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The Electronic Structure and Formation Energy of a Vacancy in Aluminum*

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The electronic structure of a vacancy in Al was calculated self-consistently using norm-conserving ionic pseudopotentials obtained from ab initio atomic calculations. A 27-atom-site supercell containing 1 vacancy and 26 atoms was used to simulate the environment of the vacancy. A vacancy formation energy of 1.5 eV was also calculated (cf. the experimental value of 0.66 eV). The effects of the supercell and the nature of the ionic potential on the resulting electronic structure and formation energy are discussed. Results for the electronic structure of a divacancy are also presented.

Self-consistent calculations of defect electronic structures in real metallic systems have been scarce, and efforts to calculate the energetics of vacancy formation, even in simple metals like Al, have met with little success [1,2]. The present work, a detailed theoretical study of the electronic structure of a vacancy in Al, is based on the self-consistent pseudopotential method [3]. Pseudopotentials are weaker than actual atomic potentials, since they eliminate the need to include atomic-core states. Thus, it has been common to associate the pseudopotential concept with a perturbative approach. The self-consistent pseudopotential method does not treat the ionic potential as a weak perturbation; it simply replaces this potential with a pseudopotential. Since this transformation is valid for all systems, the method is not restricted to simple, nearly-free-electron metals. The present calculations are based on a plane-wave basis set; nevertheless, the method is easily generalized to also include localized atomic orbitals in the basis. In earlier studies, ionic pseudopotentials fitted to energy bands were used, which only approximately describe the electronic wave functions; more recently pseudopotentials have been obtained from ab initio atomic calculations [4,5].

The results of a calculation of the electronic structure of a vacancy in Al using the empirical ionic-potential approach were reported in a previous paper [3]; here we have repeated the calculations using a norm-conserving potential [5]. A comparison of the two sets of results provides important information about the sensitivity of the resulting electronic structure and formation energy to the potential. Norm-conserving potentials yield accurate charge densities outside the core region without having to be renormalized; the integrals of the pseudo and real charge densities from 0 to r agree for any $r>r_c$, the core radius. Also, the logarithmic derivatives of the real and pseudo wave functions, and their first energy derivatives, agree for $r>r_c$. In a self-consistent calculation, where the pseudo charge density is treated as a real object, these properties ensure the transferability of the potential between different chemical environments. In

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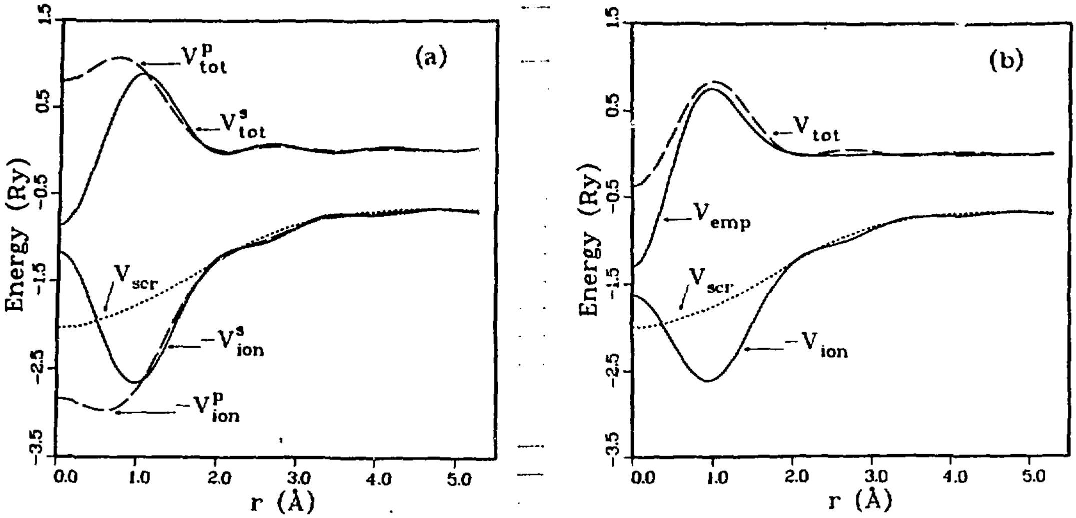
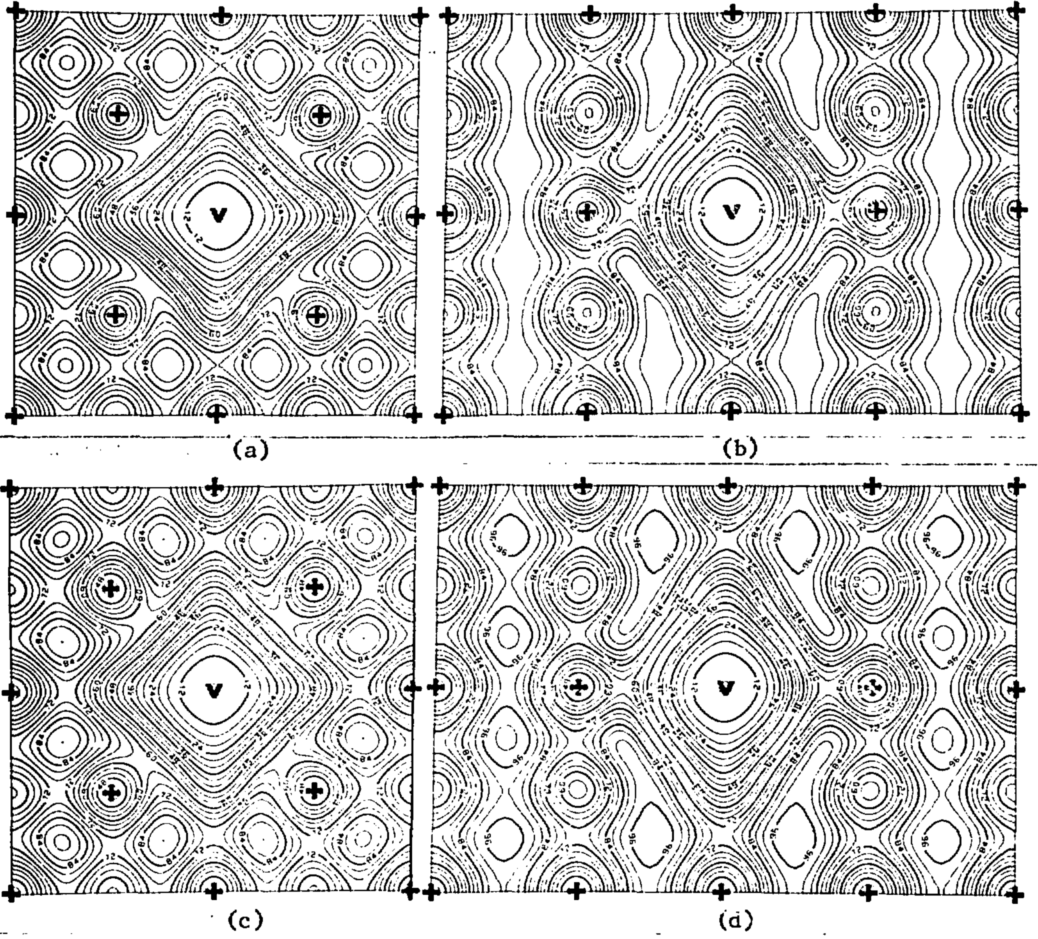


Fig. 1. The components of the vacancy potential V_{tot} for (a) the nonlocal potential compared with those of (b) the local potential [3].

contrast to the local empirical potentials, these ab initio potentials are nonlocal; i.e., they are angular-momentum dependent. Before embarking on the calculation of the vacancy electronic structure, the bulk properties of Al were calculated using both potentials [3]. The basis set consisted of ~ 50 plane waves; an additional ~ 50 were included via the Löwdin perturbation scheme [3]. The equilibrium lattice constant was determined to be 3.870 Å for the local potential and 4.047 Å for the nonlocal one (cf. the experimental 0 K value of 4.045 Å). The calculated bulk moduli were 1.2×10^{12} dyn cm^{-2} and 0.99×10^{12} dyn cm^{-2}, respectively; the experimental value is 0.88×10^{12} dyn cm^{-2}. The norm-conserving potential thus provides a more accurate description of the bulk properties of Al.

A detailed description of the calculation procedure for the electronic structure and formation energy of a vacancy in Al is given in [3]. An identical procedure was followed here, replacing the local ionic potential with the ab initio, nonlocal s- and p-ionic potentials for Al. Spherical averages of the ionic and screening components (V_{ion}, V_{scr}) of the vacancy potential (V_{tot}) for both the nonlocal and local ionic potentials are shown in Fig. 1(a,b), respectively. The vacancy potential is defined as the difference in potential between a supercell with 26 atoms and 1 vacancy and that with 27 atoms; the potential in Fig. 1(b) is essentially a compromise between the s- and p-potentials in Fig. 1(a). The nonspherical contributions to the potential are small in both cases. The same empirical potential (V_{emp}) was used to initiate both calculations. In a 27-atom-site fcc supercell, the nearest-neighbor vacancies have common third-nearest neighbors (at r = 5.0 Å), leading to some minor vacancy-potential overlap in the vicinity of these sites. However, the vacancy potentials were effectively isolated.

The total valance charge density around the vacancy is shown in Fig. 2 and compared with the results of the local-potential calculation. It is evident that the electronic structure is affected significantly, though not drastically, by the change in ionic potential. This change also resulted in the disappearance of the vacancy-associated resonance state reported in [3]; here, no evidence for a resonance state was found. The charge density at the center of the vacancy, 2.93×10^{-3} a.u., is higher than that obtained previously (2.48×10^{-3} a.u.). Also, a smaller difference between the charge densities at the atomic sites and the interstitial sites is seen in the present results. As seen in Fig. 2, the total charge density perturbation is very well localized for both potentials. However, as in [3], this does not preclude overlap of individual state wave functions of neighboring vacancies. The calculated electronic structure of the vacancy is



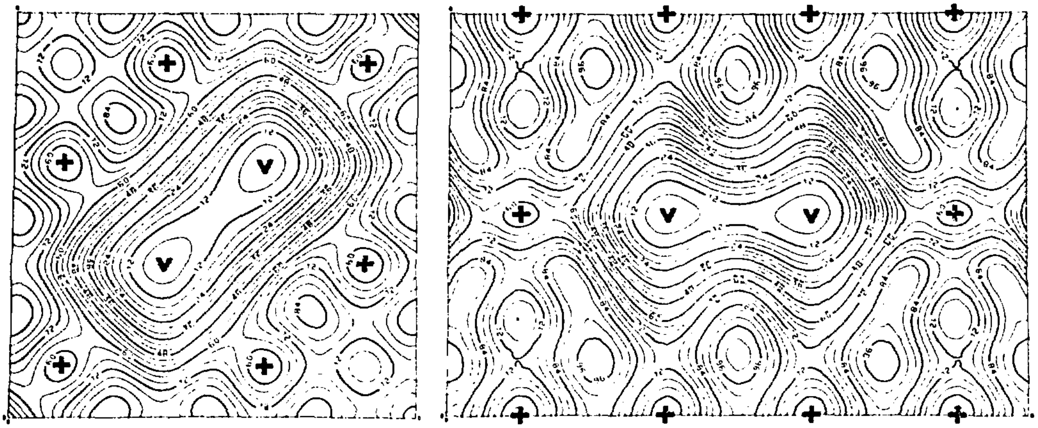
(a) (b)

(c) (d)

Fig. 2. The total valence charge density (ρ) x the supercell volume (Ω) around a vacancy (V) in (a,c) the (100) plane and (b,d) the (110) plane of the supercell for (a,b) the nonlocal potential and (c,d) the local potential [3]. The atomic positions are denoted by +.

essentially unaffected by the presence of any such small overlaps introduced by the supercell configuration; the vacancy formation energy is not so immune.

The vacancy formation energy is expected to differ significantly from the local-potential result. We obtained a value of 1.5 eV, which is a significant reduction from the previous value of 1.9 eV, but still too large compared to the experimental value of 0.66 eV [3]. Two factors could be responsible for this remaining discrepancy. The first is lattice relaxations. Work is in progress on this part of the problem, using the Hellman-Feynman theorem to estimate forces on near-neighbor atoms, using the calculated forces then to relax the atoms; no definitive answers have yet been obtained. However, the relaxation energy is not expected to be large enough to account for the remaining discrepancy, since both the nonlocal and local potentials are weak at the first nearest-neighbor (1n) sites and the relaxations estimated previously [3] were small (~ 2% radially inward for the 1n). The second and probably largest factor could be collectively termed supercell effects. These can be divided into two categories; (i) spurious overlaps introduced by the supercell, as discussed in [3], and (ii) computational difficulties associated with having a large number of atoms in a unit cell. Uncertainties associated with the first category cannot be conclusively resolved without carrying out a calculation in a larger supercell, which is not possible at present owing to



(a) (b)

Fig. 3. The total valence charge density (ρ) x the supercell volume (Ω) around a divacancy (V-V) in (a) the (100) plane and (b) the (110) plane. The atomic positions are denoted by +.

the computational times required for a sufficiently accurate calculation. A mixed-basis approach [6], involving both plane waves and localized orbitals, can reduce the size of the basis set, and hence the computational time, significantly. This approach seems to be the only one available within the supercell concept for *improving formation energy calculations*, and will have to be used to calculate the electronic structure of defects in d-band metals. At present a mixed-basis program is being applied to defect-free Al in order to determine an optimum basis set. We hope to be able to do a more accurate formation energy calculation with this approach. In order to eliminate all supercell effects, a different approach to calculating energetics is necessary. A Green's-function scheme capable of dealing with lattice relaxations, or a variational scheme [R. Benedek, private communication] which deals directly with the charge density and therefore obviates the need for detailed wave-function calculations, would be appropriate.

Finally, we present the results of a calculation of the electronic structure of a divacancy in Al (Fig. 3), which has also been carried out in the 27-atom-site supercell; it is thus expected to be of little value in studying divacancy energetics. The present calculation was done within the context of calculations of the characteristics of positron annihilation in defect-trapped states; such results should be independent of supercell configuration, since the positron is extremely well localized in the vacancy defect and the overlap from neighboring defects is too small to affect the electronic structure as seen by the trapped positron. In this context, the electronic structure of small higher-order vacancy clusters is also expected to be well defined and capable of being addressed within the supercell concept. The results of the present calculations will be presented in a more complete form elsewhere.

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