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Lattice distortion by impurities in MgB_2

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Abstract. The displacement components of B atoms around substitutional Mg-position impurities in MgB_2 were calculated *ab initio*. The size mismatch determines the dominant out-of-plane B-cage distortion in agreement with the observed (Al, Cu) cell volume changes in mixed crystals. A number of impurities can act as effective interband scatterers.

Key words: MgB_2, impurities, lattice distortion.

The discovery of the two-gap superconductor MgB_2 [1] has triggered investigations on a wide class of related binary borides and other related substances. Within these systems mixed structures of variable compositions can be built up. For this reason the investigations deal usually with highly-doped compounds. The influence of doping on electron [2,3] and phonon [4,5] spectra, structure [3,6–9], etc. of magnesium diboride has been considered. Concerning the superconductivity of MgB_2, the most impressive effect seems to be the depression (until the loss) by Al doping [3,10,11]. The effect has been explained by multiband theories of MgB_2 superconductivity [12,13].

Single impurity defect centres have not deserved so much attention. However, the scattering efficiency on defects is essential for the manifestations of the peculiarities of the two-gap superconductivity. The interband impurity scatteringis expected to quench the double-gap manifestation of the superconductivity and lower T_c through pair-breaking [14,15]. However, it is shown in [14] that substitutional impurities on B position by symmetry and on Mg position by the missing lattice distortion cause no noticeable scattering between the effective σ- and π-electron bands of the boron cage. In this aspect the calculation of lattice distortions by Mg-position defects in MgB_2 becomes topical. For a number of impurities (and Mg vacancy) such a calculation was made in [16] with the

conclusion that the calculated distortion magnitude will be sufficiently large to create measurable interband scattering. An analogous investigation was performed by the present author.

The *ab initio* calculations were carried out by using the VASP-package [17,18] with ultrasoft Vanderbildt-type pseudopotentials [19] supplied by [20]. It was supposed that the lattice distortion around Mg by a substituted impurity incorporates the displacement of 12 nearest-neighbour B atoms. The distortion centred on Mg is totally symmetric. However, for a central boron atom these displacements from regular positions lead to a broken symmetry. The defect quasimolecule with the in- and out-of-plane displacement components of B atoms is shown in Fig. 1. The supercell of $2 \times 2 \times 2$ bulk MgB_2 was used in calculations. Larger supercells, $4 \times 4 \times 2$ and $3 \times 3 \times 3$ choices, did not change the results given in Table 1 in the units of Å. Positive displacements are away from the centre.

The out-of-plane displacements dominate. The strong covalent bonding of B atoms in hexagonal rings prevents from any considerable in-plane displacements.

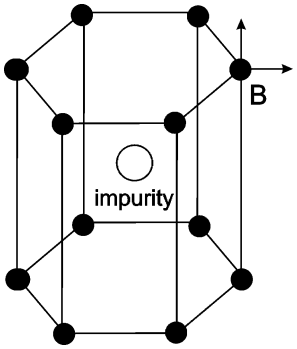

Fig. 1. The defect-centred quasimolecule. The in- and out-of-plane displacements of B atoms are shown.

Table 1. Lattice distortion components around Mg-position defects

Impurity	B out-of-plane displacement	B in-plane displacement	Ionic radius	Size defect
Mg^{2+}	0	0	0.72	0
Li^{+}	+0.002	–0.005	0.59	–0.13
Na^{+}	+0.038	+0.007	1.02	+0.30
K^{+}	+0.083	+0.020	1.51	+0.79
Ag^{+}	+0.042	+0.003	1.00	+0.28
Ca^{2+}	+0.024	+0.015	1.00	+0.28
Cu^{2+}	–0.006	–0.009	0.57	–0.15
Be^{2+}	–0.037	–0.015	0.27	–0.45
Al^{3+}	–0.033	–0.007	0.39	–0.33

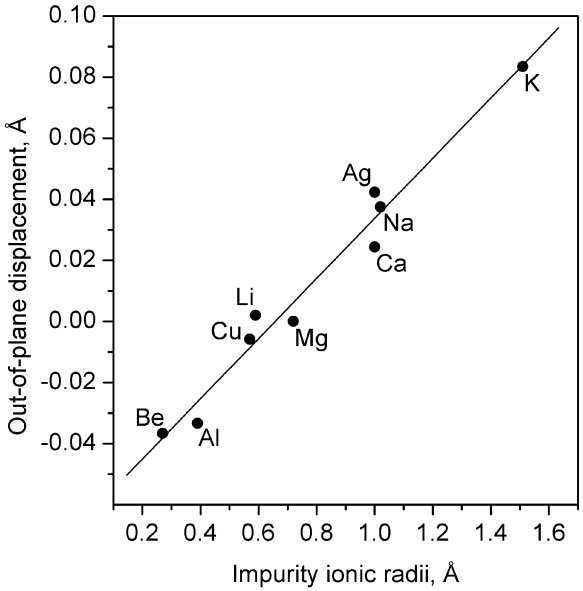

Fig. 2. B atoms out-of-plane displacements vs. ionic radii.

The same circumstance leads also to the domination of size mismatch over the charge defect influence in determining the distortion. This is illustrated in Fig. 2 where the out-of-plane displacements are given as dependent on the impurity Shannon crystalline ionic radii. In the case of Al [3] and Cu [9] the direction of the distortion agrees with the observed decrease in the cell volume with the impurity concentration. In the case of Ag doping [8] also diminished lattice parameters have been measured. The discrepancy with the present calculation can be explained by the small electron density distribution of Ag ion in positively charged configurations.

The calculation results agree in general with the ones given in [16] for commonly considered impurities. Correspondingly, it is expected that the impurities like Na, K, Be, and Al can act as sources of detectable interband scattering effects in magnesium diboride.

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Lisanditest põhjustatud võremoonutus MgB_2-s

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On arvutatud *ab initio* B-aatomite nihkekomponendid Mg-sõlme asenduslike lisandite ümber MgB_2-s. Aatomraadiuste erinevus määrab B-võrgustiku tasandivälise moonutuse kooskõlas jälgitud raku ruumala muutustega segukristallides. Rida lisandeid võib põhjustada efektiivset tsoonidevahelist hajutamist.