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First-principles electronic-structure approach for phase diagrams of binary alloys

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A combined statistical-mechanical and electronic-structure approach for the first-principles calculation of binary-alloy phase diagrams is presented. The grand partition function, constructed from volume-dependent internal energies obtained from local-density total-energy supercell calculations, permits the determination of the entropy and thus, in principle, all thermodynamic quantities. Illustrative results of first calculations for the Al-Li system show: (i) structural properties versus concentration in very good agreement with experiment and (ii) features on the Al-rich side of the phase diagram of the fcc solid solution which are important for alloy formation.

The calculation of phase diagrams of binary alloys, entirely from first principles, remains a long sought and important goal. A first, realistic attempt is found in Kikuchi's cluster method.[1] Starting with the evaluation of the entropy of characteristic clusters in an alloy, and supported by a calculation of the internal energy in a pair-potential approximation, the free energy and related quantities are obtained. This line of thought leads to the cluster variational method,[2] in which the evaluation of the energy is greatly improved. Later approaches to calculate alloy phase diagrams involve the alternative route of computer simulations.[3] In this paper, we follow the ideas of Kikuchi, but note that the energy and entropy are dependent quantities in thermodynamics. Therefore, we base our results on calculated electronic energies only, which is possible because the precision of total-energy calculations has increased rapidly.[4] Today, for example, structural properties of ordered compounds are well reproduced with state of the art density functional methods. Importantly, the recent enormous increase of computer power (both in speed and memory) allows the study of increasingly complex crystal structures with highly precise methods.

This paper presents a first step towards the calculation of phase diagrams of binary alloys starting from a local-density total-energy supercell formulation. After constructing the grand partition function which permits the determination of the entropy from our calculated total electronic energies, we are, in principle, able to obtain all thermodynamic quantities. While this approach faces the same problem as obtaining the entropy in cluster variational methods since one is presently restricted to relatively small unit cells, there are a number of important advantages: (1) solid solution and ordered phases can be calculated with the same numerical method and precision; (2) any sufficiently precise band-structure method can be used; (3) local environment effects such as charge transfer and chemical bonding are accurately described; (4) any crystal structure for which the total energy has been calculated can be easily included in the grand partition function; (5) the model is self-contained and only needs the total energies; (6) no fitting[5] and no breaking into pairwise interactions is necessary.

The calculation of a binary phase diagram necessitates the description of a solid solution, $A_{1-x}B_x$, for an arbitrary composition x. A standard approach to obtain the electronic structure of solid solutions is the single-site coherent-potential approximation based on a multiple scattering formulation of the Korringa-Kohn-Rostoker Green's function method (KKR-CPA).[6] This approach describes the solid solution in terms of a disordered alloy by embedding single atoms in an effective medium which depends on the composition of the alloy components. Very recently,[6] it even became possible to directly calculate total electronic energies by including self-consistently the effects of the different charge densities of the embedded atoms. In addition, the KKR-CPA has also been generalized to treat embedded clusters instead of single atoms.[7]

In contrast to the KKR-CPA, which describes the configurational average by an effective medium, we describe the solid solution by a thermodynamical average of ordered supercells including all configurations of A and B atoms in the supercell, and perform the configurational average of thermodynamic quantities using the grand partition function. We only apply our approach to obtain thermodynamic quantities, and do not evaluate electronic properties like energy eigenvalues and Fermi surfaces. We have tested this approach for a two-dimensional Ising model where the magnetization is equivalent to concentration. The results show that the Ising model for even small unit cells gives, qualitatively, the correct behavior of the specific heat as a function of temperature. The exact value of the transition temperature, of course, depends strongly on the size of the cells when they are small. In a real alloy, however, the dependence of the total energy upon composition is much more complicated than in the Ising model. Because our results for the *structural* properties of the fcc solid solution, $\mathrm{Al}_{1-x}\mathrm{Li}_x$, are in very good agreement with experiment we gain confidence in our thermodynamic model. Unfortunately, to our knowledge there are no experimental data available for the *energetics* which might serve as an even harder test for our procedure of configurational averaging. But the results obtained so far encourage the application of our model to attempt the calculation of a phase diagram.

In order to attain the thermodynamic limit one has to consider larger and larger cells inside the alloy, and in the end the effects of the boundary of this cell (i.e., contributions to the internal energy from bonds across the boundary) become unimportant. In our approach, we use periodic boundary conditions and thus force the structure of adjacent supercells to be identical; therefore, ordered structures are possibly favored when this approach is restricted to small supercells. Including larger supercells will probably lower the free energy of the solid solution and an ordered structure which is found to be stable in a calculation with small supercells might become unstable with respect to the solid solution. If any of the ordered structures associated with a small supercell is already unstable, it will remain unstable in a calculation with larger unit cells. Additionally, for small supercells the shape of the cells also becomes important. Our approach relies on the so-called local approximation[8] which was used for calculations of averaged densities of states of binary alloys.[9] Here, we go far beyond these previous supercell attempts by calculating total energies as a function of volume and calculate the average of quantities such as total electronic energies, equilibrium volumes and bulk moduli.

In order to perform the configurational average we follow the recipe for the construction of a grand canonical ensemble[10] in statistical mechanics. The grand partition function Z for a subvolume V of the total system of electrons, for both nuclei A and B, is given by

$$\mathcal{Z}(z_e,z_A,z_B,V,T)=\sum_{N_e}\sum_{N_A}\sum_{N_B} z_e^{N_e} z_A^{N_A} z_B^{N_B} Q(N_e,N_A,N_B,V,T) \ . \quad (1)$$

The canonical partition function Q for the temperature T ($\beta=1/kT$) is defined by

$$Q(N_e,N_A,N_B,V,T)=\mathrm{Tr}\exp(-\beta H) \quad (2)$$

and the fugacities z_i are related to the corresponding chemical potentials μ_i by $z_i=\exp(\mu_i\beta)$. The trace is performed over all states of the system with N_e electrons and N_A,N_B atoms in V. All thermodynamic quantities then follow after taking the limit V to infinity.

Even for a small volume V the summation in Eq. (1) is still formidable. At this point we make the following assumptions: First, we consider only neutral supercells. (This is certainly justified in a system where charge fluctuations are screened out in a distance short enough when compared to the size of the cells.) Second, we perform the total electronic energy calculations at $T=0$ and neglect finite-temperature effects on the electronic structure. (At present, this could be accounted for by including a semi-empirical term in the total energy of each configuration, derived from the specific heat as related to the densities of states at the Fermi energy. One expects, a significant influence of this effect only at very high temperatures.) Third, we invoke the Born-Oppenheimer approximation and at this point neglect any contributions from phonons. (Again, one could find a semi-empirical correction which is related to the Debye temperature which can be estimated through the calculated values of the bulk moduli. These terms are expected to have a pronounced effect only at temperatures above room temperature.[11]) Fourth, we do not vary the total number of atoms in a given volume. (Our calculations show that for four- and eight-atom fcc supercells the energy of formation of vacancies is very high, since in these small supercells there is insufficient freedom for relaxation. Vacancies have to be described with much larger supercells, which then implies that their effects on the phase diagram will be small.)

Taking into account all these assumptions, we express the partition function by

$$\mathcal{Z}(z_{\mathrm{eff}},V,T)=\sum_{\nu} z_{\mathrm{eff}}^{N_A(\nu)}\exp[-\beta E_\nu(V)] \ , \quad (3)$$

where E_ν is the volume-dependent total electronic energy for the νth configuration with $N_A(\nu)$ atoms of type A as obtained from our electronic-structure calculations. We left out the irrelevant factor z_B^N which does not depend on ν. Since we fix the total number of atoms, there only remains one effective fugacity, z_{eff}, which is determined by the average number of A atoms

$$\langle N_A\rangle = z_{\mathrm{eff}}\frac{\partial}{\partial z_{\mathrm{eff}}}\ln\mathcal{Z} \ . \quad (4)$$

The internal energy and the Helmholtz free energy are then derived from the statistical average of the quantities E_ν and from $\ln\mathcal{Z}$ in a standard way.[10] Further, since the calculated E_ν is a function of V, the Helmholtz free energy is a function of V. By minimizing the Helmholtz free energy one derives the T-dependent equilibrium volume and bulk modulus. Also the fugacity z_{eff} depends on T and V. The entropy is then obtained as the difference of the internal and the free energy divided by T. At this point the entropy is only configurational, since we have neglected the contributions of phonons and electronic excitations. It is thus clear that this statistical model only needs the total energies, $E_\nu(V)$, which one obtains from first-principles calculations; no additional information is required.

To demonstrate our method, we chose the Al-Li system because of its great technological importance and because it is a severe test of any new method. Al and Li are chemically rather different atoms due to their valency, size, and electronegativity. Hence, one expects sizable charge transfer and strong local environment effects due to the strong chemical bonding; this was confirmed in calculations for the ordered Al-Li Zintl phase.[12] To demonstrate our approach we focus on a simple case, namely on the Al-rich side of the alloy system and only calculate the solid solution for the fcc lattice. To cover the whole composition range of the phase diagram[13] all other important structures such as the ordered Al-Li Zintl structure must be considered as discussed below. Of great importance for the mechanical and elastic properties of Al-rich alloys is the formation of a metastable Al_3Li ordered phase (of $L1_2$ structure),[14] which is one of our supercell configurations. Therefore, it is also of physical interest to merely study the thermodynamic balance of fcc solid solution and Al_3Li by considering an ensemble of fcc supercells.

According to the local approximation[8] a supercell should be as close to a sphere as possible. With this in mind, we constructed an fcc supercell of twice the lattice spacing needed for one atom. Such a supercell contains eight atoms and in total 256 different configurations of A and B atoms have to be considered; however, because of symmetry, the number of inequivalent configurations can be reduced to 16. For all these 16 configurations we applied the self-consistent full potential linearized augmented plane-wave method[15] to obtain very precise total energies as a function of volume. A detailed discussion of the calculations and the convergence with the size of the supercell will be published elsewhere.

The entropy of mixing is shown in Fig. 1 as a function of T and composition, x. At very high temperatures (5000 K) we approach the limit of ideal mixing for eight-atom supercells,

$$S/k=-8[x\ln(x)+(1-x)\ln(1-x)] .$$

Close to $T=0$ we find dips at $x=0.25$, 0.5, 0.75, and 0.875 which reflects the interpolation between the most stable supercells. The entropy at $T=0$ is not zero because of symmetry degeneracy within the infinite periodic lattice; e.g., in the case of the $L1_2$ structure there are four different configurations with the same total energy and therefore $S/k=\ln(4)$. In the thermodynamic limit, however, this number is small compared to the total number of atoms N in the supercell and hence at $T=0$ the entropy per atom S/N will go to zero. A remarkable feature in Fig. 1 is the dip at $x=0.25$, due to the Al_3Li configuration with $L1_2$ structure, which remains even at 700 K.

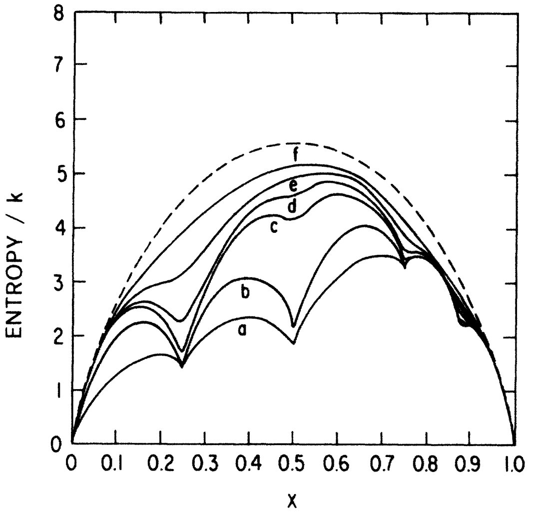

FIG. 1. Configurational entropy S/k of fcc $Al_{1-x}Li_x$ vs composition x as a function of temperature for $T=50$, 200, 500, 700, 1000, and 1500 K ($a,b,c,d,e,$and$f$, respectively). Dashed curve: $S/k=-8[x\ln(x)+(1-x)\ln(1-x)]$.

The equilibrium volume is a very important concept in the metallurgy of alloys. The Al-Li system provides an especially severe test for electronic structure calculations because of the strong deviations of the alloy volume from the linearly interpolated volume of Vegard's law. Although the equilibrium volume per atom of pure Li is 20% *larger* than the volume per atom of Al, mixing of Li to Al *shrinks* the volume [Fig. 2(a)] by up to 1% at $x=0.25$. The calculated absolute values of volume are 1% smaller than experiment (which is the usual error in local-density calculations). As seen from Fig. 2(a), the configurationally averaged relative volume change agrees well with the experimental results[16] for the solid solution. (It should be kept in mind that, at this stage, we have not included any contributions from lattice vibrations.) As shown in Fig. 2(b) the bulk moduli decrease linearly with increasing amounts of Li in very good agreement with measured values.[17] Hence, our averaging procedure gives good results for the structural properties of the fcc solid solution. We believe also that our calculated average total energies are reasonable quantities but we cannot pro-

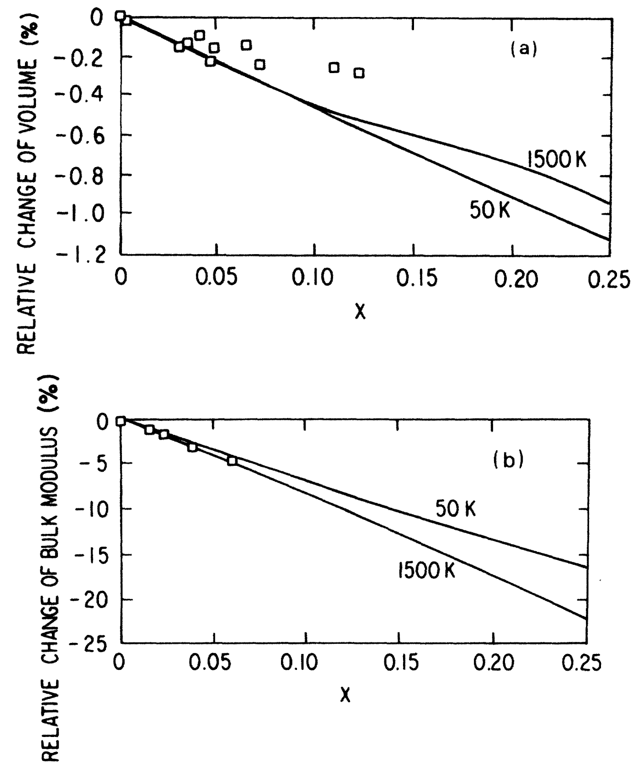

FIG. 2. Change of (a) equilibrium volume and (b) bulk modulus of $Al_{1-x}Li_x$ relative to fcc Al vs composition x for $T=50$ and 1500 K compared with the experimental values (Refs. 16 and 17, respectively).

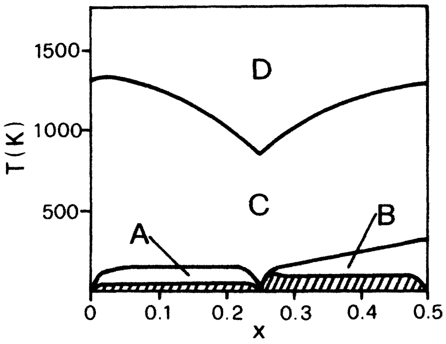

FIG. 3. Phase diagram as obtained by lines of maximum C_p as a function of temperature T for the fcc only $Al_{1-x}Li_x$ system. Here A indicates a mixture of mainly the Al and Al_3Li ($L1_2$ structure) supercells, B denotes a mixture of mainly $Al_3Li(L1_2)$ and $Al\text{-}Li(L1_0)$ cells, and C denotes another mixture of supercells. Finally, D denotes the region for which total disorder is reached at high temperatures. The hatched areas symbolize miscibility gaps.

vide a definite statement because no experimental data are available.

Figure 3 reveals the information pertaining to the phase diagram for the Al-rich side. As stated, the physics we consider is the thermodynamic competition between solid solution and some ordered phases represented by particular configurations in the supercell. To clarify our approach, we emphasize that our supercells are not individual phases but that a mixture of cells, as defined by Eqs. (3) and (4), is used to get the lines shown in Fig. 3. These lines in Fig. 3 are defined by maxima in the specific heat at zero pressure as a function of T for a fixed composition. It appears to be a sensible way to define phase boundaries for *finite* systems, although this procedure might not be able to distinguish between first- and second-order phase transitions. The consequences of our phase diagram for alloy formation will be discussed elsewhere but it should be noted that the occurrence of an $Al_3Li(L1_2)$-rich phase (phase A in Fig. 3) and a miscibility gap agree well with experiment. A quantitative comparison of the phase diagram is not meaningful because (i) we have not included lattice vibrations or any theory of melting and (ii) the Al-Li Zintl phase has to be included for a complete equilibrium phase diagram on the Al-rich side. Within our thermodynamical model including the (Al-Li) Zintl result (and others) is very easy but for a realistic description of the experimental equilibrium phase diagram well-known nonstoichometry effects (vacancies and antisite atoms), especially in the Al-Li Zintl phase, have to be calculated. All this, however, goes beyond the aim of this paper.

The hatched areas in Fig. 3 represent miscibility gaps. At compositions and temperatures in this range the free energy is lowered by separating the system into two phases of different compositions. On the other hand, in the area labeled A we need a mixture of mainly two types of *cells* [pure Al and $Al_3Li(L1_2)$] to maintain the prescribed composition according to Eq. (4). This is a microscopic mixture, indicating that one has a solid solution with a high degree of short-range order. Region B can be described in a similar way by a mixture of $Al_3Li(L1_2)$ and $Al\text{-}Li(L1_0)$. In region C we find a more complex mixture of supercells, while in region D total disorder is reached at high temperatures.

The results obtained in this paper for the Al-rich side of the phase diagram appear to be encouraging. Since we are limited to small supercells, the present method should only be applied to regions in experimentally known phase diagrams where complicated ordered structures do not occur and where concentration waves with long wavelength are not important. If a system is known to have only short-range interactions, the use of *small* supercells is justified. Even in the case where long-range interactions do exist, however, small supercells can still give good results, as long as the long-range interactions do not stabilize complex ordered structures with large unit cells. Therefore, at present, experimental phase diagrams have to guide the applications of our approach (as for many other approaches). Experimentally, there are no ordered structures (stable or metastable) with more than four atoms in the unit cell for Li concentrations less than 50%. Therefore, we can expect to obtain good results with our eight-atom supercells in this regime. Also, our four-atom supercell calculations for the free energy give very similar results for the Al-rich side as compared to the eight-atoms case. The Li side of the phase diagram is more complicated and in order to describe the observed Al_2Li_3 and Al_4Li_9 ordered structures we need larger supercells. While we need to restrict ourselves at this stage to regions of phase diagrams where only simple ordered structures are known to be important, it appears that our combined statistical mechanical and electronic-structure method shows promise for studying alloy phase diagrams from first principles. In that respect we join the efforts to combine quantum and statistical methods from a first-principles point of view,[18] a problem for which there is yet no simple solution.

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