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Ising-like Description of Structurally Relaxed Ordered and Disordered Alloys

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We demonstrate the ability of generalized Ising-like cluster expansions to describe the energetics and thermodynamics associated with large atomic displacements in alloys. Although the expansion is constructed only from the energies of a few (small-unit-cell) ordered structures, it provides

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VOLUME 75, NUMBER 17 PH YS ICAL REVIEW LETTERS 23 OcTQBER 1995

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20 E

15

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i:I ~ 0 Direct, 1000-atom/cell—

axed)—

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1.0

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0.8 0.6 0.4

LRO parameter, q

0.2 0.0

FIG. 3. Formation energies of Ga05lno5P alloys as a function
of LRO parameter, g. Directly calculated results from 1000-atom simulations are shown as are the results of the k-space CE, using as input only rl = 1 energies. rl = 1 (0) indicates complete and perfect order (randomness).

composition-temperature phase diagram (open squares of
Fig. 4). Here we apply the Monte Carlo algorithm to DHOLE[(5;)] with only spin degrees of freedom, finding the CE prediction for the phase diagram (solid line in Fig. 4). The phase diagram computed using unrelaxed en-ergies AHd;««H5,); V; (R;) = 0] is also shown for com-
parison. In the Monte Carlo simulations using the CE, a
cell of 1024 atoms with periodic boundary conditions was used. Simulations were performed in the Grand Canoni-cal ensemble, 200—500 Monte Carlo steps were used for equilibration, and subsequently, averages were taken over 1000 steps. For each temperature, phase boundaries were determined from the discontinuity in concentration ver-
sus chemical potential. The effect of relaxation is dras-

tic, as it lowers the miscibility gap temperature TMG by —2800 K. On this scale, the direct calculation and CE

4000

Direct (Unrelaxed)
Direct (Relaxed + Vibrations)
k-space CE (Relaxed)

3000 0
0

0
0
cd 0
(p 2000

CL 0
E
1000

0
0
5 Tf 17ter, (p

0

temperature

0.