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Extensive Interstitial Solid Solutions of Metals in Metals*

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A new type of metallic solid solution has been prepared in which ≤12.5 at.% of comparatively small metal atoms (Cu) fill interstitial sites in a host metal composed of larger atoms (Y). At higher solute concentrations, both interstitial and substitutional sites are occupied. These solid solutions are metastable; they were formed by ultrarapid quenching from the liquid.

Two types of binary, crystalline, metallic, solid solutions are known: substitutional and interstitial. Extensive terminal (primary) substitutional solid solutions (i.e., with >5-at.% solute) are formed between metals similar in size and electronegativity; generally, atomic radius differences of <15% are required.[1] The correlation of apparent size changes (departures from a "Vegard's law" straight line) in these solid solutions is complex.[2,3] Interstitial terminal solid solutions may be formed by small nonmetal atoms such as H, B, C, and N as solutes in metallic solvents if the size ratio $r/R<0.59$[4]; here r and R are the solute and solvent radii, respectively. Interstitial solid solubility in twelve-coordinated metals [$A1$ (ccp) and $A3$ (hcp) types] is much larger than in metals of the $A2$ (bcc) type because of the size of the available interstitial sites; e.g., the maximum solubility of C in γ-Fe ($A1$ type) is ~80 times larger than in α-Fe ($A2$ type). Interstitial solid solutions of metals in metals have never been directly demonstrated by lattice-parameter and density measurements; however, there is good indirect evidence for at least partial interstitial solubility of noble metals in In,[5] Sn, and Pb[6,7] (diffusivity,[5-7] hardness[8]), Au in La[9] (diffusivity), Au and Co in Pr[10] (diffusivity), and Co in In[11] (recoil-free fraction in Mössbauer measurements); for a recent review, see Anthony.[12] In these systems, the solid solubility of the small species in the large one is typically very low (e.g., ≤0.02 at.% Au in Pb; 0.2 at.% Ag in Pb[13]) and the fraction of interstitial to substitutional atoms has not been determined.[12] Extensive interstitial metal-metal solid solutions are not known.

Evidence for the existence of the missing type of solid solution has now been found in metastable yttrium-copper alloys and is reported in this Letter. Y-Cu alloys with up to 20 at.% Cu were prepared as foils of 0.1 to 5 μm thickness by ultrarapid quenching from the melt (at cooling rates of $\sim 10^8$ °C/sec) using the "splat-cooling" technique.[14-16] The experimental details of alloy preparation, quenching, and study by x-ray diffraction follow closely those reported earlier.[17,18] In addition, the densities of quenched foils were measured by weighing 10-15-mg samples in air and toluene with an electromicrobalance. The observed densities have a standard deviation of ±0.086 g/cm^3; the atomic volumes found by x-ray measurements have a standard deviation of ±0.043 Å^3.

In yttrium-rich Cu alloys at 20°C, α-Y solid solution (<1 at.% Cu) is in equilibrium with YCu (CsCl-$B2$ type).[13] By rapid quenching, formation of YCu was suppressed. Instead, a metastable extension of the α-Y solid solution to ~20 at.% Cu was found, corresponding to a metastable solubility increase by a factor of >20. Density and unit-cell volumes change as shown in Figs. 1(a) and 1(b). The unit-cell volume increases slightly with increasing Cu content and shows a large positive deviation from a Vegard's-law straight line: $\Delta V/V = 17.5\%$ at 20 at.% Cu.

The unit-cell contents derived from the measured cell volumes and densities [Fig. 1(c)] indicate clearly the unusually high degree of space filling; the total number of atoms per unit cell exceeds the number of atomic sites in the hcp $A3$ type by ~10% at 10 at.% solute and by 15% at 17.5 at.% solute. Within the experimental accuracy, the number of Y atoms per unit cell stays constant at two up to ~12.5 at.% Cu. As it is energetically not possible for the large Y atoms to occupy interstitial sites, all $A3$ sites are filled and unavailable for Cu. The existence of an extended interstitial solid solution of small metal atoms in a large metal has thus been demonstrated. By comparison, the maximum interstitial solubility of C in γ-Fe is 9.2 at.% C.

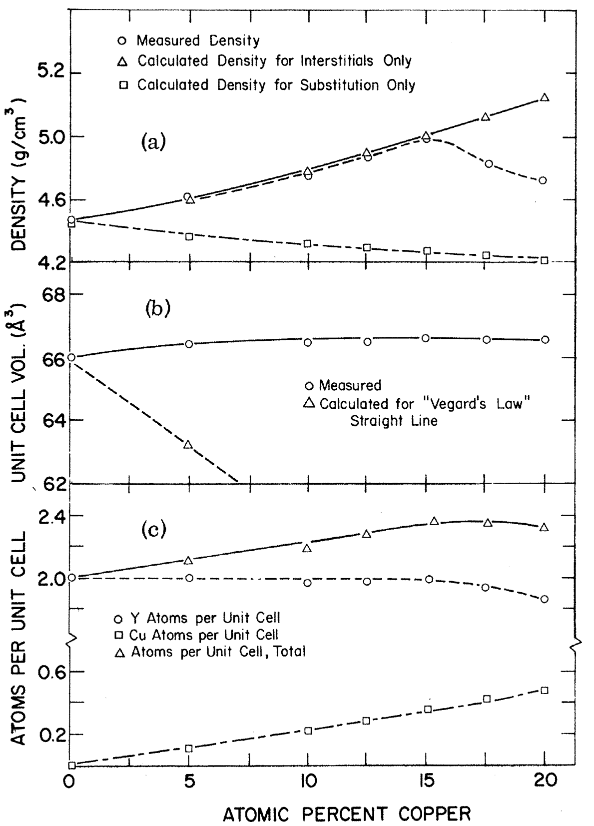

FIG. 1. Densities, unit-cell volumes, and numbers of atoms per unit cell for solid solutions of Cu in Y. Solid solutions with <15 at.% Cu are interstitial; solid solutions with >15 at.% Cu are both interstitial and substitutional.

Above about 12.5 at.% Cu, the solid solution is partly substitutional; at 20 at.% Cu, the Cu atoms are distributed between substitutional and interstitial sites in the ratio 1:2. In this case, an association of both defect types would be elastically favorable, and clusters of Cu atoms are expected to form at $A3$-structure sites. At 20 at.% Cu, complete association would correspond to clusters of three Cu atoms per Y site. This aspect is under further study in Y-Cu and related alloy systems.

The existence of a metastable solid solution has also been verified by annealing experiments and measurements of the positive heat of formation; the rate of its decomposition into Y and YCu at room temperature is negligible. Electronic-property measurements and a Mössbauer study to ascertain the f values and site symmetry of the interstitial atoms are in progress.

Some conclusions about the nature of the interstitial solid solution can be drawn. Comparing the sizes of octahedral and tetrahedral holes in a close-packed host structure gives $r_T/r_0 = 0.56$; considering this as well as the position of C in γ-Fe, it is likely that Cu occupies octahedral sites in Y. The occurrence of two-atom defects of lower symmetry, i.e., split interstitials,[19] is also possible. Inspection of the $A3$ structure shows that there is one octahedral site for each host-atom position but that only one quarter of these sites may be filled if occupancy of two sites sharing an edge is to be excluded. This assumption would lead to a maximum solubiltiy of 20 at.% Cu; the observed limit for pure interstitial solution formation [Fig. 1(c)] is about $\frac{2}{3}$ of this limiting value. It is likely that some short-range ordering of the occupied octahedral sites exists.

According to Hägg's rule,[1,4] interstitial formation in simple metallic structures is possible if $r/R < 0.59$; however, for Y-Cu, $r/R = 0.71$ if twelvefold coordinated Goldschmidt radii[1] are used. The existence of the solid solution shows that Hägg's rule is not valid for metallic interstitial solutes, even if allowance is made for a size decrease of 4% on decreasing the coordination number of Cu to 6 in an octahedral position.[1] In a hard-sphere model, a volume increase would be expected whenever $r/R > 0.414$. The absence of a substantial volume increase [~0.7% upon introduction of 10 at.% Cu into Y, Fig. 1(b)] shows this model to be inapplicable to the Y-Cu interstitial metal-metal solution even as an approximation. By contrast, an addition of 10 at.% C to γ-Fe would lead to an extrapolated volume increase of ~6%,[18] reflecting the higher relative valence and Debye temperature of this solute. Further, nonoverlap of the inert-gas cores Y^{3+} and Cu^+ is a necessary requirement to avoid prohibitive repulsive energies; with $r(Cu^+) = 0.96$ Å and $R(Y^{3+}) = 0.93$ Å,[20] $r + R < d$(Y-Cu) $= 2.54$ Å, as required.

While the solid solution is not thermodynamically stable, the excess ΔG of its free energy over the equilibrium phase mixture cannot be large, otherwise it would not have been retained even by splat-cooling.[8] The small excess ΔG is partly due to the entropy term which favors solution formation at temperatures 100-200°C below the melting point, where solidification occurs.[16] The excess enthalpy also can not be large. As the lattice parameter remains almost unchanged, there is almost no strain energy which generally makes interstitial solid solutions energetically unfavorable. The additional kinetic energy due to the added electrons must be largely balanced by the decreased electrostatic energy and the reduction in the electron-electron repulsion which is due to the added positive charge. An earlier suggestion[21] of correlation interactions between the filled $3d$ shell of Au^+ and Pb^{4+} has since been withdrawn[22]; it is difficult to see how such forces could be active between Cu^+ and Y^{3+}, although the close solute-solvent approach would favor interactions by short-range forces. General conditions favoring interstitial solubility include[12] a polyvalent, electropositive solvent; low solute valence; and a small solute size. These criteria are satisfied for Cu in Y.

Extensive interstitial metallic solutions should have interesting properties. The additional point defects increase the phonon scattering, and may thus affect superconducting properties. Solute-atom diffusion will have low thermal activation energies and high diffusivities, as observed for Au in Pb; in addition, high concentration gradients make a large flux possible. Mechanical strength should be enhanced; the extent of this effect will largely depend on whether or not the interstitials produce an isotropic or anisotropic stress field. It has been reported that interstitial Ag and Au produce solution hardening in Pb which is ~50 times larger per addition atom than predicted for substitutional solutes.[8]

Many other alloy systems without appreciable solid solution formation have solute-solvent size ratios near 0.7. Among these are systems with alkaline earths, rare earths, Th, Pb, or Bi as solvents and first-period transition metals, noble metals, and Be as solutes. A number of these systems are presently under study.

We wish to thank Mr. M. Segnini who carried out the density measurements.

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Low-Lying Even-Parity Resonances in KI:Ag^+

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Lattice resonances of E_g symmetry (16.35 cm^{-1}) and A_{1g} symmetry (25 cm^{-1}) have been found in KI:Ag^+ using far-infrared spectroscopic techniques. The two even-parity modes are found to be anharmonically coupled to the T_{1u}-symmetry resonant mode at 17.3 cm^{-1}, giving rise to the combination bands observed at 30 and 44.4 cm^{-1}.

An optically active T_{1u}-symmetry resonance at 17.3 cm^{-1} in KI:Ag^+ has been known for some time.[1] In general, there can also be impurity-activated quasilocalized resonances with even parity. Such modes are not optically active, and in the simplest approximation they involve motion only of the defect nearest neighbors. We wish to report here the identification of two even-parity resonances in KI:Ag^+, one at 16.35 cm^{-1} with E_g symmetry, the other near 25 cm^{-1} with A_{1g} symmetry. These modes were detected by far-infrared absorption measurements with the KI:Ag^+ sample in an external electric field. The field induces a strong mixing of the nearly degenerate E_g and T_{1u} modes, resulting in linear shifts of the mode frequencies. The A_{1g} mode also shifts linearly with applied field, but the field-induced mixing in this case is more complicated.

In addition, weak absorption lines at 30 and 44.4 cm^{-1} in zero field are attributed to the T_{1u}-E_g and T_{1u}-A_{1g} combination bands, respectively. The absorption strengths of these bands are a measure of the anharmonic coupling of the even modes to the odd mode.

The far-infrared absorption measurements were made using a lamellar interferometer[2] and a liquid-He^3-cooled germanium bolometer.[3] The instrumental resolution was typically 0.25-0.35 cm^{-1}. The techniques involved in making the electric-field-dependence measurements have been described elsewhere.[4]

The KI:Ag^+ far-infrared absorption spectrum is shown in Fig. 1 for a sample temperature of 1.2°K. In addition to the strong resonant-mode transition at 17.3 cm^{-1}, there are five relatively weak lines. Also observed, but not shown in Fig. 1, is a strong gap mode at 86.2 cm^{-1}. The two highest frequency lines, 55.8 and 63.5 cm^{-1}, can be correlated with host-crystal density-of-states peaks, after Dolling *et al.*[5] The 30- and 44.4-cm^{-1} lines are both asymmetric, with integrated absorption strengths relative to that of the resonant mode of 0.29 and 0.19, respectively. It is these two lines which are important in the interpretation of the results to be presented here.

The results of a typical electric-field run are shown in Fig. 2. The dashed curve shows the KI:Ag^+ T_{1u}-symmetry resonant-mode absorption line in zero field. The solid curve shows the observed absorption spectrum with an external electric field (E_{dc}) of 130 kV/cm applied in the [100] crystallographic direction and the E vector of the incident radiation (E_{ir}) polarized parallel to E_{dc}. With the field applied, there are two absorption lines in the 17-cm^{-1} region. The higher frequency of these two peaks is due to the field-shifted component of the T_{1u} mode. Clearly, the absorption strength of this line decreases with increasing field. The lower-frequency peak appears only when a field is applied. It increases

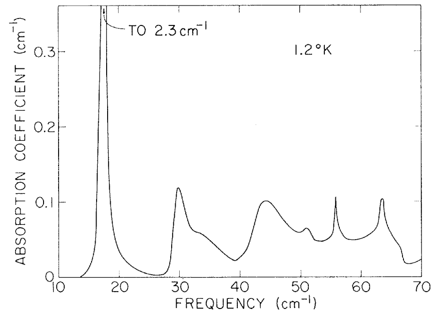

FIG. 1. KI:Ag^+ far-infrared absorption spectrum.