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## Ab initio study of structural distortion and its influence on the magnetic properties of metallic dilute alloys

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### Abstract

We report a systematic study of lattice relaxation effects around 3d and 4sp impurities in aluminum, using the full-potential Korringa–Kohn–Rostoker Green function method. Our results for the magnetic properties of the impurities seem to resolve the discrepancy between experiment and previous calculations. In addition, the calculated atomic displacements and total volume changes are in good agreement with the corresponding experimental data.

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Lattice relaxation around point defects plays an important role in the determination of various electronic and structural properties of materials. In the case of dilute alloys, for instance, the local strain field due to the size mismatch between impurity and host atoms influences the interaction of solute atoms with other defects and the tendency towards long-range ordering or clustering. Such studies aim to advance our understanding of diffusion processes, as well as the influence of defects on the mechanical properties of the materials.

Over the years, ab initio electronic structure calculations based on density-functional theory [1,2] have enormously enhanced our knowledge about the electronic properties of solids. However, the study of structural distortion around point defects is more

difficult and was usually neglected. This was due to the fact that the energy associated with the distortion of the ideal lattice arising from a point defect is rather small, of the order of a few hundredths of an eV. The first attempts to deal with lattice relaxation and dynamical properties of solids using ab initio methods were mostly done for semiconductors, mainly because of the great technological importance of these materials, but also because their treatment is easier as compared with, e.g., the case of transition metals. Several ab initio calculations have been carried out to describe the lattice distortion in semiconductors and simple metals utilizing the pseudopotential supercell technique [3–11] or the pseudopotential Green function method [12–18], while the finite cluster approach has been also used for metals [19,20], semiconductors [21], and ionic systems [22].

The defect problem can be efficiently treated using the Korringa–Kohn–Rostoker (KKR) Green

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function method. This approach, which has recently been extended to allow for the treatment of moderate lattice distortions [23], has the advantages of an all-electron, first principles method while it is free from the approximations imposed on supercell or cluster techniques. The ground state geometry in the vicinity of a point defect can be in principle determined by minimizing the total energy of the system with respect to the atomic displacements, or by seeking the atomic configuration where the forces on all the atoms vanish. Both schemes can be computationally very demanding because they require a large number of self-consistent calculations. However, by a lattice-statics simulation using the forces and the force constants from an *ab initio* calculation in the ideal-lattice geometry, we can estimate the equilibrium atomic positions straightforwardly. Then, recalculating the forces and the force constants in the shifted configuration predicted from the simulation, lattice statics can be used again to predict a new geometry, until convergence of this procedure leads to the ground-state configuration. Using this scheme the computational effort to calculate the lattice relaxation is minimized. In practice the first estimate of the relaxed geometry from the forces and the force constants calculated from the ideal-lattice configuration gives already an excellent approximation of the ground-state geometry.

In a previous work [23] we studied lattice distortion effects around *d* and *sp* impurities in Cu. Here we will extend our study to Al dilute alloys. Recently Chetty et al. studied a vacancy and light impurities in Al including the lattice distortion by using a pseudopotential supercell method [24]. Their results for the heat of solution, as well as the volume change due to the defect, were in agreement with the experimental data. However, transition-metal impurities are more difficult to treat using a pseudopotential approach and no systematic study of the lattice distortion around transition-metal impurities in Al has been reported so far to our knowledge. We carried out a systematic study of lattice relaxation effects due to 3*d* and 4*sp* substitutional impurities in Al using the full-potential KKR Green function method. Our calculations are based on the local-spin-density approximation of the density-functional theory [1,2], and employ the exchange–correlation potential of Vosko, Wilk and Nusair [25]. A detailed

description of our method is reported elsewhere [23]. Here we restrict ourselves to say that a cutoff  $l_{\max} = 4$  is used to truncate the angular momentum expansions of the Green function and the wavefunctions, while potentials and charge density are calculated up to  $l_{\max} = 8$ . The correct shape of the Wigner–Seitz cells is described by the proper shape truncation functions. The perturbation induced by the impurity atom is calculated self-consistently for 79 atoms in the vicinity of the defect thus including 5 shells of perturbed potentials around the impurity atom, while the potentials of the outer Al atoms are assumed to be unperturbed. The lattice constant of the fcc Al host, as calculated by total energy minimization, is found to be  $a_0 = 7.548a_B$  where  $a_B$  is the Bohr radius.

We carried out self-consistent calculations for different radial shifts of the first nearest neighbors (NN) of the impurity. The forces on the first NN calculated using the Hellmann–Feynman (HF) theorem agree very well with those obtained from the derivative of the total energy with respect to the atomic displacement. This fact ensures the accuracy of our calculation. Using the calculated forces exerted on the atoms in the vicinity of the impurity as well as the corresponding force constants, we can get a very good estimate of the groundstate geometry with the help of lattice-statics simulations based on the Kanzaki model. In this model the equilibrium atomic positions around a defect can be obtained by introducing forces in the ideal crystal. The Kanzaki forces are defined so that they induce the same local distortion in the host crystal as the true forces cause in the defect system. The relaxed geometry is determined by minimizing the elastic energy of the hypothetical ideal crystal in the presence of the Kanzaki forces. The dynamical matrix of the host crystal can be calculated from first principles but in this work it was taken from experimental data [26]. More details about the above described procedure can be found elsewhere [23]. The consistency of our results is checked by recalculating self-consistently the forces on the atoms in the distorted geometry, which are always found to be rather small.

In Fig. 1 we present the predicted atomic displacement for the first NN around impurities in Al. Our results are in good agreement with the available experimental data from extended X-ray absorption

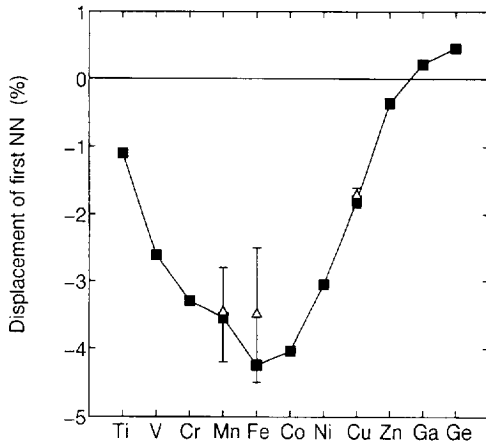


Fig. 1. Change of the first NN distance from the ideal-lattice position for 3d and 4sp substitutional impurities in Al. The triangles show the EXAFS results from Refs. [27,28].

fine-structure (EXAFS) measurements [27,28]. The Al lattice contracts upon alloying with 3d elements in the dilute limit. The atomic displacements show a parabolic behavior with the minimum at Fe, while in the case of 4sp impurities we find only a very small lattice distortion.

As it turns out, lattice relaxation effects are crucial for the magnetic behavior of the 3d impurities in Al. Previous *ab initio* calculations [29] predicted the existence of a magnetic moment for Cr, Mn, and Fe substitutional impurities in Al, without taking into account the lattice distortion. Recently Guenzburger and Ellis [19] studied lattice relaxation effects around an Fe impurity in a finite Al cluster and found that the Fe moment vanishes if lattice distortion is taken into account. However, the latter calculation seems to be subject to errors since the calculated relaxation energy was unphysically large, about 5 eV, while the predicted lattice contraction was also rather big compared with experiment.

The magnetic behavior of transition-metal impurities diluted in simple metals has been studied previously [30]. It was shown that close to the transition from a spin-polarized to a non-spin-polarized impurity state the local magnetic moment,  $M$ , is proportional to  $\sqrt{1 - \rho/\rho_c}$ , for  $\rho < \rho_c$ , where  $\rho$  is the free electron density of the host and  $\rho_c$  is a critical density above which the magnetic moment vanishes. In the case of a local lattice distortion, we can

describe a similar magnetic transition considering the distance of the first NN from the impurity as a variable parameter, instead of  $\rho$  in the homogeneous expansion (compression) case. Using arguments similar to those presented in [30], it can be shown that close to the transition the square of the local moment should vary linearly with the first NN distance. This is indeed confirmed by our calculations as shown in Fig. 2 where we present the magnetic moment versus the distance between impurity and its first NN. We find that the magnetic moment of Fe vanishes in the ground-state configuration while for Mn the moment decreases from  $2.6\mu_B$  in the ideal-lattice geometry to  $1.33\mu_B$  in the relaxed configuration. For Cr we find that the lattice distortion strongly reduces the local moment but the relaxation is not large enough to suppress the moment completely so that, finally, we obtain a moment of  $0.7\mu_B$ . Our results are in accordance with the experimental findings that Fe is non-magnetic in Al while Mn and Cr are typical cases of spin-fluctuating systems with Kondo temperatures of about 500 K and 1500 K, respectively [31,32].

The energy associated with the lattice distortion is generally proportional to the square of the displacement. In the case of Fe and Co, which induce the biggest distortion in the Al lattice, the relaxation energies are 0.44 eV and 0.42 eV, respectively. For a

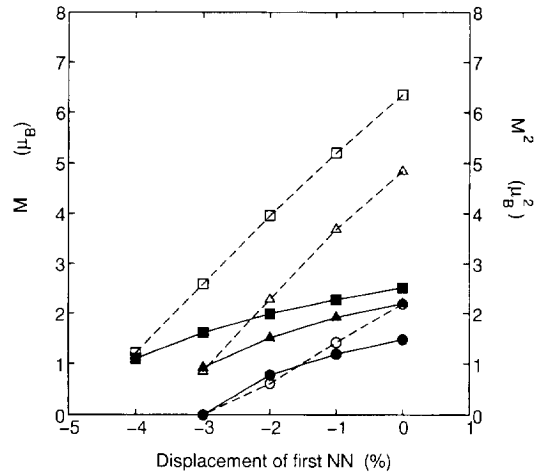


Fig. 2. Variation of the impurity magnetic moment (filled symbols) with the first NN distance for Fe (circles), Cr (triangles), and Mn (squares) impurities (left axis). The empty symbols show the square of the magnetic moment (right axis).

Cu impurity the calculated relaxation energy is 0.08 eV while for the sp impurities it is one order of magnitude smaller.

In a previous study of the lattice distortion around impurities in Cu we have found a big influence of the semicore electrons of the impurity on the force calculation. Similar effects, although smaller, also occur for impurities in Al. In our calculations we consider the semicore states of the impurities which lie up to 3.3 Ry below the Fermi energy as valence states. For the impurities of the 3d series, the influence of the treatment of the 3p semicore states on the force calculation is biggest for Ti. Using the usual spherical core treatment within the muffin-tin sphere, we find that the force on a first NN at ideal-lattice position is  $-3.6 \text{ mRy}/a_B$ , whereas treating the 3p semicore state as valence state we obtain  $-5.2 \text{ mRy}/a_B$ . In the case of V the effect is already smaller since the approximate core treatment gives a force of  $-11.1 \text{ mRy}/a_B$ , to be compared with the correct force  $-12.0 \text{ mRy}/a_B$ , while for Cr the difference is about 4%.

The presence of 3d impurities compresses the Al lattice, in agreement with experimental data from lattice-parameter measurements [33]. In Fig. 3 we present our results for the volume change, together with the experimental data. As we can see, the magnitude of the observed lattice compression is nicely reproduced from our ab initio calculations,

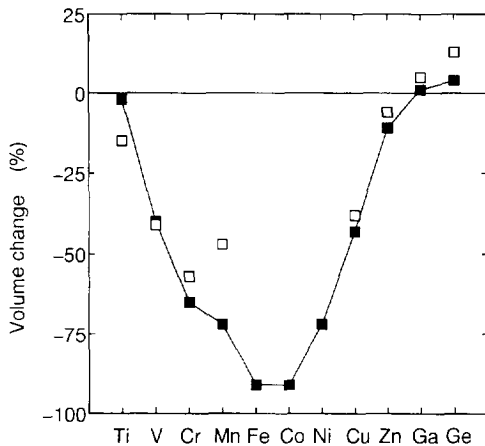


Fig. 3. Relative volume change per impurity in Al-based dilute alloys with 3d and 4sp impurities. The results of lattice-parameter measurements [33] are also shown (empty squares).

except for Mn where the experimental value is somewhat smaller than the calculated one.

In summary, we have reported here ab initio calculations of lattice relaxation effects around 3d and 4sp substitutional impurities in Al. Our results resolve the discrepancy between experiment and previous first-principles calculations on the local magnetic properties of 3d impurities in Al. Moreover, the calculated shifts of the first NN and the macroscopic volume changes induced by the impurities are in good agreement with the experimental data obtained from EXAFS and lattice-parameter measurements.

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