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1991 J. Phys.: Condens. Matter 3 1957

(http://iopscience.iop.org/0953-8984/3/12/027)

J. Phys.: Condens. Matter 3 (1991) 1957–1959. Printed in the UK

LETTER TO THE EDITOR

The influence of the atomic-sphere approximation on the calculation of the vacancy formation energy of Li

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Received 29 January 1991

Abstract. By comparing the results of a plane-wave pseudopotential calculation and of a tight-binding LMTO calculation in the atomic-sphere approximation (ASA) it is shown that the application of the ASA overestimates the vacancy formation energy of Li by a factor of about 2.

The formation energy E_V^F of vacancies in metals is a very important quantity in investigations of the thermodynamic and kinetic properties of these materials (see, for instance, Seeger 1976). Increased computer power and improved computer algorithms have made it possible to perform realistic *ab initio* calculations of these quantities within the framework of the density functional theory. For simple metals such as Al (Gillan 1989, Finnis 1990) and Li (Pawellek *et al* 1991, Benedek 1990) the plane-wave pseudopotential method has been used, whereas for transition metals a full-potential—KKR—Green function method has been successfully applied (Dederichs *et al* 1991). Recently (Braun *et al* 1991), an attempt was made to calculate E_V^F for Fe by means of the tight-binding LMTO (Andersen and Jepsen 1984, Andersen *et al* 1986) supercell method in the atomic-sphere approximation (ASA), yielding a value that is a factor of 2.5 larger than the experimental one. The results were found to agree well as regards the number of k-points, the size of the basis set and the supercell size. Furthermore, both the local density approximation and a generalized gradient expansion for the exchange–correlation contribution (Perdew and Wang 1986) yielded very similar results, and it is known (Dederichs *et al* 1991, Pawellek *et al* 1991) that the structural relaxation around the vacancy (which was neglected in this calculation) changes E_V^F only moderately.

It was therefore assumed that the failure of the calculation may be due to an inadequate treatment of the non-spherical charge distribution, originating from the ASA. In the applied program, this approximation enters in two ways. On the one hand it represents an approximation for the potential. It has been shown (Andersen *et al* 1986) that for the case of Si the charge density obtained from an ASA potential is nevertheless in excellent agreement with the one obtained from a LAPW full-potential calculation. On the other hand, however, the non-spherical charge distribution calculated thus is spherically averaged over each ASA sphere again when calculating the total energy. Indeed it has been shown (Dederichs *et al* 1991) that this step in particular introduces a big error in the calculation of E_V^F in transition metals. The importance of the use of the

0953-8984/91/121957 + 03 $03.50

Table 1. The vacancy formation energy E_V^F of Li for different supercell sizes N, numbers n of k-points in the irreducible Brillouin zone and lattice constants a_0 of the perfect lattice (see the text). The last line represents the result of the pseudopotential calculation.

		E_V^F (eV)	
N	n	$a_0 = 3.53$ Å	$a_0 = 3.37$ Å
8	29	0.93	
	145	0.92	0.90
	256	0.92	
16	10	0.96	
	35	1.02	
	165	1.02	1.00
27	8	1.10	
	29	1.03	1.02
	72	1.03	
16	10	0.54	

non-averaged charge density for the evaluation of the total energy has been anticipated by Andersen *et al* (1986), but the order of magnitude of the effect for the calculation of E_V^F is nevertheless striking.

In this present letter we demonstrate that the ASA is also critical for the calculation of E_V^F in a simple metal such as Li. To do this we compare the results recently obtained from supercell calculations on the basis of the plane-wave *ab initio* pseudopotential method (Pawellek *et al* 1991) with our new supercell results from the tight-binding LMTO-ASA calculation (including combined correction terms and applying the local density approximation according to von Barth and Hedin (1972); basis set up to $l_{max} = 2$). The numbers are shown in table 1 for various supercell sizes (characterized by the number N of atoms in the supercell without vacancies) and various numbers n of k-points in the irreducible Brillouin zone. For the pseudopotential method the authors have calculated E_V^F both by allowing for volume relaxation of the supercell with vacancies and structural relaxation around the vacancy as well as without any relaxation (i.e. for a rigid lattice with the equilibrium lattice constant a_0 of the perfect lattice). Because in the LMTO calculation no relaxation has been performed, we compare the results for this latter case. In the present letter we consider supercell sizes of $N = 8$, 16 and 27, whereas for the pseudopotential calculation, sizes of $N = 16$ and $N = 54$ have been used. Our calculations are already rather well converged for $N = 16$, and we thus compare the results for this supercell size. A small problem arises because the theoretical equilibrium lattice constants a_0 of the perfect lattice are slightly different for the two calculations. Whereas the pseudopotential method yields $a_0 = 3.534$ Å, in good agreement with the experimental result of $a_0 = 3.491$ Å, the value from the LMTO-ASA calculation is $a_0 = 3.364$ Å, which is 3.6% smaller than the experimental value but which agrees well with the KKR muffin-tin result (Moruzzi *et al* 1978) of $a_0 = 3.388$ Å. It seems that in the case of Li the underestimated lattice constant as obtained in the two latter calculations does not indicate a failure of the local density approximation. It is more probably due to the above-mentioned approximations for the potential and the charge density. For comparison with the pseudopotential results we have performed some of the calculations inserting the theoretical equilibrium constant both of the pseudopotential and of the LMTO calculation.

Comparing the ASA results with the value of $E_V^F = 0.54$ eV for $N = 16$ as obtained by the pseudopotential method (Pawellek *et al* 1991), it becomes obvious from table 1 that the ASA overestimates the vacancy formation energy again by a factor of about 2, as in the case of transition metals (Dederichs *et al* 1991, Braun *et al* 1991). We believe that a considerable improvement may be obtained by using the non-spherical instead of the averaged charge density for the calculation of the total energy, as outlined by Andersen *et al* (1986) and Dederichs *et al* (1991). It should be noted that the best value for E_V^F from the pseudopotential calculation for a supercell size of $N = 54$ and full volume and structural relaxation is (Pawellek *et al* 1991) $E_V^F = 0.47$ eV, in good agreement with values deduced from experimental data (see Messer *et al* (1989), Schultz (1991) and references therein).

The computer code is based on a TB-LMTO-ASA program developed in the group of O K Andersen at the Max-Planck-Institut für Festkörperforschung in Stuttgart. The authors are indebted to P Braun, O Jepsen, P Dederichs, B Drittler, K-M Ho and C-T Chan for helpful discussions.

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