Universality of Physical Properties of Disordered Alloys

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A simple idea of statistical independence of thermal and chemical disorders in perfectly disordered solid solutions suggests the universality of their thermodynamic and transport properties at high temperatures. Our experimental data on diagrams of state, heat capacities, and resistivities of mixtures of heavy alkali metals convincingly support this idea. A generalization of Lindemann's criterion of melting for disordered alloys has been suggested and applied to a variety of mixtures.

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Diagrams of state of binary mixtures of heavy alkali metals K, Rb, and Cs exhibit deep minima with congruent melting at their deepest (azeotropic) points[1] (Fig. 1). These points for $\mathrm{Rb_{0.5}Cs_{0.5}}$, $\mathrm{K_{0.5}Cs_{0.5}}$, and $\mathrm{Rb_{0.667}K_{0.333}}$ offer the rare opportunity to crystallize these alloys from their liquid state without any trace of separation. We have used them to produce samples of perfectly disordered mixed crystals.

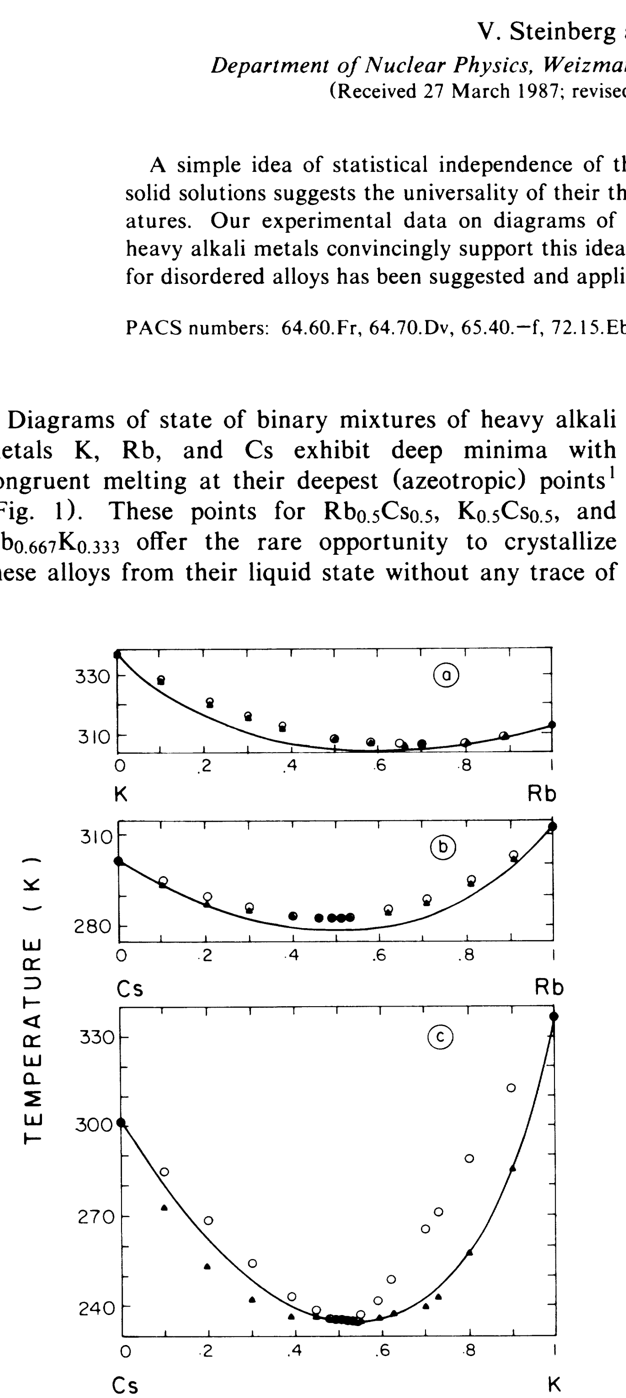

FIG. 1. Diagrams of state of alkali-metal mixtures. The two kinds of points are experimental data (Ref. 1) on freezing and melting temperatures of alloys at corresponding concentrations. The lines are our calculation in accordance with Eq. (4).

The heat capacity of c_p of $\mathrm{K_{0.5}Cs_{0.5}}$ and electrical resistivities of $\mathrm{K_{0.5}Cs_{0.5}}$, $\mathrm{Rb_{0.5}Cs_{0.5}}$, and $\mathrm{Rb_{0.667}K_{0.333}}$ have been measured together with their melting temperatures T_m. The experimental technique and sample preparation already have been reported elsewhere.[2,3] The structures, molar volumes, and elasticities of the alloys are similar to or close to additive in the corresponding properties of the pure metals.[4,5] However, their melting temperatures, heat capacities, and electrical resistivities are drastically different (see Figs. 1, 3, and 4).

The amazing result of this study is that these differences can be explained by one simple idea of *statistical independence of thermally induced vibrational disorder of an "averaged" lattice from temperature-independent disorder due to size difference of the constituent atoms.* Our explanation is valid at high temperature ($T > \Theta$, where Θ is the Debye temperature). We

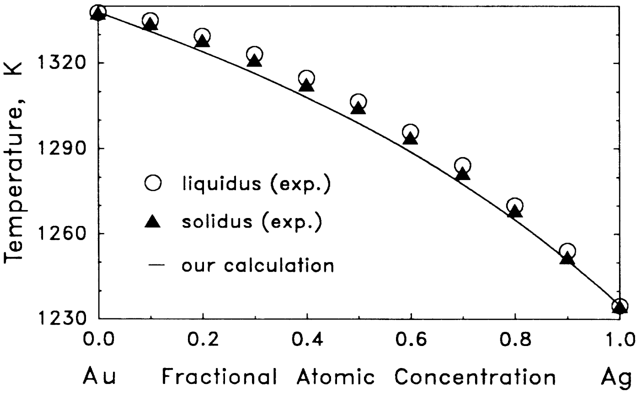

FIG. 2. Diagram of state of Au-Ag alloy. The solid line represents our calculation; the two kinds of points are experimental data on the freezing and melting.

have used this idea not only for interpretation of our own data but also to describe some experimental results already known from the literature.[6] It gives a satisfactory quantitative description of phase diagrams for different disordered alloys (see, for example, Fig. 2). The physical properties of these alloys also exhibit a trend to universality, although just on the qualitative level, mostly as a result of imperfection of the samples.

Let us consider the binary solid solution with atoms of two different sizes randomly distributed over a common lattice of the same symmetry as that of the pure components. It is known[7] that an x-ray pattern of such a crystal can be interpreted as a result of superposition of two different patterns corresponding to two different types of disorder.

A mixed lattice which includes atoms of different nature at high temperature produces the same diffraction pattern as would be produced by a simple lattice homogeneously occupied by "averaged" atoms.[7] Thermal motion will cause a reduction of the Bragg-peak intensity which is proportional to the Debye-Waller factor $D=e^{-2W}$, where W is dependent upon a relative mean square uncertainty of equilibrium positions of those "averaged" atoms[8]:

$$W \propto x_t^2 = \frac{\langle(\Delta r)_t^2\rangle}{d_{12}^2} = \frac{9\hbar^2 T}{M_{12} k_B \Theta_{12}^2 d_{12}^2}. \tag{1}$$

Here $M_{12}=p_1M_1+p_2M_2$ ("average" mass of atom of the mixture with concentrations p_1,p_2), $\Theta_{12}^{-2}=p_1\Theta_1^{-2}+p_2\Theta_2^{-2}$ ("average" Debye temperature[9]), and $d_{12}=p_1d_1+p_2d_2$ (average nearest-neighbor distance[4]). Meanwhile, a size disorder emerging from a mismatch of atoms will manifest itself like a "frozen heat motion" and introduces an additional reduction[7] $D'=e^{-2W'}$ dependent upon a relative mean square uncertainty of the atomic size: $x_{12}^2=4\langle(\Delta r_{12})^2\rangle/d_{12}^2$. The intensity which is lost by the diffraction peaks because of size dispersion of the scatterers appears in a diffuse background caused just in the same way as happens because of uncertainty of the scatterers' position from thermal motion. Indeed, such a strong, temperature-independent, diffuse background has been observed on the x-ray pattern of our $K_{0.5}Cs_{0.5}$ mixed crystal.[10] The simplest assumption is that these two scattering factors are uncorrelated. Therefore, for a perfectly disordered mixed crystal the total reduction of the integrated intensities of the Bragg peaks can be presented as a generalized Debye-Waller factor $D_g=DD'$. This assumption was used first for interpretation of x-ray patterns of disordered solid solutions by Guinier.[7]

Let us introduce now a corresponding definition of a generalized mean square uncertainty of the atomic coordinate in the mixed crystal, which Guinier has never used:

$$x^2 \equiv \frac{\langle(\Delta r)^2\rangle}{d_{12}^2} = \frac{\langle(\Delta r)_t^2\rangle}{d_{12}^2} + \frac{4\langle(\Delta r_{12})^2\rangle}{d_{12}^2}. \tag{2}$$

Generally speaking, a symmetry-dependent numerical coefficient can multiply the second term. This definition means that one can postulate a new generalized Lindemann criterion of melting for disordered alloys analogous to that of the pure substances[8] as a natural limitation of the relative atomic-coordinate uncertainty within the crystalline state. It is clear that such a criterion will set up a limit not only for the vibration amplitude but for the size dispersion in a real mixed crystal as well.[11]

Combining (1) and (2), one has to assume, as has been done for the pure crystals,[8] that the total relative mean square uncertainty should be always below a certain value x_m^2:

$$\frac{9\hbar^2 T}{M_{12} k_B \Theta_{12}^2 d_{12}^2} + \frac{4\langle(\Delta r_{12})^2\rangle}{d_{12}^2} \leq x_m^2, \tag{3}$$

which gives the following equation for the melting temperature:

$$T_m = \frac{M_{12} k_B \theta_{12}^2 d_{12}^2}{9\hbar^2} x_m^2 \left[1 - \frac{4\langle(\Delta r_{12})^2\rangle}{x_m^2 d_{12}^2}\right]. \tag{4}$$

The next crucial step in our approach is the calculation of a second term in Eqs. (2) and (4) based on a concept of a temperature-dependent hard-sphere diameter of an atom.[12]

The recent development of density-functional theory confirms both the validity of the Lindemann criterion for freezing of a hard-sphere liquid[13] and the applicability of the hard-sphere model to freezing of binary mixtures.[14] Therefore we define the average uncertainty of atomic radius as $\langle(\Delta r_{12})^2\rangle = p_1p_2(r_1-r_2)^2$, where r_1 and r_2 are temperature-dependent hard-sphere radii taken from Ref. 12.

One can see from Fig. 1 that the melting temperatures calculated from Eq. (4) agree with the experimental

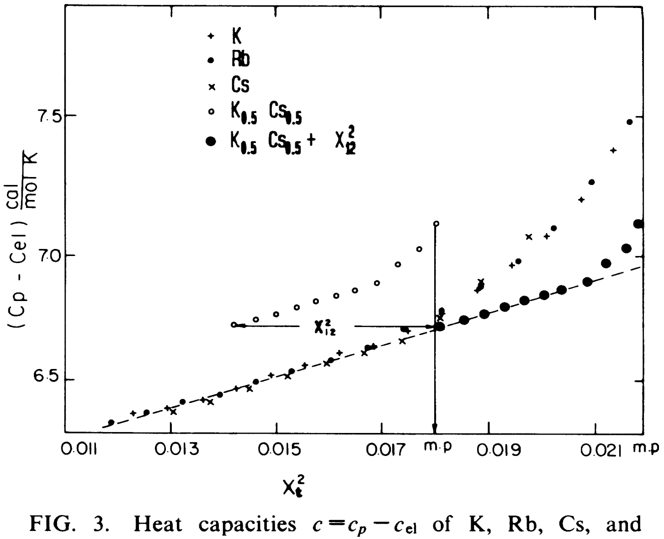

FIG. 3. Heat capacities $c=c_p-c_{el}$ of K, Rb, Cs, and $K_{0.5}Cs_{0.5}$ vs mean square uncertainty x_t^2.

values[1] which we have also checked in our own measurements. This calculation fits the experimental data much better than the corresponding calculation based on pseudopotential theory.[5] In Fig. 2 one also can see that Eq. (4) works well for Ag-Au solid solution. Here the size dispersion is small and the melting almost exactly corresponds to a prefactor in the Eq. (4).

In Fig. 3 the data on the lattice heat capacities $c = c_p - c_{el}$ (c_{el}, the electron heat capacity, was subtracted from the measured c_p following MacDonald, Shukla, and Kahaner[15]) of pure K, Rb, and Cs are plotted together with $K_{0.5}Cs_{0.5}$ as functions of the parameter x_t^2 characterizing only the thermally induced disorder. At high temperature [see Eq. (1)] this parameter is almost proportional to T.[8] One can see that c of a pure metal is close to a linear universal function of x_t^2 till it reaches about $0.8T_m$. Then the function ceases to be linear (because of vacancy formation and/or strong deviation from harmonicity) but does not cease to be universal.[16] The data on $K_{0.5}Cs_{0.5}$ appear to be strongly separated from this line. However, if instead of x_t^2 one uses the generalized parameter x^2 defined by Eq. (2), our experimental points for $K_{0.5}Cs_{0.5}$ fall on a continuation of the universal curve for pure metals with an accuracy better than 1%. The melting point of the alloy also excellently corresponds to the same value of the Lindemann constant $x^2 = x_m^2$ (see Fig. 1).

The interpretation of our resistivity data (Fig. 4) is even more striking. The mean free path of an electron is defined in the deformation-potential approximation[8] by a local relative fluctuation of volume Δ ($\Delta \equiv \Delta V/V$): $\lambda^{-1} \simeq N\bar{\sigma}\langle\Delta^2\rangle$ (N is a number density and $\bar{\sigma}$ a total cross section). We can again use Eq. (2) rewritten to correspond to relative fluctuation of volume under the same assumption of statistical independence of thermal fluctuations of scatterers from their size dispersion. It leads to the well-known Matthiessen's rule[17]:

$$\rho = \frac{\hbar}{e^2}\frac{k_F}{n}\left[\frac{1}{\lambda_t} + \frac{1}{\lambda_{12}}\right]. \tag{5}$$

Here k_F is the Fermi wave number and n is the electron concentration. The electron's mean free path due to thermal lattice vibrations λ_t has already been calculated[8]: $\lambda_t^{-1} \simeq n\bar{\sigma}\frac{2}{3}x_{tm}^2 T/T_m$, where x_m^2 is the value of x_t^2 at the melting point of the alloy.

Simple calculation of a term defined by the size difference in Eq. (5) gives for the bcc structure

$$\lambda_{12}^{-1} = n\bar{\sigma}\tfrac{9}{32}p_1p_2(V_1 - V_2)^2/(p_1V_1 + p_2V_2)^2. \tag{6}$$

Atomic volumes V_1 and V_2 should be calculated in this case from radii corresponding to electron scattering.[18] One can notice that Eq. (6) gives a generalization of the well-known Nordheim rule (and Mott's rule as its consequence), namely, that the residual resistivity of an alloy constituted from elements with close atomic volumes is proportional to p_1p_2.[19]

To single out the size-dependent effect, we have plotted reduced resistivities ρ/ρ_m (ρ_m is the resistivity of a crystal at T_m) versus reduced temperature T/T_m:

$$\frac{\rho}{\rho_m} = \frac{\frac{2}{3}x_{tm}^2 T/T_m + \frac{9}{32}p_1p_2(r_1^3 - r_2^3)^2/(p_1r_1^3 + p_2r_2^3)^2}{\frac{2}{3}x_{tm}^2 + \frac{9}{32}p_1p_2(r_1^3 - r_2^3)^2/(p_1r_1^3 + p_2r_2^3)^2}. \tag{7}$$

In Fig. 4 one can see the agreement of our experimental data with the universal Eq. (7). The deviation of the measured points from Eq. (7) at higher temperature for all alloys, but especially for $Rb_{0.667}K_{0.333}$, is easily explained by a premelting phenomenon. This phenomenon affects the two other alloys in a much milder way because of their lower melting points. From Fig. 3 one can see that the premelting phenomenon for the low-melting alloy $K_{0.5}Cs_{0.5}$ is much smaller than for pure elements (and for the high-melting alloy K-Rb correspondingly).

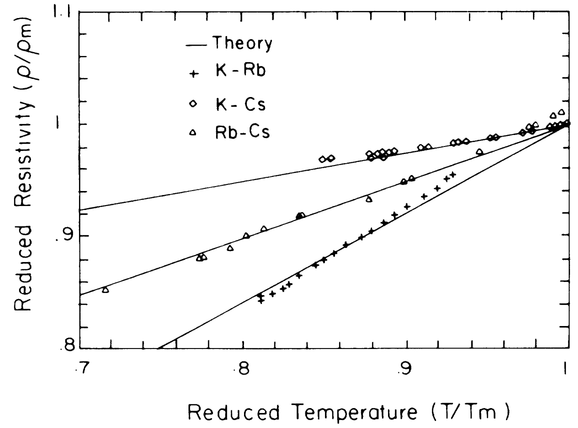

FIG. 4. Reduced resistivities of alkali-metal alloys below their melting points.

Thus, we have demonstrated that the idea of statistical independence of thermal fluctuations and size dispersion, when applied to alkali-metal disordered alloys, leads to impressive quantitative universality in macroscopic properties. The key point of our experimental study is the possibility of preparing fully disordered mixed crystals at the azeotropic points of diagrams without a trace of partial ordering or inclusions of other phases. In principle, such a high degree of disorder is achievable for any concentration of a disordered alloy. However, practically, it requires extremely long annealing times, maybe as long as several months.[20] Nevertheless, when the same idea is used to describe various binary (Au-Ag, Ar-Kr, and other) as well as ternary (K-Rb-Cs) alloys, the diagrams of state show remarkable agreement with experimental

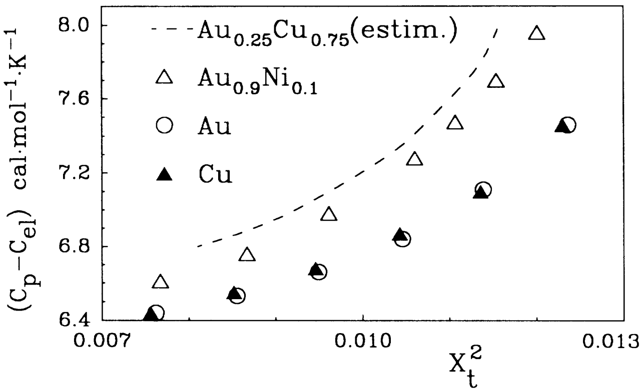

FIG. 5. Heat capacities $c=c_p-c_{el}$ of Cu, Au, and $Au_{0.9}Ni_{0.1}$, $Au_{0.25}Cu_{0.75}$ vs mean square uncertainty x_t^2. The experimental data on Cu, Au, and $Au_{0.9}Ni_{0.1}$ are taken from Ref. 6. The dashed curve is assumed in accordance with our evaluation of the poor data of both Refs. 6 and 22.

data taken from literature.[21] Unfortunately, the experimental data on heat capacity and resistivity are much more sensitive to the quality of samples, and they scatter too much to be conclusive. Nevertheless, in spite of the low accuracy of published data at high temperatures, the positive deviations from additivity (Kopp's rule) of c_p analogous to Fig. 3 has been reported for many disordered systems[6] (Au-Cu, Cu-Mg, Au-Zn, Au-Ni, Cu-Ni, Cu-Zn, Pb-In, and In-Tl). Moreover, our analysis of disordered alloys with the same fcc structure ($Au_{0.25}Cu_{0.75}$ and $Au_{0.9}Ni_{0.1}$—Fig. 5) shows a qualitatively correct trend: The more the size dispersion, the higher the positive deviation from Kopp's rule. The values of x_t^2 for fcc metals differ from those in Fig. 3 in accordance with the difference in symmetry.

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$$\Delta c_{vac} \propto (\Delta E/k_B T)^2 \exp(-\Delta E/k_B T),$$

where ΔE is a formation energy, is a universal function of a dimensionless parameter $\Delta E/k_B T$. Since the total heat capacity remains also a universal function of the parameter x_t^2 (see Fig. 2) one has to expect proportionality between these two parameters: $k_B T/\Delta E \propto x_t^2$. Using Eq. (1) we see that this relation coincides with the known expression for the vacancy formation energy $\Delta E \propto (3\hbar)^{-2} M k_B \Theta^2 \sigma^2$ [K. Mukherjee, Philos. Mag. **12**, 915 (1965)].

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