

## The Structure and Oscillational Motion of $^{57}\text{Fe}$ Atoms in Interstitial Sites in Al as Determined from Interference of Mössbauer $\gamma$ Radiation

LINUS PAULING

*Linus Pauling Institute of Science and Medicine, 400 Page Mill Road, Palo Alto, California 94306*

Received May 23, 1981

The first excited site of the  $^{57}\text{Fe}$  atom entrapped in an interstitial site in aluminum, as reported by W. Petry, G. Vogl, and W. Mansel (*Phys. Rev. Lett.* 45, 1862 (1980)) from a Mössbauer spectroscopic study of a single crystal, is analyzed by consideration of the value of the Hooke's law constant of the Fe-Al bonds obtained from the values for elemental Fe and Al. The eight wavefunctions for the eightfold nearly degenerate excited state are described as  $2s1p1d1f$  hybrids of three-dimensional harmonic oscillator wavefunctions relative to the center of the undistorted  $\text{Al}_6$  octahedron or as localized  $1s$  functions relative to the center of the distorted octahedron. These considerations provide a qualitative understanding of the observations on this system.

Petry *et al.* (1) have used Mössbauer spectroscopy to study the environment of a  $^{57}\text{Fe}$  atom (mother isotope  $^{57}\text{Co}$ ) entrapped in an interstitial site in a single crystal of aluminum. They observed that at 4.2 K the recoilless fraction  $f$  of the absorbed  $\gamma$  radiation ( $f = 87\%$ ) is isotropic, whereas at 25.5 K it is strongly anisotropic, with the largest decrease in  $f$  in the [111] and [110] directions and the smallest in the [100] directions. The observations were interpreted as showing that the iron atom occupies eight cage sites displaced in the [111] directions by  $0.52 \pm 0.02 \text{ \AA}$  from an origin at the center of a regular  $\text{Al}_6$  octahedron (Fig. 1), with the attempt frequency from one site to another equal to  $1 \times 10^{12} \text{ sec}^{-1}$ . The interpretation of these observations is related to that of observations on self-interstitial systems (2) and Al/Fe internal-friction observations (3). We have analyzed the problem in a way that, we believe, provides a reasonable explanation of the observa-

tions and suggests the structural factors that must be included in more detailed theoretical treatments.

An iron atom can easily substitute for an aluminum atom in the Al aluminum structure, but it has to be squeezed into any interstitial site. The largest hole is at the center of an  $\text{Al}_6$  octahedron (Fig. 1). If the aluminum atoms do not move, the Fe-Al distance is  $2.025 \text{ \AA}$ . The iron atom presumably retains its metallic valence 6, and thus forms a single electron-pair bond with each of the surrounding aluminum atoms (4, 5). The expected Fe-Al distance (6) is the sum of the single-bond radii,  $1.170 + 1.248 = 2.148 \text{ \AA}$ . We assume accordingly that the atoms of the  $\text{Al}_6$  cage are pushed out by  $0.393 \text{ \AA}$ , ignoring the probability that the bonds are under some pressure from the surrounding crystal and are a little shorter. The force constant (7) for the bonds in Al metal, which have bond number  $n = \frac{1}{3}$ , is  $k = 22.14 \times 10^8 \text{ dyne cm}^{-1}$ .

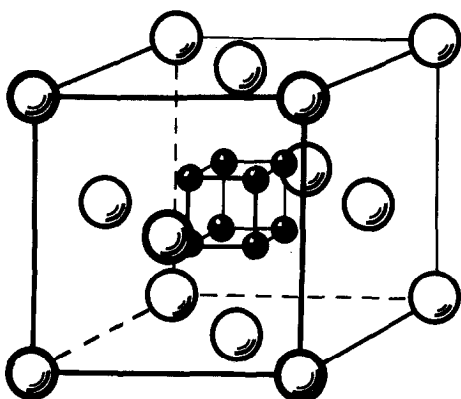


FIG. 1. The arrangement of Al atoms in a crystal of the metal (large circles) and the eight alternative positions (small circles) for an iron atom in interstitial solution, as shown by Mössbauer spectroscopy.

For a single bond a value 3 times as great,  $66.42 \times 10^9$  dyne  $\text{cm}^{-1}$ , might be expected. (Badger's equation for the sequence Na, Mg, Al, Si gives 74.7 (Ref. (7).)) For Fe, with the A2 structure (ligancy 8), the value of  $k$  is  $72.26 \times 10^9$  dyne  $\text{cm}^{-1}$ , which with the factor  $8/6$  to correct to ligancy 6 becomes  $96.3 \times 10^9$ . I shall use the geometric mean of the Al-Al and Fe-Fe values,  $80 \times 10^9$  dyne  $\text{cm}^{-1}$ , for the Fe-Al single bonds.

The Fe-Al bonds are so much stronger than the Al-Al bonds that we expect little interaction between the vibrations of the  $\text{FeAl}_6$  complex and those of the rest of the crystal.

For the normal vibrational site, in the isotropic harmonic oscillator approximation, the vibrational frequency calculated with reduced mass  $27.7 d$  (for Al-Fe-Al) is  $9.38 \times 10^{12}$  Hz, the root-mean-square amplitude of vibration is  $0.108 \text{ \AA}$ , the corresponding zero-point energy, for the 000 state, is  $9.33 \times 10^{-21}$  J, and the excitation energy to the first excited vibrational state is  $6.22 \times 10^{-21}$  J (39 meV). This value of the excitation energy is so large that no promotion to such an excited vibrational state would occur at 25.5 K. The observed excited state must accordingly correspond to an anisotropic structure.

The easiest direction in which the iron atom can move is toward the center of one of the octahedral faces of the  $\text{Al}_6$  group, with the accompanying spread of the corresponding  $\text{Al}_3$  triangle. The sequence of wavefunctions for the three-dimensional isotropic harmonic oscillator is  $1s$  for energy  $\frac{3}{2} h\nu_0$ ,  $1p$  for  $\frac{5}{2}$ ,  $2s + 1d$  for  $\frac{7}{2}$ ,  $2p + 1f$  for  $\frac{9}{2}$ , and so on. In the search for a description of the excited state by use of isotropic harmonic oscillator wave functions as the basis set we form hybrid orbitals by considering only the surface harmonic functions (of the polar coordinates  $\theta$  and  $\phi$ ), on the assumption that the radial functions are rather closely similar (3). The eight excited-state orbitals should extend toward the centers of the eight faces of the  $\text{Al}_6$  octahedron. It is found that eight equivalent orbitals with cubic symmetry cannot be formed by hybridization of  $1p$ ,  $2s$ , and  $1d$ , but can be formed by hybridization of these orbitals with  $1f$  (9).

The best  $spdf$  hybrid orbital has cylindrical symmetry about an axis in the bond directions and its dependence on the angle  $\theta'$  with this direction is (10):

$$\psi(\theta') = (35 \cos^3 \theta' + 15 \cos^2 \theta' - 15 \cos \theta' - 3)/8. \quad (1)$$

The value of the orbital and that of its square are shown in Fig. 2. The nodal cones lie at the values  $54.88^\circ$ ,  $100.43^\circ$ , and  $145.37^\circ$  with the axis of cylindrical symmetry of the function. The repulsion between the iron atom and its neighbors has its minimum values in these directions, inasmuch as the amplitude of the vibration is zero at these nodes: the iron atom vibrates about its average position in the way indicated by the square of the wavefunction. It is striking that the angle between the [111] vector and the [100] vector in a cubic crystal is  $\arcsin(\frac{2}{3})^{1/2} = 54.74^\circ$ , only  $0.14^\circ$  less than the first nodal angle. This calculation thus shows that in the excited state described by this hybrid orbital the iron atom does not vi-

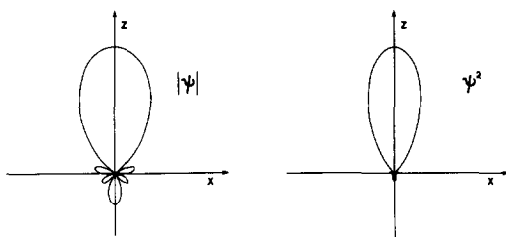


FIG. 2. Values of the angular dependence of the *spdf* hybrid orbital with the maximum value in the *z* direction (left) and values of its square (right). Each of these functions has cylindrical symmetry about the *z* axis.

brate toward the three aluminum atoms of the face toward which it is displaced (with the octahedron not distorted), but instead keeps this bond distance constant, thus helping to stabilize the system.

The other three aluminum atoms lie at the polar angle  $125.26^\circ$ , which is between the nodal angles  $100.43$  and  $145.37^\circ$ . The value of  $\psi^2$  in this lobe is small, however, so that this interaction is not an important one.

The calculation from structural principles of the amount of displacement of the iron atom from the origin for the excited state would be difficult. I accept the experimental value  $0.52 \text{ \AA}$  and calculate the amount of deformation of the  $\text{Al}_6$  octahedron with the assumptions that the Fe–Al distances remain  $2.418 \text{ \AA}$  and the sum of the squares of the displacements of the aluminum atoms from their original positions be a minimum, reflecting the interaction with the rest of the aluminum crystal. The corresponding values of the Cartesian coordinates are Fe at  $0.30, 0.30, 0.30 \text{ \AA}$ , 3 Al at  $2.65, -0.10, -0.10 \text{ \AA}$ ,  $\odot$ , and 3 Al at  $-2.08, 0.00, 0.00 \text{ \AA}$ ,  $\odot$ . The edges of the  $\text{Al}_6$  octahedron then have the lengths  $3.89, 3.31, \text{ and } 2.94 \text{ \AA}$ . The increase over the value  $2.86 \text{ \AA}$  in the undistorted aluminum crystal reflects the decrease in bond number of the Al–Al bonds resulting from the use of one valence electron by each aluminum atom in its bond to the iron atom.

If the force constant for oscillation in the

eightfold excited state had the same value as for the ground state the calculated excitation energy to the *spdf* localized orbital would be far larger than the value indicated by the transition temperature,  $17 \text{ K}$ . It is likely, however, that in each of the eight  $[111]$  positions the iron atom can be described as occupying a localized  $1s$  orbital, centered about a point  $0.52 \text{ \AA}$  from the center of the ground-state orbital and orthogonal to it. (This localized  $1s$  orbital is nearly identical with the *spdf* hybrid orbital described above.) The vibrational frequency for the atom in this localized  $1s$  orbital may be taken as about the same as that for the ground state, so that the problem presented by the large value of  $h\nu_0$  in the isotropic harmonic oscillator approximation does not arise.

The calculated root-mean-square displacement of the six aluminum atoms from their original positions,  $0.33 \text{ \AA}$ , is less than the value for the regular octahedron,  $0.39 \text{ \AA}$ , which suggests that the increased strain energy associated with this deformation is not great.

The frequency of tunneling resonance of the iron atom among the eight positions, with the corresponding changes in the deformation of the  $\text{Al}_6$  octahedron, may be low because of the small overlap of the localized wavefunctions. With the value  $\alpha$  for the resonance integral between adjacent sites (zero otherwise) and orthogonality of the wavefunctions, this resonance splits the eightfold degenerate vibrational state into one at  $3\alpha$ , three at  $\alpha$ , three at  $-\alpha$ , and one at  $-3\alpha$ . There are, of course,  $16 \text{ spdf}$  hybrid orbitals, 8 in addition to the 8 concentrated at the cube corners. One or more of these may interact strongly with the eight localized orbitals and may have only slightly higher energy. Motion of the iron atom among the eight sites could involve thermal excitation to these states, as reported by Petry *et al.* Their value of the activation energy,  $18 \text{ meV}$ , is reasonable, in that it

would result from about a 30% increase in the zero-point vibrational energy, as would be expected from the less favorable angular distribution for these less well directed orbitals.

A more detailed discussion of this structure might be carried out by evaluating a realistic potential energy function for the iron atom by consideration of the changes in length of the Fe-Al and Al-Al bonds and the correlation of the deformation of the Al<sub>6</sub> octahedron and the rest of the Al crystal with the coordinates of the iron atom. Such a discussion might provide additional information about force constants and other structural parameters.

#### Acknowledgments

I thank Dr. Zelek Herman for his help with this

work, which was supported in part by a grant from the National Science Foundation.

#### References

1. W. PETRY, G. VOGL, AND W. MANSEL, *Phys. Rev. Lett.* **45**, 1862 (1980).
2. G. VOGL, W. MANSEL, AND P. H. DEDERICHS, *Phys. Rev. Lett.* **36**, 1497 (1976).
3. L. E. REHN, K.-H. ROBRACK, AND H. JACQUES, *J. Phys. F* **8**, 1835 (1978).
4. L. PAULING, *Phys. Rev.* **54**, 899 (1938).
5. L. PAULING, "The Nature of the Chemical Bond," 3rd ed. Cornell Univ. Press, Ithaca, N.Y. (1960).
6. L. PAULING, *J. Amer. Chem. Soc.* **69**, 542 (1947).
7. J. WASER AND L. PAULING, *J. Chem. Phys.* **18**, 747 (1950).
8. L. PAULING, *J. Amer. Chem. Soc.* **53**, 1367 (1931).
9. G. E. KIMBALL, *J. Chem. Phys.* **8**, 188 (1940).
10. L. PAULING, *Proc. Nat. Acad. Sci. USA* **73**, 274 (1976).