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Bond-length relaxation in pseudobinary alloys

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The bond-length relaxation in pseudobinary alloys can be predicted by a simple radial force model. In tetrahedral structure alloys the bond-length deviation of the solute in the dilute solution is a quarter of the bond-length difference between the two components. This result agrees with the experimental work done on the $Ga_{1-x}In_xAs$ system performed by Mikkelsen and Boyce.

In calculating pseudobinary alloy properties, the nearest-neighbor distance is a very important parameter. For many years people have used the virtual-crystal approximation (VCA) which assumes that all atoms occupy the average lattice positions. In 1982 Mikkelson and Boyce used extended x-ray-absorption fine structure (EXAFS) to study the atomic scale structure of the $Ga_{1-x}In_xAs$ system.[1] They found that the Ga–As and In–As bond lengths did not follow the VCA; instead, they only slightly deviated from their natural bond lengths even in the dilute solutions, and the magnitude of the bond-length deviation at the dilute limit was about a quarter of the difference of the natural bond lengths of the two components (GaAs and InAs). These results can be explained by a simple radial force constant model in which the weaker angular forces are neglected.

Consider a compound GaAs in which one of the Ga atoms is replaced by an In atom. This configuration represents the dilute limit of In-As in a GaAs host (see Fig. 1). In this configuration, four In–As bonds are identical and the tetrahedral symmetry is preserved at the In atom. We regard any difference between Ga and In as a first-order difference. Let us call d_{GaAs} the natural bond length of the host and K the stretching force constant for the host. Adding In will change K by an amount we regard as first order, but that alone will not give the distortion. However, because the natural bond length of InAs, d_{InAs}, is larger than d_{GaAs} by a first-order amount the As atoms around the In impurity move outward by a first-order distance; we hold the second neighbors fixed and to first order can take K to be the value for the host. Let us call u the outward relaxation displacement of the As. Then Δd_{InAs}, the amount that the final In–As bond length deviates from d_{InAs}, is $d_{\mathrm{GaAS}}-d_{\mathrm{InAs}}+u$. The bond lengths of the neighboring Ga-As are decreased by $-u\cos\theta$ equal to $-u/3$ to first order. The energy associated with the distortion is

$$E=4[(k/2)(d_{\mathrm{GaAs}}-d_{\mathrm{InAs}}+u)^2+3(k/2)(u/3)^2] \ .$$

By minimizng the energy with respect to u, we obtain

$$u=\tfrac{3}{4}(d_{\mathrm{InAs}}-d_{\mathrm{GaAs}}) \ ,$$

or the deviation of the In–As bond length

$$\Delta d_{\mathrm{InAs}}=\tfrac{1}{4}(d_{\mathrm{GaAs}}-d_{\mathrm{InAs}}) \ .$$

Similarly, the bond-length deviation of dilute Ga-As in an InAs host is

$$\Delta d_{\mathrm{GaAs}}=\tfrac{1}{4}(d_{\mathrm{InAs}}-d_{\mathrm{GaAs}}) \ .$$

This predicts exactly Mikkelsen and Boyce's result.[1] Note that this displacement leaves all metallic atoms in their original sites; only the As atoms move. To a good approximation this is true in the concentrated alloy, where the metal atoms form a face-centered-cubic lattice of the weighted average lattice parameter and the As atoms move to fit local bond lengths.

One can apply this principle to the rocksalt-structure systems, e.g., $K_{1-x}Rb_xBr$, and predict that the bond-length deviation of the solute in the dilute solution is half of the

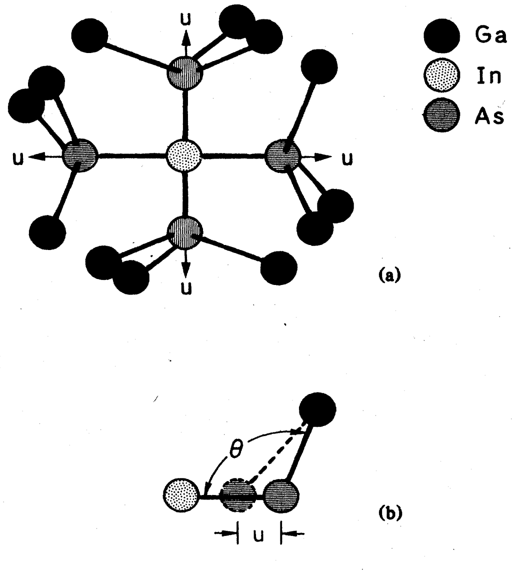

FIG. 1. (a) An indium atom substitutes for gallium in GaAs; the tetrahedral symmetry is preserved at the In atom. (b) The displacement of As atoms, u, results in the Ga–As bonds being decreased by $u\cos\theta$. The In–As bond lengths are varied by $d_{\mathrm{GaAs}}+u-d_{\mathrm{InAs}}$.

difference between the two components:

$$\Delta d_{\mathrm{KBr}} = \frac{1}{2}(d_{\mathrm{RbBr}} - d_{\mathrm{KBr}}) \ ,$$

$$\Delta d_{\mathrm{RbBr}} = \frac{1}{2}(d_{\mathrm{KBr}} - d_{\mathrm{RbBr}}) \ .$$

However, because of the lattice geometry, the approximation that all the cations stay in their original sites might not be as good. In rocksalt structure, the restoring force on the displaced first neighbor results from the atom right behind the first neighbor; one would expect that the relaxation extends more than one interatomic distance and the value of the bond-length deviation would be somewhat smaller than what is predicted by this model. This agrees with the experimental result.[2]

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[1] J. C. Mikkelsen, Jr. and J. B. Boyce, Phys. Rev. B **28**, 7130 (1983).

[2] J. B. Boyce and J. C. Mikkelsen, Jr., Bull. Am. Phys. Soc. **29**, 271 (1984).