Electronic structure and Mössbauer isomer shift of the iron atom isolated in a crystalline argon matrix

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Multiple-scattering calculations were performed on an FeAr₁₂ cluster in order to describe the iron atom trapped in a crystalline argon matrix. The total electron densities at the iron nucleus derived from these calculations are used to interpret Mössbauer-isomer-shift data. The different bonding mechanisms contributing to the metal-atom-rare-gas matrix interaction are also investigated. It is found that the overlap distortion effect of the metal wave functions plays a major role in the calculated electron densities. The iron-isomer-shift calibration constant was found to be $-0.22a_0^3$ mm sec⁻¹.

I. INTRODUCTION

Hyperfine interactions between the nuclear and the electronic energy levels as studied by Mössbauer spectroscopy are known to provide valuable information about the electronic structure and chemical bonding in a wide variety of both inorganic and organic compounds. The Mössbauer isomer shift (IS) gives a direct measure of the total electron density at the nuclear site. In a nonrelativistic approximation, the IS energy shift can be written as

$$\Delta E_{\rm IS} = \frac{2}{3} \pi e^2 Z \Delta \langle r^2 \rangle \Delta \rho(0) \quad , \tag{1}$$

$$\Delta \rho(0) = \psi_A^2(0) - \psi_S^2(0) \quad , \tag{2}$$

where $\psi_A^2(0)$ and $\psi_S^2(0)$ are the total electron densities at the absorber and source nuclei, respectively, and $\Delta \langle r^2 \rangle = \langle r^2 \rangle_e - \langle r^2 \rangle_g$ is the change in nuclear mean-square radius between excited and ground state. For a given nucleus, all factors are constant except the electron density difference term $\Delta \rho(0)$. Equation (1) may be rewritten as

$$\alpha = \Delta E_{\rm IS} / \Delta \rho(0) \quad , \tag{3}$$

where α is the IS calibration constant and contains only nuclear factors. However, an accurate determination of this constant from nuclear theory has not proved feasible. Instead, it must be determined from measured IS and calculated charge densities for the nucleus in two different chemical environments. For the iron IS calibration constant the values are at great variance, ranging from -0.1 to $-0.7a_0^3$ mm sec⁻¹.¹

The interpretation of the IS data has usually been given in terms of free-atom or free-ion models.² In order to account for the influence of the neighboring atoms, the free-atom or free-ion wave functions are modified to include covalency and overlap effects.³⁻⁵ More recently, molecular-orbital wave functions ob-

tained from *ab initio*,^{1,6} multiple-scattering⁷ or semiempirical⁸ calculations and charge densities from band-structure calculations of some iron alloys^{26, 27} have also been used.

The use of the rare-gas matrix isolation technique to solve the problem of the iron IS calibration was suggested by Jaccarino and Wertheim.⁹ In such systems, free-atom or free-ion functions should be a reasonable approximation to the true wave functions of the trapped atom. The first successful result of a Mössbauer experiment with ⁵⁷Fe atoms isolated in argon matrix was reported by Barrett and McNab.¹⁰ Shortly after the Mössbauer spectra of ⁵⁷Fe was measured in argon, krypton, and xenon.¹¹ These spectra showed an absorption line with an IS of -0.75 ± 0.03 mm sec⁻¹ with respect to an iron foil at 300 K. In addition, ⁵⁷Fe⁺ ions isolated in xenon matrix with $3d^64s^1$ (Ref. 12) and $3d^7$ (Ref. 13) configuration have also been studied. Iron atoms in N₂ (Ref. 14), CH_4 , and CO_2 (Ref. 15) matrices showed the same IS as in the case of the rare-gas matrices. Thus experiments in nonrare-gas inert matrices support the concept of an almost free isolated atom, i.e., the influence of the matrix itself can be neglected.

However, optical spectra indicate an appreciable amount of interaction between the trapped atom (mainly in the case of transition-metal atoms) and the matrix. The matrix perturbation on the atomic levels can be as great as $3000 \text{ cm}^{-1.16}$ There is also marked level splitting due to a noncubic symmetry at the impurity site (vacancies or another metal atom as one of the nearest neighbors¹¹) or the presence of the metal atom in two different crystallographic site.

The contribution of the overlap distortion effect to the measured IS in rare-gas matrices have been analyzed by several authors.^{17, 18} The overlap between the metal and ligand wave functions was included by orthogonalizing the *s*-metal functions to suitable combinations of ligand *s* and *p* orbitals

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transforming under a_{1g} symmetry, the ligand-ligand overlap being neglected. The modification of the atomic wave functions by the crystalline potential (covalent effect) have also been investigated.¹⁸

However, a deeper understanding of the different bonding mechanisms involved in trapped atom-host lattice interaction should require to include simultaneously all the effects mentioned above. It is well known that band theory in its conventional form cannot be applied to the description of localized states in solids. The application of the molecular-orbital theory is based on the assumption that a representative small cluster of atoms (usually the trapped atom and its nearest neighbors) provides a suitable representation of the electronic environment at the impurity site in the crystal. The discrete variational method in connection with the cluster model has been employed by Walch and Ellis to study the IS of the iron atom in argon matrix.¹⁸ However, the calculation does not converge to self-consistency and the calculated electron density is probably uncertain by 30%.¹⁹ Combining the calculated $\Delta \rho(0)$ with the FeF_2 IS (Ref. 11) (where the iron configuration is very close to $3d^64s^0$) gives $\alpha = -0.38a_0^3 \text{ mm sec}^{-1.1}$

The multiple-scattering method has been widely applied to the study of both perfect and locally perturbed solids.²⁰ In a recent communication²¹ it has been used to describe the electronic structure and related properties of the hydrogen impurity in crystalline argon matrix. It has been shown that the main features of the bulk electronic structure and of the locally perturbed argon matrix are adequately reproduced by the multiple-scattering cluster model.

In the present work we have carried out multiplescattering calculations for the iron atom isolated in crystalline argon matrix. Calculated wave functions are used to get the electron densities at the iron nucleus. These are correlated to the Mössbauer IS and interpreted in terms of the different bonding mechanisms involved in the metal-host lattice interaction. The IS calibration constant has also been evaluated.

II. COMPUTATIONAL METHOD

The spin-polarized multiple-scattering method²² in its muffin-tin form with Slater's $X\alpha$ local exchange have been applied to a cluster consisting of an iron atom and its twelve nearest-neighbor argon atoms. This cluster was designed to represent the iron impurity substitutionally placed on an argon site in the fcc crystal. The Ar-Ar distance was assumed to be that of bulk crystalline argon. It has been further assumed the Fe-Ar distance to be the same as the Ar-Ar distance. The values of the α parameter for the exchange potential inside the Fe and Ar spheres were those calculated by Schwarz.²³ In the intersphere and outer region a weighted average of the atomic values was used.

Calculations have been carried out with three different initial iron configurations; $3d^64s^2$, $3d^74s^1$, and $3d^64s^{1+}$. All the calculations were carried to selfconsistency, all the electrons (core + valence) included in each SCF (self-consistent field) cycle.

The multiple-scattering method has been described in detail in a number of papers.²² By using the muffin-tin approximation for the molecular potential, the wave functions may be calculated numerically without the use of basis sets. In each muffin-tin sphere *i* the orbitals are given by

$$\phi(r) = \sum_{lm} C_{lm}^{l} R_{l}(r) Y_{lm}(\theta, \phi) \quad , \tag{4}$$

where $Y_{lm}(\theta, \phi)$ are the spherical harmonic functions. In the Fe and outer region we are using l = 0 and l = 4 for orbitals of a_{1g} symmetry, l = 2 and l = 4 for e_g and t_{2g} , l = 4 for t_{1g} , l = 3 for a_{2u} and t_{2u} , and l = 1 and l = 3 for t_{1u} . In the ligand spheres we are using up to l = 1. In the interatomic region, the wave function is expanded in terms of spherical Bessel and Hankel functions. Eigenvalues and eigenvectors are obtained by the condition that the orbitals and their derivatives should be continuous across the sphere boundaries. In the case of the charged FeAr_{12}^{+} cluster, a Watson sphere with charge -1 was used. Previous calculations^{7(a)} suggested that the $\rho(0)$ values are almost completely independent of the Watson sphere charge.

III. ORBITALS AND ORBITAL ENERGIES

The calculated energy spectra for the $Fe(3d^64s^2)Ar_{12}$, $Fe(3d^74s^1)Ar_{12}$, and $Fe(3d^64s^1)Ar_{12}^+$ clusters are given in Figs. 1–3. The terms inside the brackets indicate the iron configuration assumed at the beginning of each calculation. The energy levels are labeled according to the irreducible representations of the cubic symmetry group O_h . For comparison purposes, the energy spectrum of the $ArAr_{12}$ cluster²¹ is also included in Fig. 1.

In the case of the neutral cluster we obtain different results which are dependent of the configurations initially assumed. This fact is consistent with the almost free nature of the metal atom trapped in the rare-gas matrix, i.e., there is no charge transfer between the iron and the argon atoms (see below) and also with the experimental evidence which suggests that the iron atom in a rare-gas lattice can exist with different configurations for the same oxidation state [the Fe⁺ may be isolated with $3d^64s^1$ (Ref. 12) and $3d^7$ (Ref. 13) configurations in xenon matrix].

We shall briefly discuss the main features arising from the cluster calculation of the argon crystalline bulk. For the argon crystal, many energy-band calculations have been reported²⁴ and the comparison of



FIG. 1. Energy-level spectra for the Fe $(3d^{6}4s^{2})$ Ar₁₂ and ArAr₁₂ clusters. The energies are referred to the HOMO level in the Ar 3*p* band (t_{1g}) which has been taken as the zero of the scale.

the direct band-gap and valence-band widths to the experimental optical properties have been the usual criteria to test the accuracy of a given calculation. The energy difference between the HOMO (t_{1g}) and LUMO (a_{1g}) is found 0.68 Ry, which is in good agreement with the crystal band gap obtained from band calculations using the $X\alpha$ exchange approximation.²⁴ However, it differs from the experimental value (1.04 Ry) and also from band calculations using the Hartree-Fock exchange. Virtual levels calculated in the $X\alpha$ model do not, in the case of the van der Waals solid, correspond to the physical conduction levels.²⁴ Thus results are more reliable when related to bulk ground-state properties. The bandwidth of the 3s and 3p band are 0.047 and 0.079 Ry, respectively, in reasonable agreement with previous results from band calculations.²⁴

The argon bulk electronic structure is not substantially modified after replacing the central argon atom



FIG. 2. Energy-level spectrum for the $Fe(3d^74s^1)Ar_{12}$ cluster.



FIG. 3. Energy-level spectrum for the $Fe(3d^64s^1)Ar_{12}^+$ cluster.

	Central atom	Argon atom	Interatomic region	Outer sphere
ArAr ₁₂	17.89	17.87	1.69	0.02
$Fe(3d^{6}4s^{2})Ar_{12}$	25.59	17.88	1.80	0.10
$Fe(3d^{6}4s^{1})Ar_{12}^{4}$	25.00	17.87	1.54	0.08
$Fe(3d^{7}4s^{1})Ar_{12}$	25.70	17.87	1.73	0.10

TABLE I. Total charge distributions in muffin-tin regions for ArAr₁₂ and FeAr₁₂ clusters.

by an iron atom. The net effect is the disappearance of the a_{1g} and t_{1u} levels localized on the central argon atom from the 3s and 3p band, respectively, and the appearance of the Fe 3d, 4s, and 4p (unoccupied) valence levels in the crystal fundamental gap. In the case of the Fe $(3d^64s^1)$ Ar⁺₁₂ cluster the e_g and t_{2g} spin up iron 3d levels fall inside the Ar 3p band. The small changes in the argon bulk electronic structure are mainly due to the spin-polarization effects produced by the unpaired 3d electrons of the iron atom. Polarization of the ligand atoms by the metal will in turn increase the crystalline potential. However this effect is very small and completely overcome by the much stronger overlap distortion effect (see Sec. IV). The impurity levels are highly localized on the metal atom and do not mix with the ligand wave functions

TABLE II. Orbital energies and integrated charge density (in fraction of one electron) for the orbitals of a_{1g} , e_g , and t_{2g} symmetry for Fe($3d^64s^2$)Ar₁₂ cluster.

	Orbital	Charges in muffin-tin spheres			
	energy			Outer	
Orbital	(-Ry)	Fe	Ar	sphere	Interatomic
a_{1a} (Ar 3s)	1.800	0.0	0.995	0.0	0.005
$ a_{1\sigma} $ (Ar 3s)	1.800	0.0	0.995	0.0	0.005
$2a_{1g}^{\dagger}$ (Ar 3p)	0.794	0.024	0.942	0.002	0.032
$2a_{1g}$ (Ar 3p)	0.792	0.017	0.950	0.002	0.031
$3a_{1a}$ (Fe 4s)	0.421	0.787	0.089	0.001	0.123
$3a_{1g}\downarrow$ (Fe 4s)	0.337	0.737	0.105	0.002	0.156
$1e_{-1}(Ar 3s)$	1.772	0.0	0.998	0.0	0.002
$1e_{a}$ (Ar 3s)	1.772	0.0	0.998	0.0	0.002
$2e_1(Ar 3n)$	0.783	0.019	0.951	0.001	0.029
$2e_{a}\left(\operatorname{Ar} 3p\right)$	0.783	0.001	0.969	0.001	0.029
$3e_{a}$ (Ar $3p$)	0.758	0.052	0.932	0.003	0.013
$3e_{a}$ (Ar $3p$)	0.757	0.001	0.983	0.004	0.012
$4e_{a}$ (Fe 3d)	0.733	0.924	0.072	0.0	0.004
$4e_g\downarrow$ (Fe 3d)	0.410	0.985	0.003	0.0	0.012
112-1(Ar 3s)	1.775	0.0	0.997	0.0	0.003
1_{2g} (Ar 3s)	1.775	0.0	0.997	0.0	0.003
$2t_{2a}^{2g}$ (Ar $3p$)	0.789	0.023	0.949	0.001	0.027
$2t_{2g}$ (Ar 3p)	0.788	0.001	0.971	0.001	0.027
$3t_{2a}$ (Ar $3p$)	0.765	0.063	0.918	0.002	0.017
$3t_{2p}$ (Ar 3p)	0.763	0.002	0.979	0.003	0.016
$4t_{2a}$ (Fe 3d)	0.732	0.912	0.085	0.0	0.003
$4t_{2g}\downarrow$ (Fe 3d)	0.410	0.985	0.005	0.0	0.010

to any significant extent. In Table I we are giving the charge distributions in the different muffin-tin regions of the $ArAr_{12}$ and $FeAr_{12}$ clusters. Only a very small fraction of the total number of electrons is in the interatomic and outer region. Thus the muffintin approximation seems to be a realistic approximation to the true crystal potential. On the other hand, the charge in the argon sphere remains unchanged when going from the argon to the iron clusters. In the Fe($3d^{6}4s^{1}$)Ar₁₂ case all the iron electrons are inside the muffin-tin sphere. In the other cases, some of the 4s charge is in the intersphere region. Table II gives the energies and charge distribution for orbitals of a_{1g} , e_g , and t_{2g} symmetry for the Fe($3d^64s^2$)Ar₁₂ cluster. The $3a_{1g}$, $4e_g$, and $4t_{2g}$ are almost pure 4sand 3d iron levels without any significant ligand admixture. In the case of $Fe(3d^74s^1)Ar_{12}$ the situation is completely similar. In the Fe $(3d^64s^1)$ Ar⁺₁₂ the $2a_{1g}$ spin-up level has a slight iron 4s component (about 12% of an electron) and as result of this interaction it is lowered in energy (see Fig. 3). From data in Tables I and II we can conclude the marked atomiclike character of the iron and argon atoms, i.e., covalent effects in the trapped atom rare-gas matrix are almost negligible.

IV. ELECTRON DENSITIES AT THE IRON NUCLEUS AND THE ISOMER SHIFT CALIBRATION CONSTANT

In Table III we are giving the total electron density at the iron nucleus and the contributions from the different a_{1g} orbitals for the FeAr₁₂ clusters and the free-iron atom. For the Fe $(3d^6rs^2)$ Ar₁₂ cluster we obtain $\Delta\rho(0) = +1.77$ a.u. relative to the free atom. Our result is in disagreement with the value previously reported by Walch and Ellis (-0.94). However a positive $\Delta\rho(0)$ for the trapped iron relative to the free atom can be explained by two different mechanisms: the contraction of the radial part of the iron 4s orbitals which leads to an increased 4s electron density at the nucleus and the contribution from the Ar 3p orbital transforming under a_{1g} symmetry. The inner Fe orbitals are not substantially modified.

Different bonding mechanisms can be regarded as contributing to the metal-atom rare-gas lattice interaction. According to Adrian²⁵ the effect of a raregas matrix upon a trapped atom may be divided in three different parts; the attractive van der Waals interaction, the repulsive interaction, and the overlap distortion effect. In the following we shall discuss the relative importance of these interactions in determining the calculated electron densities at the iron nucleus.

The first two effects may be identified with the 6 and 12 terms of the "6-12" Lennard-Jones potential, respectively. The net effect is a slight expansion of the wave functions of the interacting species, i.e., the mean atomic radius is increased slightly. Such an expansion of the atomic wave functions (in the case of the iron atom, the 4s functions are the most affected) will tend to reduce the electron density at the iron nucleus. The net effect of the van der Waals interaction is therefore a negative contribution to

TABLE III. Electron charge densities (in atomic units) at the Fe nucleus for FeAr₁₂ clusters and Fe atom. $\Delta \rho(0)$ values are relative to the free atom.

Orbital	$\operatorname{Fe}(3d^{6}4s^{2})\operatorname{Ar}_{12}$	$Fe(3d^{6}4s^{1})Ar_{12}^{+}$	$Fe(3d^74s^1)Ar_{12}$	Fe $3d^64s^2$
Fe†1s	5 376.081	5 375.990	5 376.990	5 375,904
Fells	5 376.143	5 376.032	5 376.115	5 375.962
Fe†2s	488.566	488.578	488.889	488.528
Fel2s	490.319	490.363	490.175	490.358
Fe†3s	71.257	72.198	70.507	71.277
Fe13s	70.426	70.420	69.996	70.439
$1a_{1r}$ (Ar 3s)	0.0	0.0	0.0	· · · ·
$1a_{1e}$ (Ar 3s)	0.0	0.0	0.0	
$2a_{1p}$ (Ar 3p)	0.101	0.746	0.063	
$2a_{1p}$ (Ar 3p)	0.057	0.101	0.027	
$3a_{1s}$ (Fe 4s)	5.615	6.088	4.770	5.084
$3a_{1g}\downarrow$ (Fe 4s)	4.598		• • •	3.839
Total	11 883.163	11 880.516	11 876.657	11 881.391
$\Delta ho(0)$	+1.77	-0.88	-4.73	



FIG. 4. Radial charge distributions for the a_{1g} \uparrow (Fe 4s) orbital in Fe($3d^{6}4s^{2}$)Ar₁₂ and the 4s \uparrow free-atom function.

 $\Delta \rho(0).$

The overlap distortion effect can be described as a shrinking of both the metal and ligand orbitals having the same spin in order to reduce the forbidden overlap between them. The consequence is a repulsive interaction energy between the atoms involved, which tends to push charge on the nucleus of the atomic species involved. It is clear that the net result of this interaction will be to increase the electron density at the nuclear site. For the FeAr₁₂ clusters [with the exception of the Fe($3d^74s^1$)Ar₁₂ cluster] the contraction of the 4s iron orbitals is the main positive contribution to the calculated $\Delta \rho(0)$. Figure 4 shows this effect for the $3a_{1g}$ spin-up orbital.

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(Fe 4s). The other iron orbitals are not significantly modified. In the case of the $Fe(3d^74s^1)Ar_{12}$ the increased 3d population leads to an increased shielding of the nuclear charge which in turn produce a marked expansion of the 3s and 4s iron functions. This shielding effect is much stronger than the overlap distortion and as a consequence the 4s contribution to the total electron density is considerably lower than that of the free atom (see Table III).

The calculated electron density for the $Fe(3d^{6}4s^{2})Ar_{12}$ cluster gives one point of the two required for the IS calibration constant. For the other we shall use FeF_2 .^{1,11} The IS of the FeF_2 is 1.57 ± 0.01 mm sec⁻¹ relative to the iron at 300 K. For the FeF₂ electron density we have used that of the FeF_6^{-4} cluster obtained from a multiplescattering- $X\alpha$ calculation. According to Larsson et al.^{7(a)} a regular octahedral structure with a Fe-F distance equal to 2.06 Å was used, the muffin-tin radius for the Fe and F being 1.76 and 2.14 a.u., respectively. The calculated charge density at the iron nucleus was 11872.36 a.u. We finally obtain the iron IS calibration constant to be $-0.22a_0^3$ mm sec⁻¹. This value is in good agreement with recent ab initio and band-structure calculations.^{1, 6, 26, 27}

It is interesting to observe that these elaborate methods of calculating wave functions confirm the previous value obtained by the use of Pauling's model of the chemical bond.⁴

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