Mössbauer investigation of the relation between the electron structure and the diffusion properties of impurity atoms

B. S. Bokshteĭn and A. A. Zhukhovitskiĭ
Moscow Institute of Steel and Alloys
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The nuclear γ resonance (Mössbauer) method was used to investigate the relationship between the electron density at the nucleus of an impurity atom in a dilute solution and the activation energy of the diffusion of the same atom. It was found that an increase in the density of the s electrons at Fe impurity atoms altered strongly the energy of the intermediate state and increased correspondingly the activation energy of diffusion. It was concluded that this increase was associated with an increase in the covalent component of the binding and a reduction in the degree of metallic bonding. A similar although weaker effect was observed for Sn forming hybrid sp^3 bonds.

There are many empirical relationships between the activation energy of diffusion and various parameters representing the interactions between atoms (heats of fusion and evaporation, melting point, characteristic temperatures, elastic moduli, etc.). These relationships are justified qualitatively by the fact that diffusion involves, in some form or other, either partial or complete breaking of bonds. However, it must be stressed that the rate of diffusion depends not so much on the strength of the binding as on the type of bonds and their spatial distribution (directivity). These more detailed characteristics of the atomic interactions are governed primarily by the distribution of electrons, i.e., by the electron structure of the diffusing atoms. A study of the relationship between the diffusion characteristics and the electron structure of impurities in solutions is thus of considerable importance in the theory of diffusion. This relationship can be regarded as of "primary" importance, compared with the others mentioned above, because the binding strength and geometrical parameters of the lattice are, in the final analysis, governed by the electron structure.

Information on the electron structure of impurity atoms, particularly transition elements, can be obtained by various resonance methods such as electron-positron annihilation,[1] x-ray spectroscopy,[2] neutron diffraction, and nuclear magnetic resonance. The Mössbauer spectroscopy has gained widespread acceptance in recent years.[3] Like the Knight shift in the NMR spectra, the isomeric or chemical shift of the Mössbauer line gives direct information on the electron density and impurity nuclei. Measurements of the chemical shifts of the lines of the same Mössbauer nucleus in different solvents yield information on the change in the electron density at a nucleus reflecting the change in the electron structure and in the nature of the chemical bond. In some cases, there is a clear correlation between the chemical shift of the line of an impurity nucleus and the force constants of the matrix.[4] These experimental capabilities make it possible to investigate the relationship between the electron density and the diffusion characteristics.

We recorded the Mössbauer absorption spectra using a single-channel unit operating under constant-velocity conditions and coupled to a scintillation detector. The velocity resolution was at least 0.04 mm/sec. The random error was ±0.5%. The source of γ quanta, used in recording the spectra of iron-bearing materials, was Co^{57} embedded in austenitic stainless steel.

TABLE I

Solvent	Chem. shift, mm/sec	Ref.	Q, kcal/g-atom	Раство тель	Chem. shift, mm/sec	Ref.	Q, kcal/g-atom
Be	0.52	[5]	51.8	Co	0.30	[8]	60.5—62.7
V	0.08—0.18 *	[6]	70.5—71.0	Cu	0.48	[6]	51.0—51.8
W	0.26—0.42	[7, 8]	66.0	Ni	0.30 *		60.4—61.0
Fe-α	0.26	[6]	60.0	Nb	0.16 *		77.7
Fe-γ	0.18	[6]	64.5	Ag	0.55	[8]	49.0
(source)				Ta	0.29 *		71.4
Au	0.62	[5]	41.6	Cr	0.07	[6, 8]	79.3

*Our results.

The absorbers were either foils about 30 μ thick or powders precipitated from a suspension on a 0.1—0.15 thick aluminum or beryllium foil. The source and the absorbers were at room temperature. The chemical shifts δ of the iron-bearing materials were measured relative to a standard absorber, which was sodium nitroferricyanide (nitroprusside).

Table I gives the values of the chemical shifts of the line (or the center of gravity of a split spectrum) representing the absorption by the Fe^{57} nuclei in different solvents. The table also lists the diffusion activation energies of iron atoms in the same solvents. The absorption spectra of V, Nb, and Ta containing Fe were recorded because the experimental data exhibited large scatter. This scatter was probably due to the formation of hydrides during annealing of the sources in a hydrogen atmosphere. Therefore, the samples were prepared as follows: iron was deposited electrolytically on both sides of 30-μ thick rolled foils which were then annealed in 10^{-5} mm Hg vacuum at 1300°C for 30 min. The iron remaining on the surface was then removed. The absorption spectra of Nb and Ta were quadrupole-split, whereas the spectrum of V consisted of a single line.

The diffusion activation energies Q listed in Table I seemed to be most reliable and were taken from[9].

A comparison of the diffusion activation energies of the Fe atoms in different solvents and of the chemical shifts of the lines of the Fe^{57} nuclei in the same solvents (Fig. 1) left no doubt about the existence of a definite correlation between them.

Since the chemical shift is proportional to the difference between the electron densities at the same nucleus in the absorber and in the source,

$$\delta = A\{\psi^2_{\text{abs}}(0) - \psi^2_{\text{sour}}(0)\} \qquad (1)$$

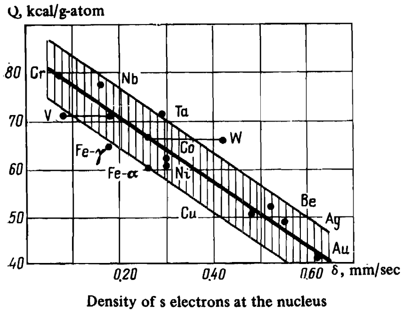

FIG. 1

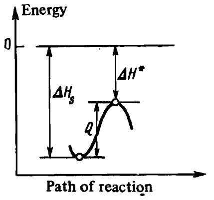

FIG. 2

FIG. 1. Comparison of the activation energies of the diffusion of the Fe atoms in different solvents and of the chemical shifts of the line of the Fe^{57} nuclei in the same solvents. All solutions were dilute.

FIG. 2. Schematic representation of the change in the energy of an atom during a diffusion jump.

and since $A < 0$ for Fe, an increase in the chemical shift means that the density of the s electrons at the absorber nuclei decreases. Thus, an increase in the density of the s electrons at the nuclei of the Fe^{57} impurities increases considerably the activation energy of the diffusion of the Fe atoms.

It is known that the activation energy of the diffusion of an impurity atom can be represented (within the framework of the intermediate state theory) by the difference between two quantities: the binding energy of an impurity in the lattice, equal to its heat of evaporation ΔH_s, and its binding energy in the intermediate state ΔH^*. Thus, it follows from Fig. 2 that

$$Q = \Delta H^* - \Delta H_s. \qquad (2)$$

Obviously, the activation energy of the diffusion of an impurity atom in different solvents can change because of the change in its heat of evaporation and because of the change in the height of the potential barrier. The rise of ΔH_s and the reduction in the absolute value of ΔH^* both increase Q.

The heat of evaporation of a Fe impurity atom can be represented as the sum of two quantities: the heat of evaporation of an Fe atom from iron ΔH_{s0} and the heat of solution of a Fe atom in a solvent ΔH_1,

$$\Delta H_s = \Delta H_{s0} + \Delta H_1. \qquad (3)$$

Since ΔH_{s0} is independent of the solvent metal, it follows that the change in ΔH_s on the transfer of Fe from one solvent to another is due to the change in the heat of solution ΔH_1. The values of the heats of solution Fe in different metals are listed in Table II[10] and show that this heat varies little (by about 2 kcal), whereas the activation energy of diffusion changes by almost 40 kcal.

Thus, we reach the conclusion that the change in the electron density affects mainly the energy of the intermediate state: the absolute value of this energy should decrease with increasing electron density at the nucleus because of the increase in the height of the diffusion barrier. Consequently, the electron structure affects the diffusion jump by altering the activated (intermediate) state, at least in the case of atoms of the transition metal Fe.

It is frequently assumed[11] that an increase in the density of the s electrons at the nucleus of an atom in a crystal implies an increase in the degree of localization of the electrons and can be regarded as a strengthening of the covalent component of the atomic binding or a weakening of the degree of metallic binding. From this point of view, the results obtained would indicate that the binding of Fe impurity atoms in transition-metal solvents, particularly those with the bcc lattice (V, Nb, Ta, Cr, and W), is strongly covalent. This enhancement of the rigid and directional covalent bonds should hinder strongly the diffusion jumps.

TABLE II

Solvent	Molar fraction of iron	T, °C	ΔH₁, kcal/g-atom		Solvent	Molar fraction of iron	T, °C	ΔH₁, kcal/g-atom	
			experiment	Calc.*				experiment.	Calc.*
V	< 0.1	—	0	—	Mn	0.1	1127	—0.43	—
Au	0,1	850	+0.48	—	Cu	0,1	1550	—	+0.12
Co	γ-phase	1020	0	—	Cr	0,1	1355	—	+0.70
Si	0,1	25	—1,9	—					

*The calculated value of the heat of solution was deduced from the free energy of dissolution on the assumption that the solutions were perfect.

In order to test the generality of the obtained result, we applied the same analysis to impurity atoms of Sn^{119} (outer shell configuration $5s5p^3$) and Au^{197} ($5d^{10}6s^1$). In the case of Sn, the tendency was found to be the same as for Fe: the activation energy decreased with increasing degree of metallization of the bonds but the influence of the electron density on the diffusion activation energy was at least an order of magnitude weaker than in the case of Fe. No relationship between the activation energy and the electron density was found in the case of Au.

Thus, the electron density has a strong influence on the activation energy of the diffusion of transition elements with outer partly filled d shells but has less effect on the elements with an outer sp shell and no influence on the elements in which the d shell is filled but there are no p electrons.

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17