ factors. It appears from Table 1 that there is good qualitative conformity between the experimental values and the corresponding values derived theoretically.

Effect of pressure on the IS value for Fe-bcc

The isomer shift for a series of measurements carried out for the same Mössbauer source is usually interpreted with the use of formula [5]; $IS = \alpha\Delta\rho(0)$ where α is a constant dependent on the Mössbauer nuclide type (for the ^{57}Fe isotope it amounts to $-0.24\,a_0^3$ mm/s) and the $\Delta\rho(0)$ is the change of the electronic charge density occurring in the absorbent nucleus compared with the standard material. In this paper, a relative change $\Delta\rho(0)$ for different values of pressure has been calculated in relation to the values

Table 1. Pressure and volume derivatives of the magnetic moment (μ), Fermi contact hyperfine field (B_c) and isomer shift (IS) calculated by means of *ab initio* methods and determined experimentally.

	$\partial\ln\mu/\partial P$ (kbar^{-1})	$\partial\ln B_c/\partial P$ (kbar^{-1})	$\partial IS^{tot}/\partial\ln V$ (mm/s)	$\partial\ln B_c/\partial\ln V$
TB-LMTO	-2.89×10^{-4}	-3.84×10^{-4}	1.28	1.148
FP-LAPW	-2.95×10^{-4}	-4.07×10^{-4}	1.17	1.157
Experiment	$-3.20\times10^{-4*}$	$-1.66\times10^{-4**}$	1.62**	0.372**

*Ref. [7]. **Ref. [10].

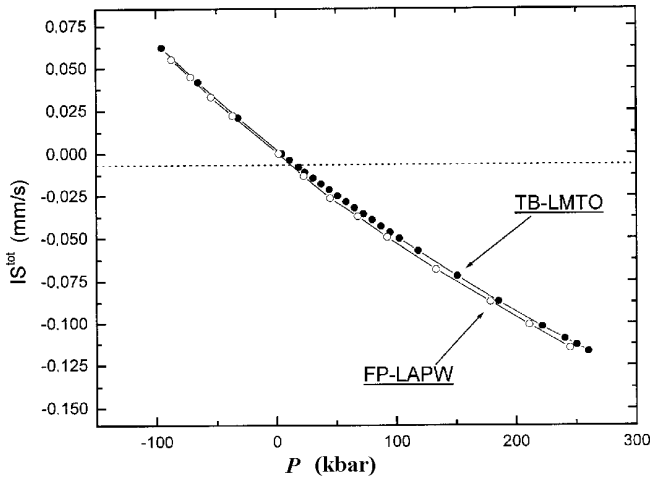

Fig. 2. Isomer shift – pressure curves for both discussed methods.

$\rho(0)$ at $P = 0$ kbar. In the relativistic calculations of the electronic structure, the point charge approximation for the electrostatic nucleus potential $V_j(r)$ is employed which is divergent for $r \to 0$. This singularity of potential results in the divergence of the $\rho(r)$ for $r \to 0$. In the non-relativistic approach, the IS parameter is calculated basing on the $\rho(r)$ difference in point r_1, which is the first (different from zero) radial point occurring within the sphere representing atom in *ab initio* calculations. In the relativistic calculations the $\rho(r)$ of the core *s*-electrons attains in this first point the values of 10^5 order and every (event slight) displacement of this calculation point leads to the non-physical variations of the density value. This situation takes place in the TB-LMTO method [1], where the position of the first radial point depends on the Wigner-Seitz (W-S) sphere volume. To avoid this non-physical results, when calculating within the TB-LMTO method, the IS values have been calculated utilizing the electronic charge density from the nucleus surface (r_J). The above mentioned difficulty does not occur in the FP-LAPW method [2] where the first radial point in the muffin-tin (M-T) sphere occupies a fixed position. Figure 2 represents the pressure dependence of the total IS calculated with aid of the two presented methods. One can see that the differences in the course of curves are incon-

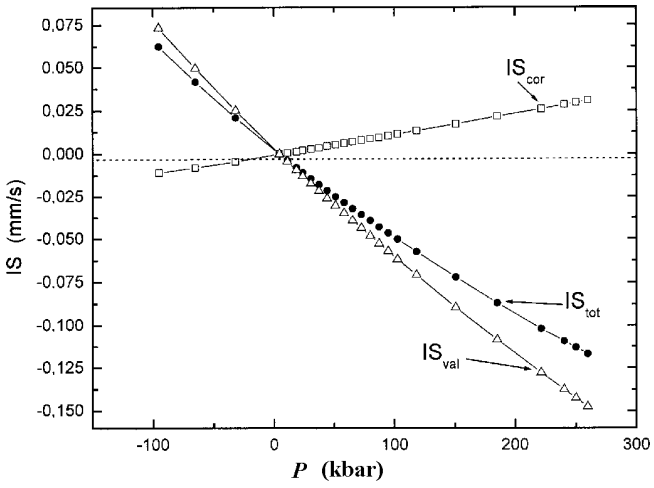

Fig. 3. Core contributions and isomer shift conduction related to pressure. Results were obtained using the TB-LMTO method.

Table 2. The parameters a (mm/s kbar), β (mm/s kbar) and γ (mm/s kbar^2), calculated from matching to the relationship IS(P) of function IS = aP for P = 0–70 kbar and IS = $\beta P + \gamma P^2$ for the full pressure range.

	TB-LMTO	FP-LAPW	Experiment
a	$-(5.07 \pm 0.07)\times10^{-4}$	$-(5.41 \pm 0.03)\times10^{-4}$	$-(7.94 \pm 0.24)\times10^{-4}$*
β	$-(5.33 \pm 0.21)\times10^{-4}$	$-(5.83 \pm 0.17)\times10^{-4}$	$-(9.48 \pm 1.14)\times10^{-4}$*
γ	$-(0.40 \pm 0.05)\times10^{-6}$	$-(0.70 \pm 0.02)\times10^{-4}$	$-(1.41 \pm 0.82)\times10^{-6}$*

*Ref. [10].

siderable ones and do not exceed 7% what confirms the correctness of the IS calculation method based on the TB-LMTO results. The total value of the IS is influenced both by the variations of the core electron densities (1*s*, 2*s* and 3*s*) and by change of the 4*s*-electronic density. The total value of the isomeric shift can be expressed as $IS^{tot} = IS^{cor} + IS^{val}$.

Figure 3 presents the calculated contributions to the IS^{tot} in function of P. As results from Fig. 3, the predominant contribution is IS^{val}. Its systematic drop with growth of pressure can be caused by the compression of wave function of the conduction electrons, what is confirmed by the growth of 4*s* electron number within the W-S (M-T) sphere. The IS^{cor} contribution is positive and by one order of magnitude weaker. It grows linearly with incresing pressure, lowering slightly the value of the total isomeric shift. The growth of IS^{cor} can be related to the screening of the nucleus due to the increasing 4*s*-electronic density. For the sake of analytical results, in different pressure ranges, different forms of functions describing the shape of dependence of the IS(P) have been adopted [10]. For the pressure range from 0 to 70 kbar a linear relation IS = $a \cdot P$ has been employed, whereas in the full pressure range the quadratic term is added and the relation takes the form IS = $\beta P + \gamma P^2$. The results of the fitting procedures have been recorded in Table 2. It results from the presented graphs and results given in Table 2, showing that the values of the calculated IS and its variation with pressure are similar for both calculation methods and are in good qualitative agreement with experimental data (conformity in regard to the sign and order of magnitude).

Effect of pressure on the value of the hyperfine field

The hyperfine field B_f affecting the nucleus ^{57}Fe constitutes the superposition of three different contributions [5]: orbital momentum term, magnetic dipolar term and Fermi contact term (B_c). The predominant contribution to the total hyperfine field is from the contact Fermi interaction. The results for the Fermi contact hyperfine field presented in this paper were calculated by means of the relativistic formula derived by Blügel *et al.* [3]. The total B_c value depends on the difference in the spin density in nucleus region both of core states 1*s*, 2*s* and 3*s* (B_c^{cor}) and the conduction states 4*s* (B_c^{val}). The total value of the Fermi term can be expressed in form: $B_c^{tot} = B_c^{cor} + B_c^{val}$.

The effect of pressure on the value of Fermi contact term of the hyperfine field in bcc iron (Fe) shows Fig. 4. Table 3 gives the values of the hyperfine fields (B^{tot} and B^{cor}, B^{val}) for the equilibrium values of latice parameter. The equilibrium values of B_c agree very well with the experimental data. Drop of the core states spin density with growing pressure (Fig. 4) results from the strong exchange interaction of the polarized 3*d*-orbitals with electrons in the 2*s* and 3*s* core states. With increasing pressure the μ_{3d} magnetic moment decreases resulting in the decrease of the electronic spin density of the core states in the region of the atom nucleus. The observed decrease of the spin density of the band 4*s* electrons of Fe nucleus is also caused by the decrease of μ_{3d} with increasing pressure. The mechanism of this conjugation is of dual nature. The spin polarization of 4*s* electrons on the Mössbauer nucleus depends directly on the magnetic momentum of this atom, but also on the spin polarization of the neighbouring atoms. In the case of the bcc-Fe, there is a linear dependence between the hyperfine field and the magnetic moment within the full pressure range (Fig. 5). The deviations from the linearity observed in iron-based alloys is caused by the effect of the magnetic moments of neighbouring atoms on the spin polarization of the 4*s* electrons in region of the Mössbauer ion.

Table 3. The calculated hyperfine field B_c^{tot} with separated core (B_c^{cor}) and valence (B_c^{val}) contributions.

	B_c^{cor} (T)	B_c^{val} (T)	B_c^{tot} (T)
TB-LMTO	–28.87	–4.16	–33.03
FP-LAPW	–28.15	–3.17	–31.32
Experiment	–	–	–33.9*

*Ref. [7].

Conclusions

Calculations of the effect of pressure on the Fermi contact hyperfine field (B_c) and isomer shift (IS) for ^{57}Fe have been performed using the TB-LMTO and FP-LAPW methods. The results are in good qualitative agreement with those derived from experiments. Both methods of IS calculation

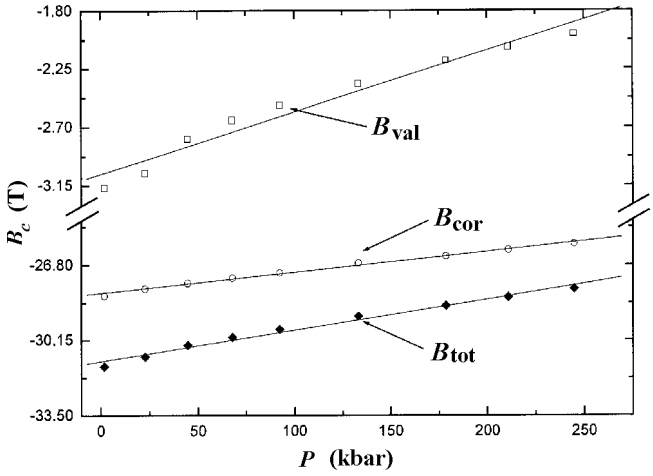

Fig. 4. Effect of pressure on the particular B_c contributions originating from core and conduction electrons. Results obtained according to the FP-LAPW method.

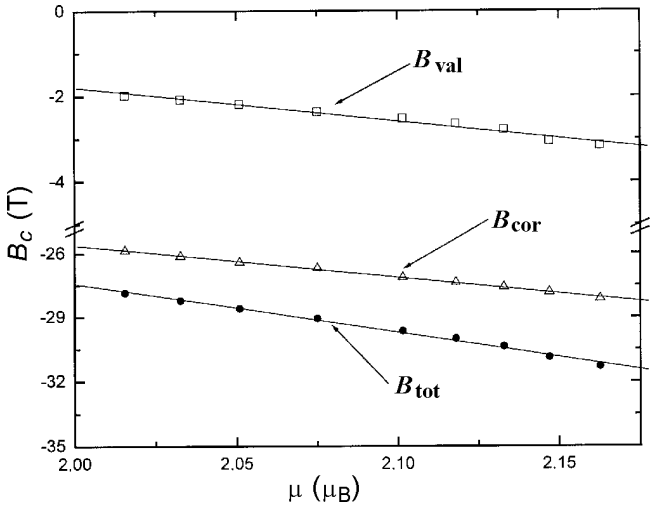

Fig. 5. Calculated by the FP-LAPW method relationship between the contact term of hyperfine field and magnetic moment.

(IS = $\alpha\Delta\rho(r_1)$ and IS = $\alpha\Delta\rho(r_J)$) give consistent results. The IS^{cor} contribution is positive and increases linearly with pressure. The dominant contribution, coming to IS from band electrons, is negative and its absolute value increases with increasing pressure. The Fermi contact hyperfine field in pure iron is dominated by the core electrons contribution. The 4*s*-band part is by one order of magnitude smaller. The values of both terms decrease linearly with incresing pressure.

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