PHYSICAL REVIEW B VOLUME 46, NUMBER 19 15 NOVEMBER 1992-I

Ab initio calculations of oxygen diffusivity in group-IB transition metals

M. E. Eberhart
Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, Colorado 80401

M. M. Donovan
Department of Energy, Washington, D.C. 20585

R. A. Outlaw
National Aeronautics and Space Administration, Langley Research Center, Hampton, Virginia 23681

(Received 4 February 1992)

First-principles investigations of oxygen transport through Cu, Ag, and Au have revealed subtle changes in the response of the total charge density to the presence of O atoms in the octahedral holes of these metals. In both Cu and Ag, these changes are characterized by a decrease in the magnitude of the curvature of the charge density normal to the metal-metal first-neighbor atoms. In Au there is an increase in the magnitude of this curvature. Associating the curvature of the charge density normal to the internuclear axis with the barrier to oxygen diffusion provides a consistent explanation of the difference in diffusivity of O through Cu, Ag, and Au.

INTRODUCTION

As one approach to describing the electronic structure of the solid state we have recently employed a model of chemical bonding developed by Bader.[1-4] This model provides a simple graphical basis from which changes in total charge distribution accompanying some processes can be interpreted. What is particularly attractive about this model is that complex changes of the total charge distribution can be represented by changes at a few special points. Bader has shown that the essence of molecular structure is contained in the scalar field of the charge density, $\rho(\mathbf{r})$. There are four kinds of critical points (defined as the zeros of the gradient of this scalar field) in a three-dimensional space: a local minimum, a local maximum, and two kinds of saddle points. These critical points (CP) are denoted by an index which is the number of positive curvatures minus the number of negative curvatures. For example, a minimum CP has positive curvature in the three orthogonal directions, therefore it is called a (3,3) CP, where the first number is simply the number of dimensions of the space, and the second number is the net number of positive curvatures. A maximum would be denoted by a $(3,-3)$ CP, since all three curvatures are negative. A saddle point with two of the three curvatures negative is denoted as a $(3,-1)$ CP, while the other saddle point is a (3,1) CP. Bader has pointed out that a bond in molecules can be seen in terms of the topology of $\rho(\mathbf{r})$. A bond path connects two nuclei [where the charge density possesses $(3,-3)$ CP's] through a $(3,-1)$ CP such that the charge density is always a maximum with respect to any neighboring path. This idea has recently been extended[5] to the solid state, where the notion of the metallic bond was discussed.

While the location of CP's is seen from the zeros of the gradient field of $\rho(\mathbf{r})$, the magnitude of CP's is quantified by the value of the scalar Laplacian field which represents the concentration of the charge distribution. Different types of bonding can be categorized by the value of the Laplacian at the $(3,-1)$ CP. A covalent bond has a large concentration of charge in the internuclear region. Along the bond path, the curvature of the charge-density distribution, $\nabla_{\parallel}^2\rho(\mathbf{r})$, would be positive but smaller than if the internuclear region were depleted. The depleted case would correspond to an ionic bond where the charge density is concentrated on nuclei. The curvatures in a direction perpendicular to the bond path, $\nabla_{\perp}^2\rho(\mathbf{r})$, would always be negative (by definition of the bond path), but one would expect that in the instance where there is a strong concentration of charge in the internuclear region, $\nabla_{\perp}^2\rho(\mathbf{r})$ would be more negative than in the case where the region is depleted. What is found in practice is that strong covalent bonds are characterized by $\nabla^2\rho(\mathbf{r})\ll 0$ at the bonding CP, while strong ionic bonds have $\nabla^2\rho(\mathbf{r})\gg 0$. Metallic bonds have the Laplacian at the bonding CP dominated by the positive curvature along the bonding direction, but not to the extent of the strong ionic bond. In the metallic bond, all the curvature components have a rather small magnitude at the bonding CP and $\nabla^2\rho(\mathbf{r})>0$ characterizes a metallic bond.

Figure 1 shows a plot of the bulk modulus versus the Laplacian of the charge density, for a variety of fcc met-

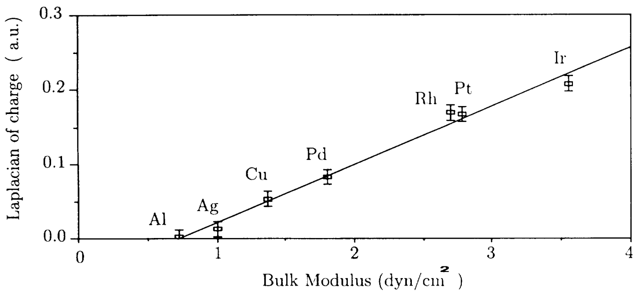

FIG. 1. Bulk modulus vs the Laplacian of the charge density for various fcc metals.

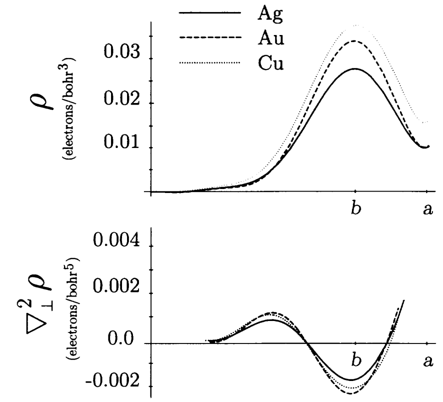

FIG. 3. The charge density (top) and curvature of the charge density (bottom) along the line a-b shown in Fig. 2 for Ag, Au, and Cu.

als at the $(3,-1)$ CP. The linear relationship between bulk modulus and curvature demonstrates that, to first order, bond stiffness or strength can be interpreted as arising from or being dominated by the nature of the charge density at the $(3,-1)$ CP only. Thus one is provided with a simple procedure for analyzing the net flow of charge density by simply noting the movement of the $(3,-1)$ CP and the changes in value of the Laplacian of $\rho(r)$ at these points. Maps showing the change in position of these $(3,-1)$ CP's accompanying some processes are reminiscent of the type of diagrams used by organic chemists to show the redistribution of electron pairs in organic reactions.

Using this approach to represent a bond, it is possible to rationalize aspects of solid-state behavior. For example, we have employed this procedure as an explanation of the difference in cleavage energy between two different alloys with the same structure.[5] These explanations then provide guidance for more detailed theoretical or experimental investigations. It is in this spirit that we seek to establish a correlation between features of the total charge distribution and the barrier to diffusion in crystalline solids.

RESULTS AND DISCUSSION

The specific problem presented here deals with the difference in diffusivity of oxygen through Cu, Ag, and Au. Oxygen is observed to diffuse readily through Cu and Ag, but shows no appreciable solubility or diffusivity through Au at any temperature, even if the source of the oxygen is as atoms already adsorbed on the surface.[6] Table I shows the diffusivity and solubility equations for oxygen in the three metals as well as the general characteristics relating to oxygen transport. It is interesting to note that Cu and Ag have similar oxygen transport properties with the exception of the oxide that forms on Cu at high temperatures. Furthermore, since Ag and Au possess nearly identical atomic radii (therefore nearly identical octahedral site radii) and have quite similar chemisorption characteristics for oxygen (both have stable oxygen layers adsorbed on the surface), their difference in diffusivity cannot be explained with stearic arguments. Rather, it can only be attributed to a difference in activation energy for the movement of O from one octahedral site to another with the barrier to diffusion occurring between nearest-neighbor atoms of the fcc lattice at point b shown in Fig. 2.

Our approach to examining the difference in diffusivity of O through Cu, Ag, and Au is to use two methods of

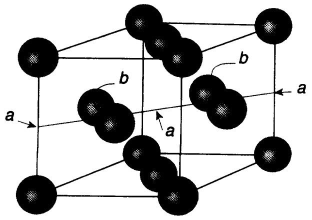

FIG. 2. The proposed diffusion path for oxygen in fcc lattice. The activation barrier is presumed to occur at point b while the stable site is believed to be point a.

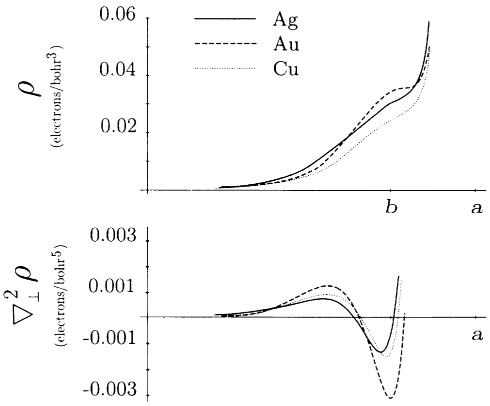

FIG. 4. The charge density (top) and curvature of the charge density (bottom) along the line a-b shown in Fig. 2 for O in Ag, Au, and Cu octahedra.

TABLE I. Diffusivity and solubility equations for Cu, Ag, and Au.

Property	Cu	Ag	Au	Ref.
Atomic radius	0.1278 nm	0.1444 nm	0.1441 nm	8
Surface	Stable oxide	Chemisorbed atom layer	Chemisorbed atom layer	9,10
Diffusivity	$9.68\times10^{-7}\exp(-7360/T)$ ($m^2 s^{-1}$)	$2.96\times10^{-7}\exp(-5560/T)$ ($m^2 s^{-1}$)		11,12,13
Solubility	$7.25\exp(-14\,290/T)$ (mf)	$2.35\times10^{-4}\exp(-5969/T)$ (mf)		11,12,13

electronic structure theory,[6,7] the layer Kohn-Korringer-Rostocker (LKKR) method for extended systems and the multiple-scattering local-density-functional (MS-LDF) cluster method, to determine the changes in the curvature of the charge density at the $(3,-1)$ CP. We expected that if the differences in diffusivity could be attributed to some feature of the bonding, this should manifest itself in changes in the curvature of $\rho(\mathbf{r})$ at this point.

Figure 3 compares the charge density as calculated with the MS-LDF method along the line *b-a* for the fcc metals Cu, Ag, and Au. Also shown is the curvature of the charge density along this line. While the absolute magnitude of the charge density is different for cluster and LKKR calculations, the same features and orderings of the $(3,-1)$ CP's are observed. Note that if one adopts the concepts presented by Bader of identifying the curvature of the charge density with a property of the bond (as in Fig. 1, where we correlate the Laplacian with bond stiffness) then the bond ordering $\mathrm{Au}>\mathrm{Cu}>\mathrm{Ag}$ occurs, in agreement with the observed bulk moduli. On the other hand, if one identifies the magnitude of charge at point *b* as a measure of stiffness then the ordering $\mathrm{Cu}>\mathrm{Au}>\mathrm{Ag}$ is realized, contrary to observation.

Figure 4 shows the charge density and curvature along the line *b-a* near the point *b* for oxygen centered isolated octahedra of Cu, Ag, and Au. While the charge density along this line is strikingly different from that determined for the empty octahedra (Fig. 3), the curvatures of these charge densities are similar. Both empty and O-centered octahedra show a $(3,-1)$ CP in the total charge density near the point *b*, indicating the existence of a bond between the metal atoms of the octahedra. The change in the magnitude of the curvature of the charge density at point *b* upon the addition of O is different for the various metals modeled. Both Cu and Ag show a decrease while Au shows an increase in $\nabla_{\perp}^2\rho(\mathbf{r})$ with the presence of O. Though not shown, the changes in the parallel component of the curvature, $\nabla_{\parallel}^2\rho(\mathbf{r})$, at point *b* is only slightly affected by the oxygen atom at the center of the octahedra.

These observations lead us to conjecture that a qualitative measure of the activation barrier for the movement of an oxygen atom from one octahedral site to another is given by the magnitude of $\nabla_{\perp}^2\rho(\mathbf{r})$. If this conjecture can be supported by additional calculations, this approach provides a rapid method by which the atomic mechanisms of diffusion can be inferred. In systems where there are multiple paths for diffusion, a few calculations will allow one to determine which are the most likely to dominate the process. More complicated calculations to actually determine the magnitude of the activation barrier to diffusion and how this may be changed through alloying can then be performed. Such approaches will be important in some technologically important systems where there are many possible paths for diffusion, an example being the diffusion of hydrogen in many of the alloy systems being investigated for high-temperature applications.

SUMMARY

Experimentally, it is well known that oxygen diffuses readily through Cu and Ag but not through Au. There exists, however, no acceptable rationale to explain these observations. We have identified the curvature of the charge density at the $(3,-1)$ CP between near-neighbor atoms with the directionality of these bonds. Through this identification we conclude that oxygen weakens the metal-metal bonds in Cu and Ag, giving rise to a higher probability of jumping from site to site. In Au, oxygen actually strengthens the nearest-neighbor bonds which, conversely, inhibits interstitial movement. The arguments presented here are qualitative but internally consistent, showing another correlation between the curvature of the charge density at $(3,-1)$ CP and properties. These correlations provide an explanation for the marked difference in the diffusivity of O through Cu, Ag, and Au.

ACKNOWLEDGMENTS

We are grateful for funding from NASA Ames Research Center and the U.S. Office of Naval Research.

---

[1] R. F. W. Bader and H. J. T. Preston, Int. J. Quantum Chem. **3**, 327 (1969); R. F. W. Bader, P. M. Beddall, and J. Peslak, Jr., J. Chem. Phys. **28**, 557 (1973).

[2] G. R. Runtz, R. F. W. Bader, and R. R. Messer, Can. J. Chem. **55**, 3040 (1977).

[3] R. F. W. Bader, T. T. Nguyen-Dang, and Y. Tal, Rep. Prog. Phys. **44**, 893 (1981).

[4] R. F. W. Bader and P. J. MacDougall, J. Am. Chem. Soc. **107**, 6788 (1985).

[5] M. E. Eberhart, D. P. Clougherty, and J. N. Louwen, MRS

Bulletin **16**, 53 (1991); M. E. Eberhart, M. M. Donovan, J. M. MacLaren, and D. P. Clougherty, Prog. Surf. Sci. **36** (1991).

[6] J. M. MacLaren, S. Crampin, D. D. Vvedensky, and J. B. Pendry, Phys. Rev. B **40**, (1989); S. Crampin, D. D. Vvedensky, J. M. MacLaren, and M. E. Eberhart, *ibid.* **40**, 3413 (1989).

[7] K. H. Johnson and F. C. Smith, Jr., Phys. Rev. B **5**, 831 (1972); J. C. Slater and K. H. Johnson, *ibid.* **5**, 844 (1972).

[8] B. D. Cullity, *Elements of X-ray Diffraction* (Addison-Wesley, Reading, MA, 1967).

[9] H. A. Engelhardt and D. Menzel, Surf. Sci. **57**, 591 (1975).

[10] C. T. Campbell, Surf. Sci. **157**, 43 (1983).

[11] E. Albert, R. Kirchheim and, H. Dietz, Scr. Metall. **15**, 673 (1981).

[12] R. A. Outlaw, S. N. Sankaran, G. B. Hoflund, and M. R. Davidson, J. Mat. Res. **3**, 1378 (1988).

[13] W. Eichenauer and G. Muller, Z. Metallkd. **53**, 321 (1962).

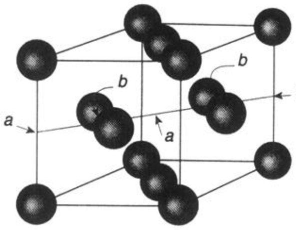

FIG. 2. The proposed diffusion path for oxygen in fcc lattice. The activation barrier is presumed to occur at point *b* while the stable site is believed to be point *a*.