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BRIEF REPORTS

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Bonding properties of Li_2Ca and Mg_2Ca

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We previously determined that the monovalent intermetallic compound Na_2K has a negative formation enthalpy only because of relatively large energy band contributions which result in large multiatom covalent bonds. Here we calculate the bonding properties of the divalent Mg_2Ca and mixed valence Li_2Ca compounds crystallizing in the same $MgZn_2$ structure as Na_2K. [S0163-1829(96)06645-3]

The $MgZn_2$ structure, although not well known to physicists, is fairly ubiquitous; Pearson's Handbook[1(a)] lists 394 intermetallic phases crystallizing in that structure. Its strong bonding properties are exemplified by Na_2K. Sodium and potassium do not like to mix in the solid state. Less than 4.3% of Na will dissolve[2] in K and less than 0.73% of K will dissolve in Na. One might expect NaK to exist in the CsCl structure since it would leave the atoms in their body centered cubic environment while opening up energy gaps at the Fermi surface but neither it nor any other ordered compound, with the exception of Na_2K, is believed to exist at atmospheric pressure.[2] We[3] recently performed *ab initio* pseudopotential calculations for Na, K, NaK, and Na_2K. The formation enthalpy obtained for NaK was 7.5 meV/atom and for Na_2K was -16.1 meV/atom, consistent with the fact that Na_2K exists and NaK does not. Contour plots showed very large multiatom covalent bonds in Na_2K. A measure of this is the ratio of the maximum pseudocharge density to the average pseudocharge density in the crystal. This was calculated to be 1.68 for Na_2K while, for comparison, it was 1.13 in Na. We demonstrated that the volume dependent part of the energy favors each element at its own equilibrium density rather than a mixture of the two at some average equilibrium density. Furthermore, the bcc Ewald energy of point ions in the average electronic charge density exceeds that of Na_2K in the $MgZn_2$ structure with the same charge density. Thus the existence of Na_2K must be attributed to its strong covalent bonding.

After Ref. 3 was completed we became aware of the work of Hafner[4,5] who used linear response theory (LRT), i.e., he worked only to first order in perturbation theory. In addition to the errors inherent in LRT there appear to be several other shortcomings to his method. (1) The depletion hole due to the orthogonalization of the pseudofunctions to the core eigenfunctions was replaced by a point charge. (With the more modern norm conserving pseudopotentials the depletion hole averages out the rapid oscillations of the actual depletion hole but exists over the same region.) (2) This hole was estimated by summing the holes of single plane waves within the Fermi sphere; this results in an overestimate of the depletion hole because the pseudofunctions have a smaller amplitude in the core than a single plane wave. (3) The pseudopotential used was a variation of the Phillips-Kleinman[6] pseudopotential in which its ''arbitrariness'' is removed to achieve an arbitrary smoothness criterion. It is this ''arbitrariness'' which allows the eigenfunctions, which may be obtained from the pseudofunctions, to be orthogonal to the core functions. Without it the valence eigenfunctions do not become orthogonal to the core functions until enough plane waves have been used to converge the core functions. Because of the overestimate of the depletion hole and the concommitant renormalization of the charge density we are not able to directly compare Hafner's

TABLE I. Valence electron ionization energy $-E$ (in eV/atom) and lattice constants (in bohrs) of Mg, Li, and Ca compared with experimental values in parenthesis.

	Mg	Li	Ca
$-E$	24.1777 (24.18)	6.9429 (7.02)	19.6165 (19.82)
a	6.0551 (6.066)	6.820 (6.597)	10.639 (10.545)
c	9.7915 (9.845)		

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TABLE II. Lattice constants a and c (in bohrs), atomic position parameters χ and ζ (in units of a and c, respectively), the c/a ratio, ratio of compound to constituent volumes, and heat of formation $-H$ (in meV/atom) of Na_2K, Li_2Ca, and Mg_2Ca compared with (Hafner's results) and [experiment].

	Na_2K	Li_2Ca	Mg_2Ca
a	13.959 (14.400) [14.173]	12.087 [11.832]	11.825 [11.777]
c	22.966 (24.170) [23.225]	19.659 [19.370]	19.305 [19.124]
χ	0.1680 (0.1675) [0.170]	0.1688 (0.1635)	0.1688 (0.1680)
ζ	0.0627 (0.0635) [0.070]	0.0629 (0.0618)	0.0635 (0.0625)
c/a	1.645 (1.680) [1.639]	1.626 (1.634)	1.633 (1.623)
V/V_0	0.9771 [1.020]	1.0058 [1.012]	0.955 [0.946]
$-H$	16.1 (5.4) [10.9]	-31.6	57.3 [139]

charge density contour plots with our own. Nevertheless, we can compare the ratios of the strong covalent bond charge density inside a triangle of Na atoms to the weak K-K bond density and find them to be 1.85 for both calculations. This was unexpected because we[3] could demonstrate that the strong covalent bonding in diamond is a nonlinear effect and because when we made a LRT calculation for Ni_2K the ratio obtained was 1.53. In this Brief Report we calculate bonding properties of the divalent Mg_2Ca and mixed valence Li_2Ca to compare with the monovalent Ni_2K, with Hafner's results, and with experiment.

In Ref. 3 we averaged two different first principles pseudopotentials in order to obtain the experimental lattice constants for Na and K. Here we use a single pseudopotential obtained from an atom in which the valence electrons see a Hartree-Fock potential from the core and a local spin density exchange-correlation potential from themselves.[7] In Table I the calculated lattice constants and total energy of Mg, Li, and Ca are compared with experiment,[8] the experimental energy taken to be the sum of the cohesive and ionization energies. The results are somewhat disappointing for Li and quite good for Mg. The calculations are well converged using all plane waves with $(\mathbf{k}+\mathbf{K})<30$ Ry for Li and <40 Ry for everything else.[9] We sampled 330 (about half of which are occupied) and 182 $\mathbf{k}$ points in the $\frac{1}{48}$th Li and Ca irreducible Brillouin zone (BZ) wedges and 108 and 48 points in the $\frac{1}{24}$th BZ wedges of Mg and the $MgZn_2$ compounds.

We compare our results for Na_2K, Li_2Ca, and Mg_2Ca with Hafner's[4,5] and experiment[1,10] in Table II. The general principle that an intermetallic compound has a greater density than its constituents[11] is satisfied by all our calculated values of V/V_0 except for Li_2Ca where its value is consistent with the fact that our calculation yields a positive formation enthalpy. The experimental V/V_0 are greater than unity for Li_2Ca and Na_2K because the Li, Na, and K lattice constants are low temperature values[8] whereas the compounds[1(b)] are measured near room temperature. Hafner gives no information about his constituents and thus no values for V/V_0. In fact for Li_2Ca and Mg_2Ca he only gives χ and ζ, the atomic position parameters, for which there is no experimental data and c/a ratios which are in very good agreement with experiment. For Na_2K Hafner's zero temperature lattice constants are much larger than the room temperature experimental values and his c/a ratio much larger than experiment. His atomic position parameters χ and ζ (see Ref. 3 for a complete description of the unit cell) are close to ours. Experimental χ and ζ are given only for Na_2K and are not expected to be very accurate since they are obtained by fitting the x-ray data with a superposition of atomic charge densities. Hafner's heat of formation is smaller than ours and experiment, which we would have expected from LRT had his covalent bonds[5] not been comparable to ours.[3] Note that because of its covalent bonds, one would expect the Debye temperature of Na_2K to be larger than the average of Na and K; thus zero point vibrations should lower the calculated

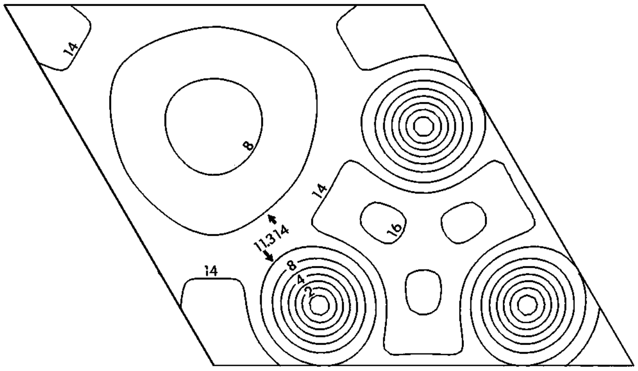

FIG. 1. Contours of constant charge density in millielectrons/bohr^3 in the Mg_2Ca (0001) plane containing a triangle of Mg atoms. Unlabeled contours are a factor of $\sqrt{2}$ larger than the nearest smaller contour.

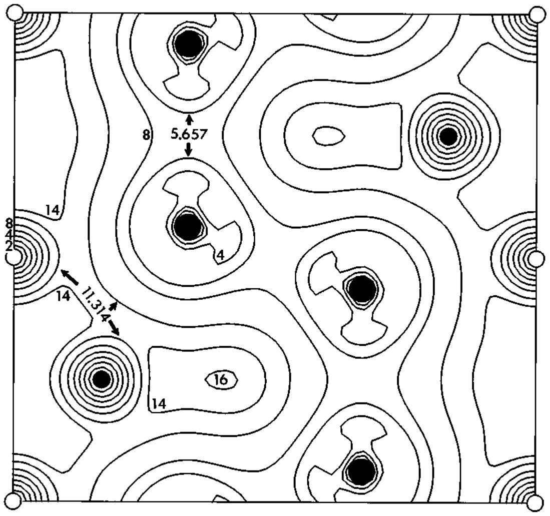

FIG. 2. Contours of constant charge density in the Mg_2Ca plane perpendicular to and containing the long diagonal of the (0001) plane. The open circles are edge Mg. The small black circles are triangle Mg and the large black circles are Ca atoms.

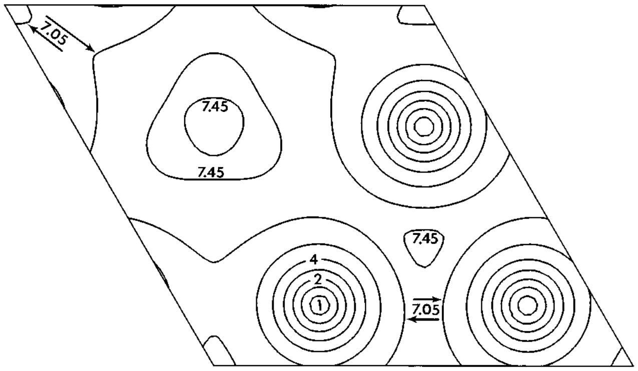

FIG. 3. Same as Fig. 1 but for Li_2Ca.

heats of formation by a few meV. We do not expect our Li_2Ca and Mg_2Ca results to be as accurate as those for Na_2K because their pseudopotentials were not adjusted to fit the constituent crystals. However, we did not expect their formation enthalpies to be in such poor agreement with experiment. The Mg_2Ca is off by 82 meV; although there is no experimental value for Li_2Ca, it is almost certainly negative. Thus for Li_2Ca our calculated values is off by at least 35 meV.

As the Li and Ca lattice constants are a few percent larger than experiment, so are they for Li_2Ca, while for Mg_2Ca they are only a fraction of a percent larger. Our values of χ and ζ do not vary much from crystal to crystal and are in general agreement with Hafner's except that his Li_2Ca χ is anomalously small. Our c/a ratios are all in fair agreement with experimental whereas his are in excellent agreement for Li_2Ca and Mg_2Ca and poor agreement for Ni_2K.

Figure 1 is a plot of constant pseudocharge density contours in the Mg_2Ca (0001) plane containing Mg triangles. The pseudocharge gets extremely small in the atomic cores, making the Mg triangle stand out. This triangle is capped by Ca atoms above and below the plane. There is a second triangle consisting of the corner Mg plus two Mg atoms outside the unit cell. This triangle is capped by Mg atoms along the edge of the cell. This can be seen in Fig. 2 where contours are plotted in plane perpendicular to and containing the long diagonal of the (0001) plane. The 8 millielectron/bohr^3 contour in the upper left half of Fig. 1 is the center of a Ca-Ca bond. The ratio of the largest contour in the Mg triangular bond to the Ca-Ca bond is 2.00, somewhat larger than the corresponding ratio of 1.85 in Na_2K. However, Hafner obtains 1.59 for the Mg_2Ca ratio, consistent with our assertion that LRT does not yield strong covalent bonds correctly. For Li_2Ca, because of the difference in atomic valence, we find this ratio to be 1.0 whereas Hafner obtains 0.74. Note that Hafner finds the pseudocharge density at the Li nucleus to be considerably larger than in the Li triangular bond. This is a consequence of his point charge depletion hole which is not included in his contour plots but should not have any effect on the ratio of charge densities far from atomic sites (see also Figs. 3 and 4).

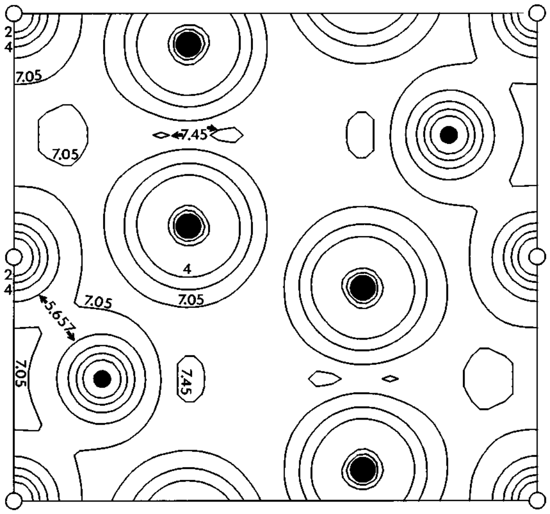

FIG. 4. Same as Fig. 2 but for Li_2Ca.

In conclusion, we have calculated bonding properties of Li_2Ca and Mg_2Ca and compared them and our previously calculated Na_2K results with Hafner's results and experiment. For Na_2K our charge density is similar to Hafner's, our lattice constants in much better agreement with experiment than his, and our formation enthalpies both in good agreement with experiment although ours is better if zero point vibrations are considered. Our Mg_2Ca results are in good agreement with experiment except for the heat of formation which is badly underestimated. Our Li_2Ca lattice constants are too large but their errors scale with those of Li and Ca. Our Li_2Ca heat of formation has the wrong sign but the magnitude of the error is probably not as large as for Mg_2Ca. We do not understand the reason for these errors and note that Hafner did not reveal his Li_2Ca and Mg_2Ca heats of formation. There are considerable differences between our charge density contour plots and those of Hafner for Li_2Ca and Mg_2Ca which we attribute to LRT being less applicable to these compounds than to Na_2K.

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