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Abstract. The equilibrium lattice constant and the bulk modulus of fcc Fe are calculated by the FP-LMTO method. The use of the generalized gradient approximation in calculating the electron structure and lattice properties of γ-Fe is discussed. A local minimum is observed on the curve of total energy versus the amplitude of the atomic displacements corresponding to transverse vibrations at the W point of the Brillouin zone. The temperature dependence of the anharmonic mode effective frequency calculated within the framework of the pseudoharmonic approximation is found to qualitatively agree with the experimental one. The possibility of interpreting the structural phase transition as a transition of the 'active' phonon mode from the excited to the basic state is discussed.

1. Introduction

Interest in the theoretical investigation of martensitic phase transitions is being constantly stimulated by the abundant experimental evidence being accumulated while studying this problem, which is of prime importance in both basic and applied physics. In the microscopic description of martensitic phase transitions from first principles, the model based on the study of the peculiarities of the lattice dynamics [1] has been intensively used in the last few years. The current status of the band theory and the development of consistent *ab initio* methods for calculating the electronic structure of crystals have opened up new avenues for theoretical investigation of the lattice dynamics in the case of d-metal systems [2]. The band theory based on the density functional concept and the Kohn–Sham method allows the ground-state properties, including the total energy and the electron density distribution, to be calculated self-consistently.

After having calculated the total energy, one can find the phonon frequencies for chosen vibrational modes by the frozen-phonon technique [3] via calculation of the difference in total energy between the perfect and distorted lattices. The atomic displacements in the distorted supercell correspond to the chosen normal mode. Next, knowing the normal-mode amplitude, one finds the phonon frequency with the wave vector commensurate with a vector of the reciprocal lattice.

The recently developed variational linear-response method [4], unlike the frozen-phonon technique, does not require the construction of a supercell, and can be used for the calculation of phonon frequencies with any wave vector in an arbitrarily complex cell. In such an approach, the dynamic matrix may be expressed in terms of the dielectric matrix describing the response of the electron density to perturbation. The variational linear-response method

consists in finding the first-order corrections to the wave functions of the filled electron states under weak perturbation of the crystalline potential. Such a correction is the solution of an inhomogeneous second-order differential Schrödinger-like equation. Until recently, the linear-response method was, as a rule, based on the pseudopotential scheme. The authors of [5] proposed the muffin-tin orbitals as a rapidly convergent basis set, which immediately ensured a thorough calculation of the transition metal phonon spectra in good agreement with experiment. The current state of the art of investigations in this field, and a comparative analysis of the linear-response technique have been presented in a recent review [6]. Though the linear-response method surpasses the frozen-phonon technique in efficiency, the accuracy of the calculation of the phonon frequencies, forces, and displacement-induced electron density is actually the same. Note that both methods are based on the computational scheme of the full-potential linear-muffin-tin-orbital (FP-LMTO) method [6, 7] which allows for the effects of nonsphericity of the electron density and crystalline potential.

The goal of this work is to take account of the anharmonicity effects when investigating the stability of systems undergoing a structural phase transition in a model based on *ab initio* calculations of the lattice dynamics. Of course, in the *ab initio* molecular dynamics method of Car and Parrinello [8], the anharmonic effects are taken into account automatically: the forces acting on atomic nuclei in the system are calculated from first principles in terms of the electron density in a large lattice cell, while the system anharmonicity is explicitly taken into account in solving the equations of motion. Because of the time-consuming computations involved, the Car–Parrinello method is currently confined to consideration of systems of no more than several tens of atoms. In such molecular dynamics simulation, the electron states have been until now calculated by the pseudopotential method, whose validity in the case of transition metals is still under study [1, 9]. It should be noted that systems of transition metals are of particular interest in investigating the structural phase transitions. Hence, the use of the *ab initio* molecular dynamics method is hardly justified in considering the phase transitions when the anharmonic 'active' mode responsible for the structural phase transition is known. In our opinion, the conventional approaches are sufficient for describing the dynamics of the anharmonic mode.

In this paper, we use the self-consistent phonon (pseudoharmonic) approximation to examine the temperature dependence of the dynamical behaviour of the transverse W phonon in γ-Fe. The choice of the subject of investigation is due to the results of our paper [10], in which a quasi-harmonic approximation was used to analyse the changes in dynamical and elastic properties of α- and γ-Fe with lattice constant variation. A soft mode with transverse polarization localized at the point W: $k = (2\pi/a)(0.5, 1, 0)$ of the Brillouin zone (BZ) was found to exist in the γ-phase of Fe. The mode is likely to be responsible for the $\gamma-\alpha$ transition in iron. The atomic displacements in this mode are analogous to the observed ones [11]. An attempt to compute the phonon frequencies of fcc Fe by the FP-LMTO frozen-phonon method was made in a recent paper [12]. Several high-symmetry points of the BZ were examined; however, the point that we are interested in was not considered. The suggested theoretical investigation may be of great interest, since experimental data for the high-temperature Fe phase under consideration are still not available.

In the next section of the present paper, the total energy of fcc γ-Fe, one of the structural modifications of iron, is calculated from first principles by the FP-LMTO method [7]. Then the frozen-phonon technique is used to calculate the dependence of the total energy on the amplitude of the atomic displacements corresponding to W phonon. As this dependence is far from quadratic, we use the pseudoharmonic formalism to find the temperature-dependent frequency of the W phonon, and discuss the results obtained.

2. Calculation of the band structure of γ-Fe

The magnetic structure and electron properties of γ-Fe are still not clearly understood because of the difficulties associated with the experimental study of fcc iron. The *ab initio* LMTO method generalized to the case of helical magnetic structure was used in reference [13] to show that under strong moment–volume instability, the minimum of the total energy in fcc Fe corresponds to a noncollinear magnetic structure. An analogous result for a wide range of lattice constant values was obtained in [14] by the augmented-spherical-wave method using the same approximations: the local spin-density approximation and the atomic sphere approximation. According to [14], in γ-Fe, the absolute minima of the total energy for the helical magnetic and nonmagnetic configurations coincide. This supports our model used in the investigation of the dynamic properties of fcc iron in which we consider the iron as nonmagnetic, because, distorting the lattice, we will seek the variation of the system total energy with respect to the absolute minimum. It should be noted that the calculations mentioned above are nonrelativistic and, as we discussed earlier in [15], taking into consideration the spin–orbit interaction via solving the Dirac equation for 3d magnets results in a change in the electron kinetic energy which is comparable, in order of magnitude, to the correction for noncollinearity of the magnetic structure.

The local spin-density approximation (LDA) for the exchange–correlation energy is known to give a value of the equilibrium lattice constant somewhat lower than the experimental one. Repeated attempts to exceed the limits of the local approximation have been made, and one of the latest realizations, known as the generalized gradient approximation (GGA) [16], is used in this work for the band calculation of fcc Fe. The use of the GGA in combination with the *ab initio* full-potential band LAPW technique allowed the authors of [17] to carry out, for the first time, a reliable calculation of the absolute minimum of the total energy corresponding to a ferromagnetic state with bcc structure. In practically all of the previous calculations within the local density approximation, the total energy minimum obtained for fcc Fe was 4–7 mRyd lower than that for the bcc structure [18].

The present fcc Fe calculation was performed by the FP-LMTO method in the scalar relativistic approximation, with inclusion of one energy panel for valence electrons. The charge density of the core electrons was recalculated at each iteration of the self-consistency procedure. Integration over the BZ was performed using 72 special k-points in its irreducible part. Good convergence was ensured by using a double set of basis orbitals with fixed and properly spaced κ (κ^2 is the mean kinetic energy of an electron in the interstitial region). The maximum values of the angular momentum l in the expansion of the basis functions in spherical harmonics inside and outside the MT spheres, as well as in the crystalline potential and charge-density expansions, were chosen in such a way that further increase of l does not affect the total energy calculated.

Table 1 illustrates the FP-LMTO total energy calculation for fcc Fe with and without the use of the GGA (in the latter LDA case, the exchange–correlation potentials of Hedin and Lundqvist [19] and of Ceperley and Alder [20] were used). In considering the effect of including the GGA, we should note that, first, the position of the minimum of the specific energy curve shifts towards the experimental value of the equilibrium volume V_0 corresponding to the lattice constant $a_0 = 6.78$ au, and, second, with the GGA included, the total energy minimum is considerably lowered. Besides the equilibrium lattice constant and the total energy, table 1 presents the cohesive energy and the bulk modulus B_0 from our calculation, in comparison with the data of [18]. Unfortunately, in reference [12], based on the same model as we use, the theoretical values of the equilibrium lattice constant and B_0 for γ-Fe are not presented.

Table 1. Structural properties of fcc Fe calculated within the GGA and the LDA with the Hedin–Lundqvist and Ceperley–Alder exchange–correlation potentials (a_{eq} is the equilibrium lattice constant, E_{total} is the corresponding total energy, B_0 is the bulk modulus, and E_{coh} is the cohesive energy).

	a_{eq} (au)	B_0 (Mbar)	E_{total} (Ryd)	E_{coh} (Ryd)
Experiment	6.78			
Reference [18]: FP-LAPW (C–A)	6.38	3.44	−2541.200	
FP-LMTO (H–L)	6.485	3.11	−2540.5314	0.703
FP-LMTO (C–A)	6.482	3.30	−2541.1032	0.733
FP-LMTO (GGA)	6.623	2.54	−2545.6444	0.612

The shape of the $E_{total}(V/V_0)$ curve obtained with the use of the GGA is such that the bulk modulus and cohesive energy values are markedly lower than those calculated within the LDA. As the experimental data on γ-Fe are extremely meagre, we cannot as yet conclude that the GGA is the approach of choice in calculating the electronic structure. Note that one continues searching for an optimum GGA form for calculating the ground-state properties, especially for materials with magnetic ordering [21].

3. Calculation of the temperature-dependent W phonon frequency

Upon calculation of the equilibrium lattice constant a_{eq} of fcc iron, we can construct for it an eight-atom supercell. The coordinates of the atoms in units of a_{eq} are listed in table 2. The vibrational mode corresponding to the W phonon can be defined, at the point $k = (2\pi/a)(0.5, 1, 0)$ of the BZ, through a distorted cell with four displaced atoms. The displacements given in table 2 correspond to transverse vibrations in a plane that is perpendicular to the z-axis.

Table 2. Positions of Fe atoms in the tetragonal supercell in units of the cubic lattice constant.

Atom	x	y	z
1	0.0	0.0	0.0
2	1.0	0.0	0.0
3	0.0	0.5	0.5
4	1.0	0.5	0.5
5	$1.5 - u_x$	$0.5 + u_y$	0.0
6	$1.5 + u_x$	$1.0 - u_y$	0.5
7	$0.5 + u_x$	$0.5 - u_y$	0.0
8	$0.5 - u_x$	$0.0 + u_y$	0.5

In figure 1 the difference in total energy between the perfect and distorted supercells of fcc Fe is plotted as a function of the amplitude of the atomic displacements u_q corresponding to transverse vibrations at the W point of the Brillouin zone.

In calculating the total energy of an eight-atom cell, we used the Ceperley–Alder exchange–correlation potential, and the equilibrium lattice constant obtained, $a_{eq} = 6.482$. The details of the FP-LMTO calculation remained unchanged. As, however, the distortion of the fcc lattice resulted in a lowered symmetry of the problem, integration over the irreducible part of the BZ was performed using 80 special k-points.

We have expressly examined the important question of the choice of MT-sphere radii
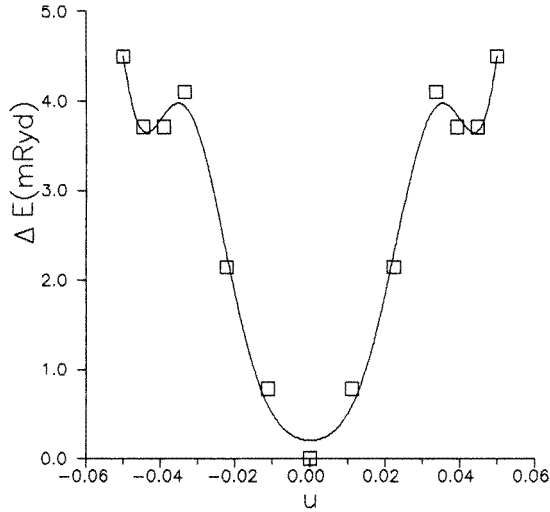
Figure 1. The total energy of the system versus the atomic displacement amplitude u_q (in units of the lattice constant) for transverse vibrations of the normal W mode. The open squares correspond to calculated values, and the solid line shows the polynomial approximation.

r_{MT}. The magnitudes of the nonoverlapping MT radii should be such as to enable atomic displacements in the cell. The relative volume of the MT spheres should be kept large with respect to the cell volume, so as to avoid the use of empty spheres. In this calculation, for all Fe atoms, $r_{MT} = 2.2$ au. The volume of the MT spheres accounted for 0.61 of the cell volume. Reducing the MT radii leads to a noticeable loss of accuracy in calculations of the total energy and forces.

To calculate the normal-mode frequency by the frozen-phonon technique, one should define the total energy of the system as a function of the amplitude of the atomic displacements corresponding to the given mode. This function $\Delta E(u_q)$ is the lattice potential for the mode. When the potential is close to the quadratic one, $\Delta E(u_q) = K_2 u_q^2/2$, at $T = 0$ one can use the harmonic approximation, taking

$$\omega_q = (K_2/M)^{1/2} \qquad (1)$$

where M is the reduced mass.

The lattice potential that we obtained for the W phonon is far from quadratic (see figure 1). It should be especially noted that at $u_q \simeq 0.04$ there exists a maximum of $\Delta E(u_q)$, the height of which, $E_b \sim 500$ K, is below the temperature range of γ-Fe stability ($T \sim 900$–1000 K). At these temperatures, the vibrations cannot be localized at either local or global potential wells, and, therefore, the frequency is not determined by the curvature of $\Delta E(u_q)$ near the potential well bottom, i.e. the standard procedure of the frozen-phonon technique cannot be used.

In an anharmonic potential, the frequency of the oscillator depends on its energy, and hence it is determined by the system temperature. Since, when describing the dynamics of systems undergoing a phase transition, it is important to determine the temperature dependence of the dynamics of the 'active' mode responsible for this transition, one should use the relevant approaches.

In this paper, to describe the dynamics of the W phonon, which we believe to be responsible for the γ–α transition in Fe [10], the pseudoharmonic approximation was used.

According to this approximation, the motion of a particle in an anharmonic potential $U(r)$ can be described as a harmonic motion, but subjected to a different (effective) potential $\tilde{U}(r)$ [22]

$$\tilde{U}(r) = \exp(\langle u^2 \rangle / (2\partial^2 / \partial r^2)) U(r) \qquad (2)$$

whose temperature dependence is expressed in terms of the correlator of the root mean square shift $\langle u^2 \rangle$ from the equilibrium position, r_0. In turn, r_0 is also a function of temperature, and can be found from the condition $\partial \tilde{U} / \partial r = 0$. Having chosen a suitable approximation for finding $\langle u^2 \rangle$, we get the self-consistent equations from which we can obtain the temperature dependence of the effective frequency, $\omega(T)$.

To calculate $\omega(T)$, we approximated the computed values of $\Delta E(u_q)$ by the eighth-order polynomial

$$U(r) = ar^2 + br^4 - cr^6 + dr^8. \qquad (3)$$

For the chosen values of the parameters ($a, b, c, d > 0$), this potential describes quite well the behaviour of ΔE for $u_q < 0.05$, the region for which numerical calculations were performed, and the increase of the potential at large values of u_q ensures the finiteness of the motion in the stable phase.
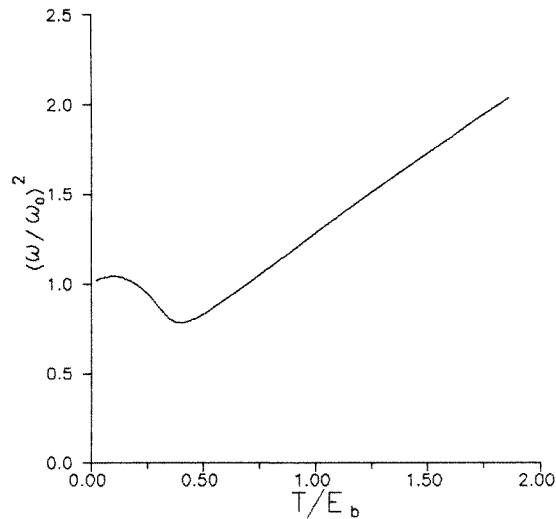

Figure 2. The effective frequency of the transverse vibrations of the normal W mode as a function of temperature expressed in terms of the energy barrier height E_b.

The dependence $\omega^2(T)/\omega_0^2$ calculated in the classical limit of high temperatures ($\langle u^2 \rangle = T/M\omega^2(T)$; $\omega_0 = 42.21$ THz is the frequency at $T = 0$) is shown in figure 2. Unfortunately, no experimental data for iron are available; however, the temperature dependence of the frequency of the phonon mode responsible for structural phase transitions that is obtained is consistent with the experimentally observed ones (see, e.g., [23]). At high temperatures, the linear dependence $\omega^2(T)$ is a universal characteristic for systems which undergo a structural phase transition [24, 25]. The point at which the minimum of the experimental dependence $\omega^2(T)$ occurs corresponds to the structural phase transition temperature. According to our model, at this point the oscillator passes from the excited state (over-barrier vibrations) to

the basic one (vibrations localized near the global minimum) [22]. Therefore the high-temperature phase is characterized by high-energy vibrations insensitive to the fine structure of the potential bottom, rather than by the localization of vibrations near the local minima.

The pseudoharmonic approximation can provide only a crude picture of the temperature behaviour of the anharmonic mode dynamics. A more rigorous approach [26] and numerical simulation [27] show that in a multi-well potential there is a probability of both basic (localized near the global and local minima) and excited vibrations at all temperatures. The density of the vibrational states of such an oscillator is represented by some peaks corresponding to these vibrations. The positions and intensities of the peaks are temperature dependent. In the conventional pseudoharmonic approximation used here, the small probability of vibrational states near the local minima is neglected, and the T-dependence of the probability of basic and excited states is assumed to have a stepwise behaviour. It is probably the use of these approximations that leads to a rather small value of $T_c \simeq 0.5E_b$ being obtained (figure 2), but this point requires more rigorous consideration. It should be noted that if the peaks of the vibrational spectrum are poorly resolved, the inelastic neutron scattering data may be interpreted within the framework of a phonon picture, but the 'phonon' peak width is of the order of the phonon energy. In this case, what should be taken as the anharmonic oscillator frequency is rather obscure. In spite of the above-mentioned shortcomings of the pseudoharmonic approximation, at this stage of the investigation the results obtained may be considered quite satisfactory.

Unfortunately, because of the lack of information on the phonon system in high-temperature γ-Fe, we cannot compare our results with experimental data. Recently, experimental data for β-Zr [28] have given impetus to new theoretical investigations [29]. We hope that the proposed method holds much promise, and that it will stimulate further theoretical and experimental work.

Acknowledgments

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