Displacement around a Dissolved Impurity Atom in a Metal: Sn in Cu

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It has been determined that the nearest-neighbor distance around tin atoms dissolved in a Cu lattice is 2.63 Å, ~0.07 Å larger than given by the average lattice constant. The determination was made by the extended x-ray-absorption fine-structure technique. The observed distortion agrees with that calculated from an anisotropic lattice model.

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An impurity atom dissolved substitutionally in a metal produces a local lattice strain. This distortion is important in determining the electronic states of an impurity, in the scattering from an impurity, and in understanding solution mechanisms and x-ray diffraction patterns of alloys.

In principle, x-ray diffraction techniques can detect this distortion. However, the confusing effects of the thermal diffuse scattering, impurity clustering, defects, and long-range impurity strain-field interactions have prevented unequivocal x-ray determinations of local strain.[1] Local distortions have been measured in a very few systems (*Pd*Gd,[2] *Al*Li,[3] *Pd*Bi,[4] and Al alloys[4]) by neutron scattering.

We report here the first extended x-ray-absorption fine-structure (EXAFS) measurement of the Sn-Cu spacing in dilute *Cu*Sn alloys, and show that it is in good agreement with a theoretical model.[5] The analysis of the experimental data uses a "model compound" to eliminate some of the uncertainties arising from the data reduction. This experiment demonstrates that at least for those cases where the impurity is of higher Z than the host, EXAFS measurements can be widely used to study interatomic distances in dilute alloys. EXAFS has the feature that it is sensitive primarily to near-neighbor (nn) distance, and can be used to examine selectively a dilute impurity. Single crystals are not required, and the impurity does not have to be magnetic.

In these experiments, transmission EXAFS geometry was used.[6] Samples were prepared by standard techniques. Dilute Sn-Cu absorbers were rolled foils, annealed and quenched after rolling. The Cu_3Sn (ϵ-phase) model compound was made into a powder, then annealed. Measurements were made at approximately 80 K to reduce the thermal atomic motion.[7] A special Dewar flask held the absorbers mounted side by side so that the x-ray beam could be directed through any of the absorbers by adjusting the Dewar flask position. Samples were also studied by ^{119}Sn Mössbauer spectroscopy and Rutherford backscattering/channeling techniques to check for phase purity and the substitutionality of the tin atoms.

The EXAFS technique measures the modulation of the x-ray-absorption cross section above an absorption edge.[8] Nearby atoms scatter the outgoing photoelectron wave, and the interference between the outgoing and scattered waves modulates the absorption cross section (see Fig. 1). The cross section is oscillatory because the interference is constructive or destructive depending on the phase shift of the scattered wave.

For s electrons, with the assumption of spherical averaging over sample orientation, the oscillatory part of the absorption cross section is given by[6]

$$\chi(k) = -\sum_j (N_j/kr_j^2)|f_j(k,\pi)| \sin[2kr_j + \psi_j(k)] \times \exp(-2\sigma_j^2 k^2)\exp[-2r_j/\eta_j(k)], \qquad (1)$$

where k is the wave vector of the outgoing elec-

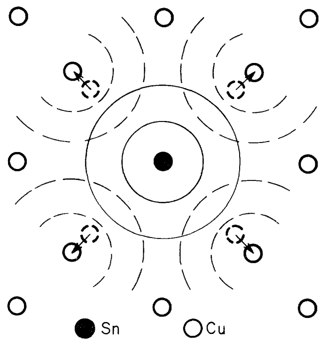

FIG. 1. The 100 plane of an fcc Cu crystal containing a single tin atom. The nearest and second- and fourth-nearest neighbors of the tin are shown. The arrows and displacements of the Cu atoms show the distortion we measure here (exaggerated for clarity). The light solid and dashed circles represent the outgoing photoelectron wave and the electron wave backscattered from the first nn Cu atoms. The interference between these waves produces the EXAFS effects.

tron, N_j and r_j are the occupancy number and distance of backscattering shell j, f is the backscattering amplitude, and ψ is the phase factor (discussed below). The last two terms represent, respectively, the damping due to thermal and zero-point atomic motion, and the attenuation of the outgoing and backscattered waves from inelastic scattering.

Figure 2 shows the Fourier transform (FT) of the EXAFS, which is related to the radial distribution function (RDF) for the neighbor shells. Even though the EXAFS FT is only a filtered and distorted version of the true RDF (Ref. 6, p. 781), the transform plot is useful as a physically intuitive representation of the data.

Cu metal is a widely used reference for EXAFS studies, and data such as those at the bottom of Fig. 2 have been published and discussed.[6,9] The identification of the peaks in the FT amplitude out to the fourth-nearest-neighbor shell is clear and unambiguous. Comparison of the FT amplitude of the Sn EXAFS of the 0.3% and 1% Sn alloys with that of pure Cu shows the strong nn peak that we use for the distance determination, and the corresponding shells out to the fourth-nn shell. This confirms that the tin atoms are indeed substitutional in the fcc Cu lattice. The similarity between the 0.3% FT and the 1% FT suggests that concentration-dependent effects are not significant. The Sn-edge FT data for the alloys is similar to that of the Cu edge in Cu since for substitutional Sn in Cu, the neighbor atoms and shell occupations are the same as for Cu metal; only the absorbing atom is different.

Furthermore, a characteristic of the fcc structure provides additional evidence of the high degree of order of the alloys. The fourth-nn peak (at 4.8 Å in the Cu FT) is anomalously strong as a result of forward scattering of the outgoing electron wave by the nn atoms (see Fig. 1) which are directly in line with the fourth-nn atom positions in the undistorted lattice.[6] In the *Cu*Sn alloys, we see that the fourth-nn peak is still strong. This tells us not only that long-range coherence is maintained out to that shell, but that the displacement vectors of the nn Cu atoms from the Sn central scattering atom are radial.

Quantitative analysis of EXAFS data requires that the phase, ψ_j, be determined. This problem is central to the evaluation of all EXAFS data, and is the principal limitation in the precise determination of interatomic distances. Considerable success has been obtained by use of theoretically calculated phase-shift values.[10] However,

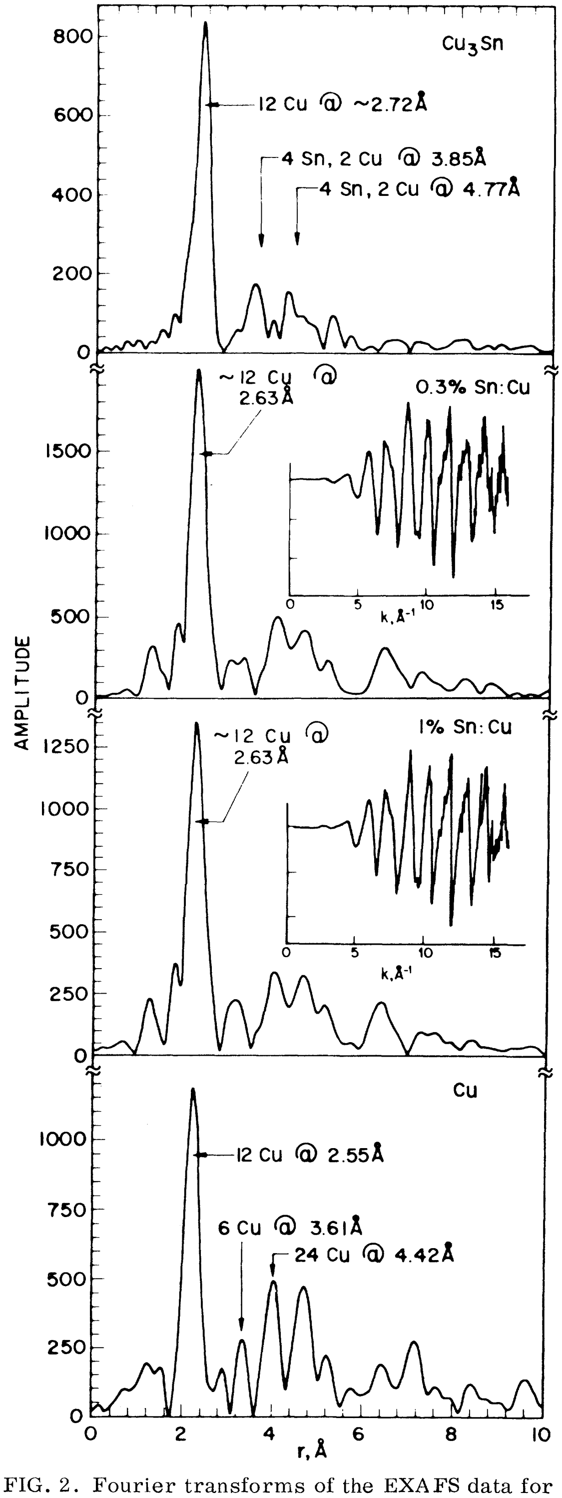

FIG. 2. Fourier transforms of the EXAFS data for the Cu$_3$Sn model compound, the dilute Sn-Cu alloys, and a Cu "standard." The top three data sets were taken with use of the tin K edge, the bottom, with use of the Cu K edge. These transforms are not the same as the RDF about the central (tin) atom, but can be used to visualize the data, as discussed in the text. The insets show $k^3\chi(k)$, the EXAFS spectra with background removed.

we have chosen the alternative approach of using a model compound, i.e., one which has tin and Cu atoms positioned similarly to those in the dilute *Cu*Sn alloy under study. With use of the idea of chemical transferability, the Cu-Sn phase from the model compound can then be used to analyze the EXAFS data for the alloy system (Ref. 6, p. 784).

The Cu_3Sn model compound is an extremely good analog for the *Cu*Sn alloy. From the known structure,[11] the tin environment consists of twelve Cu atoms, six at 2.69 Å and six at 2.76 Å, and two shells each containing four Sn atoms and two Cu atoms at 3.85 and 4.77 Å. The tin atom is surrounded by twelve Cu atoms, just as in the dilute alloy, and, as shown in Ref. 6, it is a good approximation to treat the two Cu distances in the first shell by the average distance (Ref. 6, p. 795).

We have carried out the analysis along the lines of Refs. 9 and 6 (see p. 787), by spline fitting to remove the background from the EXAFS oscillations, and then truncating the data, using the range from 4 to 18 $Å^{-1}$. The data sets were Fourier transformed, filtered, and back-transformed to extract the phases for the first shell of the Cu_3Sn and the alloys. A least-squares program then compared the phases for the model and the alloys (Ref. 6, p. 790) and gave directly the Sn-Cu distance of 2.63 Å in both the 0.3% and 1% alloys.

The measured value of 2.63 Å is ~0.07 Å larger than the interatomic distance given by the average lattice-constant measurement. This shows significant expansion of the nn shell. Table I summarizes our results and shows the distortion calculated with the model of Krivoglaz [Ref. 5, Eq. (20)]. The Krivoglaz theory is a microscopic elastic theory which takes into account the lattice anisotropy and the discrete positions of the host lattice atoms, and provides results significantly different from less sophisticated elasticity models. The good agreement between the Krivoglaz model and the experiment suggests that it is an effective way to describe the distortion.

TABLE I. Measured and calculated interatomic distances.

	Distance (Å)
Measured	
Cu-Cu (Cu metal, x ray)	2.5508
Sn-Cu (1% Sn, EXAFS, this work)	2.63
Sn-Cu (0.3% Sn, EXAFS, this work)	2.63
Mean interatomic distance in 1% Sn alloy (x ray)[a]	2.5580
Calculated[b]	2.618

[a] Ref. 12. [b] Ref. 5.

The accuracy of the EXAFS determination of the interatomic distance is limited by the following: (1) uncertainty in the atomic positions of the Cu_3Sn model (~0.01 Å); (2) statistical and other uncertainties in the data and the analysis (<0.01 Å); and (3) systematic errors from the difference between the model compound and the alloys—the mean value of $\Delta\psi = \psi_{\mathrm{model}} - \psi_{\mathrm{alloy}}$ is much less than 0.05 rad, so that the inaccuracy from this term should be less than 0.005 Å (Ref. 6, p. 791). Combining these terms, we see that ± 0.02 Å for the total error arising from all sources would be a reasonable estimate. The small size for the second term is confirmed by the good agreement between the results for the two different dilute alloys.

Two previous EXAFS experiments have studied this local distortion effect in *Al*Cu (Ref. 9) and *Ti*Cu (Ref. 13) alloys. In the first, strong clustering of the impurity and the use of calculated phase shifts complicated the interpretation. In the second, the observed distortion was just the size of the error flag. In the *Cu*Sn work reported here, clustering effects are not significant.[14,15] For the 0.3% alloy, only 3.6% of the Sn atoms have Sn nn atoms in a random alloy. We have used phase shifts from a model compound with structure similar to that of the alloy to provide precise phase information for the analysis. The *Cu*Sn system shows a relatively large change in average lattice constant with tin concentration, suggesting that the distortion is large. These features have allowed us to get a precise result, in good agreement with the Krivoglaz theoretical model.

In summary, we have carried out the first precise EXAFS measurement of the distortion around an isolated impurity atom in a metal. The result confirms the validity of a sophisticated elasticity model by Krivoglaz. These conclusions are important because of the broad range of effects which depend on the host-impurity distance.

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