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CALCULATION ON A CLUSTER MODEL FOR THE ELECTRONIC CHARGE DENSITY AT NUCLEAR SITE AND THE ELECTRONIC STRUCTURE PARAMETERS OF α IRON

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In order to investigate the Mössbauer isomer shifts and its related electronic charge densities for some substances, the electronic charge density at nuclear site of α iron have been computed for an octahedral cluster Fe_6 with SCF MS-X_α method. Some other electronic structure parameters of the cluster have also been obtained, such as the orbital energy distribution, the electron density of states, the Fermi level and various kinds of electron energies, etc. The cohesive energy of α iron have also been calculated and discussed.

PACC: 3120G; 7680; 7110

I. INTRODUCTION

^{57}Fe is the most useful Mössbauer isotope, and α iron is usually applied to calibrate the Doppler velocity for measuring the Mössbauer spectrum and conventionally as a standard for comparing the isomer shifts of various substances. According to the theory of Mössbauer spectrum[1,2], the formula of isomer shift relative to that of α iron can be simplified as[3]

$$IS_{(Fe)} = \alpha \cdot \Delta\rho(0) ,$$

where α is a constant reflecting the radius changing of ^{57}Fe nucleus during the transition from the exited state to the ground state, $\Delta\rho(0) = \rho^i(0) - \rho^{Fe}(0)$, where $\rho^{Fe}(0)$ is the electronic charge density at the nuclear site in pure α iron, $\rho^i(0)$ is that in the substance under study.

In order to investigate the problems of electronic charge density and electronic structure for various substances through their Mössbauer spectra, as a standard for comparison, the value of $\rho^{Fe}(0)$ should be known in advance. We selected an atomic cluster appropriate to our particular subject[4,5] and performed the calculation for the value of $\rho^{Fe}(0)$, using the self-consistent-field multiple-scattered-wave X_α (SCF MS-X_α) method. Besides the value of $\rho^{Fe}(0)$, some other electronic structure parameters of the cluster have also been obtained in the same computation, such as the orbital energy distribution, the density of electron states, the Fermi level, several kinds of electron energies and the total energy for cluster formation, etc. To some extent, all these calculated parameters can be applied to describe the characteristics of the electronic structure for α iron, and can be considered as a reference for further study of such problems that are related to the octahedral cluster.

II. CALCULATION METHOD AND CLUSTER MODEL

SCF MS-X_α method is effective for the calculation on the molecules or clusters which contain heavy atoms. When considering a many-body system consisting of m nuclei and their relevant n electrons, Hartree-Fork equations can be derived just taking a few basic approximations such as Born-Oppenheimer and one-electron approximation. As the exchange term in Hartree-Fork equations is still complicated, in X_α method it has been replaced by an expression, i.e., the product of an adjustable parameter α multiplying a functional of the local electron density calculated by Slater using a free electron gas model. Thus, the appropriate X_α equation are obtained as

$$\left[-\frac{1}{2}\nabla_1^2 - \sum_\mu \frac{Z_\mu}{r_{\mu 1}} + \int \rho(\boldsymbol{r}_2)\frac{1}{r_{12}}\mathrm{d}\tau_2 - 3\alpha\left(\frac{3\rho(\boldsymbol{r}_1)}{8\pi}\right)^{\frac{1}{3}}\right]\psi_i(\boldsymbol{r}_1) = \varepsilon_i\psi_i(\boldsymbol{r}_1)\,. \tag{1}$$

(for details see Ref. [6-8].)

In the case of a molecule or cluster composed of a number of atoms, the Muffin-tin model was adopted and the multiple-scattered-wave-X_α method was developed by Johnson.[7] The potential inside each atomic sphere or outside out-sphere is taken to be spherically symmetrical and their wave function solutions can be determined similarly to the situation of atoms. The potential in the space between the atomic spheres is assumed to be constant, so that the analytical wave function solutions may be written as

$$\psi_i(\boldsymbol{r}) = \sum_\alpha \sum_L a^\alpha_{i,L} J^\alpha_{i,l}(\gamma_\alpha) Y_L(\theta_\alpha, \phi_\alpha)\,, \tag{2}$$

where the radial part $J^\alpha_{i,l}(\gamma_\alpha)$ can be expressed in terms of Bessel, Newman or Hankel function. Y_L is a spherical harmonic. The overlapping coefficient $a^\alpha_{i,L}$ and the orbital eigenvalues ε_i can be obtained by solving the secular equations which satisfy the wave multiple-scattering conditions. These secular equations read

$$\sum_\beta \sum_{L'} \left\{[t^\beta_l(\varepsilon_i)]^{-1}\delta_{\alpha\beta}\delta_{LL'} - G^{\alpha\beta}_{LL'}\right\} a^\beta_{i,L'} - \sum_{L'} S^{\alpha 0}_{LL'} a^0_{i,L'} = 0\,, \tag{3}$$

$$\sum_\beta \sum_{L'} S^{0\beta}_{LL'} a^\beta_{i,L'} - \sum_{L'} [t^0_l(\varepsilon_i)]^{-1}\delta_{LL'} a^0_{i,L'} = 0\,. \tag{4}$$

The calculation for solving these equations can be done on a proper computer. All the one-electron wave functions in every region and other electronic structure parameters can finally be worked out. Thus, various one-electron properties of the cluster can then be calculated.

To meet our specific requirement for analyzing the Mössbauer spectra of some substances[4,5], we selected an octahedral cluster composed of six Fe atoms from the crystal lattice of α iron (Fig. 1). This cluster is enveloped by eight {110} planes that possess the main

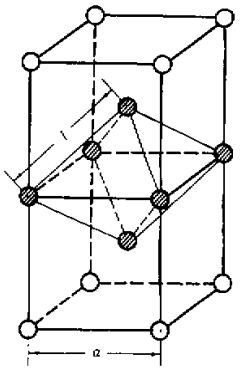

Fig. 1. The octahedral cluster in α iron $a = 5.4186a_0$ $l = 4.6911a_0$.

characteristics of the bcc structure. Moreover, as there are eight shortest, five next shorter and two third-shorter atomic spacing distances in the cluster, such a cluster should be capable of reflecting approximately the essence of the atomic bonding and the characteristics of the structure for α iron.

In the process of computation with SCF MS-X_α method, the radii of the atomic spheres were selected according to the standard overlapping approximation using Norman's regulation. The α value inside each atomic sphere or outside outer-sphere was taken to be 0.71151, being equal to the value for an isolated Fe atom, suggested by Schwartz. To solve the secular equations, the summation index $L_{\max}$ was taken to be 2 for Fe atom or 5 for outer-sphere. The convergence condition in self-consistent iteration is that the maximum changing of the electric potential between the two successive iterations must be less than 10^{-4}. This is an adequate approximation. In the computation process, the 1s through 3p electrons are treated as inner core ones, the 3d and 4s electrons take part in bonding and form the spin-orbitals of the cluster. Results of such a spin-restricted calculation are presented below.

III. RESULTS AND DISCUSSION

After the convergence of the SCF computation, the numerical solutions for all the one-electron wave functions and their self-consistent potential are obtained. The electronic charge density at Fe nuclear site $\rho^{\mathrm{Fe}}(0)$ and some other electronic structure parameters can be calculated herefrom. The cohesive energy of α iron is also calculated as a trial.

A. The calculated result for $\rho^{\mathrm{Fe}}(0)$

Table 1. Electronic charge density at nuclear site (a. u.).

obital	site of equi-symmetry		average
electron	top	side	
1s inner	5376.0857×2	5376.0680×2	
2s inner	489.5066×2	489.4964×2	
3s inner	70.4439×2	70.4375×2	
total valence	2.2748×2	2.5123×2	
Sum	11876.623	11877.029	11876.758

The electron densities at the atomic nuclei of two kinds of site, with different equivalent symmetry in the Fe_8 cluster, are given in Table 1. The fractional contributions from different orbitals are also shown. The values of $\rho^{\mathrm{Fe}}(0)$ at the two equi-symmetry sites show a small difference from each other. An appropriate average value can be taken as the electron density at Fe nuclear site approximately. This value is slightly less than that for a free Fe atom

given in Ref. [1]. This means that the relevant electron distribution becomes more widely spread when bonding functions among the Fe atoms. This result is also in good agreement with some other results, calculated by means of similar methods in Ref. [3]. Finally, taking this value as the standard of comparison, we have gotten a reasonable explanation on the relation between the Mössbauer parameter $IS_{(Fe)}$ and the calculated $\rho^i(0)$ for a kind of slag Fe_xO in steelmaking[4,5].

B. Obital energy level distribution and curve of density of state

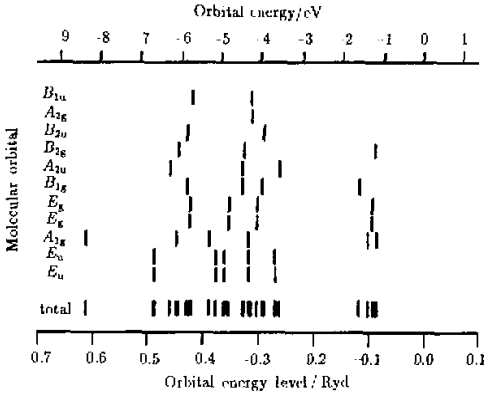

Fig. 2. Orbital energy eigenvalues for cluster Fe_8. 0.315 Ryd = 4.28 eV.

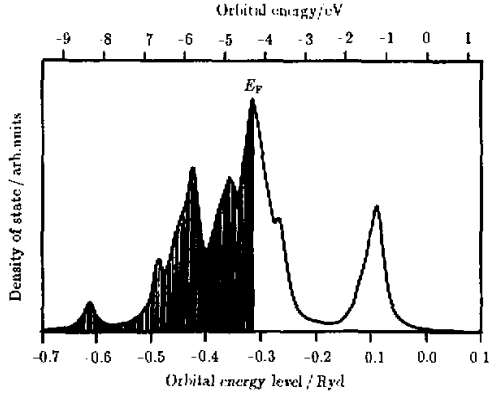

Fig. 3. Density of states and Fermi level for cluster Fe_8.

In Fig. 2 the molecular orbital energy level distribution is given. Assuming each energy level itself has a distribution of Lorentz type and selecting a proper half-height width, the corresponding electronic density of states (DOS) can be worked out. Referring to Ref. [9] and performing actual calculations, we take the half-height width $\gamma = 0.0125$ Ryd and get a DOS curve as shown in Fig. 3. The calculated Fermi level $E_F = -0.315$ Ryd (-4.28 eV). One

can find from Fig. 3 that the Fermi level happens to be situated nearly at the highest point of the DOS curve. This instance brings out the electronic factor for interpreting the fact that the bcc structure of α iron is a quite stable one. This result can also be used to discuss the problems of the function of electrons in ferrous alloy, such as the influence of the alloying element on the stability of α phase of iron. The features of DOS curve are consistent with or similar to that given in Refs. [9, 10], calculated from the tetrahedral cluster Fe_4 and the extented bcc cluster Fe_{15} etc.

C. Electronic energies and the cohesive energy

The calculated values of various kinds of electron energies for cluster Fe_8 are given in Table 2. The relation of the total energy and average kinetic energy satisfies the virial theorem pretty well, the virial ratio $R_V = 1.999992$. Under the present choice of the standard calculation parameters above, the total energy calculated for Fe_8 is -15149.412 Ryd, hence the average value for each atom in the cluster is -2524.902 Ryd. However, the total energy of a free atom E_{HF} has been known as -2524.582 Ryd (-1262.291 a.u.)[11], calculated by Mann using Hartree-Fock method. The difference between the two energy values for each atom in different states, free or in the cluster, should represent approximately the cohesive energy of α iron. The difference is 0.320 Ryd, equivalent to 104.0 kcal/mol, which approaches the experimental value 96.7 kcal/mol[12], obtained by measuring the sublimation heat.

Table 2. Electronic energies of cluster Fe_8 (unit: Ryd).

energy	vale	energy	value
nuc-nuc coulomb	3905.322	nuc-ele coulomb	−43927.313
ele-ele coulomb	10376.729	ele-ele exchage	−653.441
total kinetic	15149.292	total energy	−15149.412

When the total energy of a free Fe atom is computed using SCF X_α method under our computation condition, the calculated free atom energy $E_{at} = -2524.381$ Ryd, obtained through a spin-polarized computation taking $\alpha = 0.71151$. The corresponding cohesive energy value is 163.46 kcal/mol, which is much larger than the experimental one. However, when taking $\alpha = 0.71285$, the value E_{at} becomes -2524.586 Ryd. The resulting cohesive energy is 99.13 kcal/mol, in good agreement with the experimental value. This fact shows that the calculation result evidently depends upon the α value while the other calculated parameters are taken as standardized. The coefficient α is an adjustable parameter selected by performing computations according to some standards, for instance, to make the total energy of the system minimum, and to satisfy the virial theorem best or to make the calculated result equal to the accurate one attained by Hartree-Fork method. The α value we used are equal or close to an α value that is determined by one of the standards above. The influencing rules of α and other calculation parameters should be examined further

by performing more calculations so as to search for or improve the efficiency of this basic theoretical method in calculation for cohesive energy.

IV. CONCLUSIONS

The electronic charge density at a nuclear site and some other electronic structure parameters for Fe_6 cluster have been calculated using SCF X_α method.

1) The calculated electron densities at two kinds of nuclear sites with different equivalent symmetry in the cluster are 11877.029 and 11876.623 a. u. respectively. The data have been used as a standard to explain adequately the quantitative relation between Mössbauer isomer shift $IS_{(Fe)}$ and electronic density at the nuclear site for the substance Fe_xO.

2) The molecular orbital energy level distribution and the density of states curve for the cluster Fe_6 have been calculated and, to a certain extent, are capable to reflect the electronic structural characteristics of α iron. The calculated Fermi level is -0.315 Ryd which happens to situate nearly at the highest point of the DOS. curve. This result displays the electronic factor for understanding the stability of the bcc structure of α iron and its alloys.

3) The cohesive energy of α iron has also been calculated using the basic theoretical method. The result is close to the experimental one. Some of the parameters influencing the calculated result are discussed.

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