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Compound formation and superconductivity in Au-Si: X-ray absorption measurements on ion-beam-mixed Au-Si films

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Multilayered Au-Si thin films have been deposited with the net compositions "$Au_{1-x}Si_x$," $x=0.29$, 0.5, and 0.8. After ion-beam mixing these films exhibited superconductivity in the 0.3–1.2 K range despite the nonsuperconducting character of both Au and Si. Near-edge x-ray absorption spectroscopy (XAS) measurements on the Au L_3 edge in these films indicate that metastable Au-Si compound formation occurs in these ion-mixed materials. Specifically, the XAS measurements indicate changes in Au 5*d*-orbital occupancy and changes in the local Au structural environment which are both consistent with local compound formation.

INTRODUCTION

Elemental metallic Au and semiconducting Si do not exhibit superconductivity under ordinary conditions and do not form any equilibrium compounds. Nevertheless, superconductivity has been observed in mixtures of Au and Si prepared by a number of metastable materials-synthesis techniques.[1–3] Several mechanisms have been proposed for superconductivity in these Au-Si mixtures.[2–5] The method of ion-beam mixing provides a means of preparing metastable Au-Si mixtures in which the composition and degree of mixing can be conveniently varied.[6] Here we will be discussing ion-beam-mixed films of net compositions "Au_5Si_2," "AuSi," and "$AuSi_4$" (i.e., "$Au_{1-x}Si_x$;" $x=0.29$, 0.5, and 0.8). The quotation marks will always be used to clearly identify when net compositions are being discussed. We will first review measurements of the superconducting properties of these materials and then discuss x-ray absorption spectroscopy (XAS) results which elucidate the chemical bonding and local atomic arrangements of these materials. As we shall see, these results support the occurrence of local metastable compound formation in these ion-beam-mixed Au-Si materials.

EXPERIMENT

The starting films in our study were Au-Si multilayers prepared with different ratios of the Au and Si layer thicknesses in order to vary the Au-to-Si ratio. All of the films had six pairs of layers and were roughly 700 Å in total thickness. The Au:Si ratios and total film thicknesses were verified by Rutherford backscattering spectroscopy. Xe^{2+} beams with energies in the 150–400 keV range and fluences between 0.5×10^{15} and 4.0×10^{15} ions/cm^2 were used to mix the multilayer samples. The Xe^{2+} beam energies were chosen so that the projected ion penetration range plus straggling depth at that energy was equal to film thickness, thus insuring that most of the ions came to rest within the Au-Si film. The resistivity measurements were made using a conventional four-probe dc technique in a ^{3}He cryostat capable of cooling to 0.4 K. The XAS measurements were carried out in the total electron yield mode which is particularly suitable for thin film materials.[7] The secondary electron escape depth exceeds the film thickness; hence this method sampled the entire film.

SUPERCONDUCTIVITY AND RESISTIVITY RESULTS

The measurements of the temperature dependence of resistivity and superconducting T_c are reviewed briefly here to provide a context in which to discuss the XAS re-

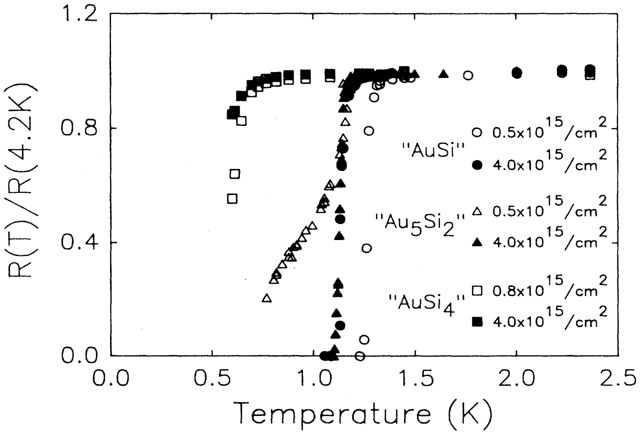

FIG. 1. Superconducting resistive transitions in ion-beam-mixed Au-Si films with different doses of Xe ions.

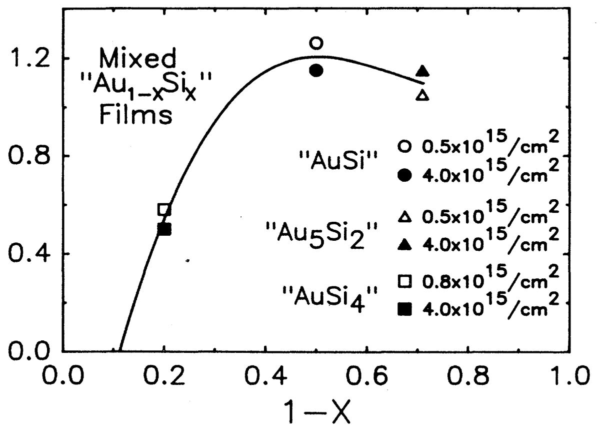

FIG. 2. Variation of superconducting transition temperature with Au fraction for ion-beam-mixed "$Au_{1-x}Si_x$" films. Note that the quotation marks denote net composition of the initial layered film throughout this paper.

sults. A more detailed discussion of the superconductivity studies is presented elsewhere.[8]

In Fig. 1 we present the resistivity results for selected ion-beam-mixed "$Au_{1-x}Si_x$" samples. In Fig. 2 we summarize the dependence of T_c on x for these samples. We note first that the "AuSi" sample with the lower mixing dose (0.5×10^{15} ions/cm^2) exhibits the highest T_c (1.26 K) and the sharpest resistive transition of the series. The "AuSi" sample with the higher fluence of 4.0×10^{15} ions/cm^2 has a lower T_c (1.15 K).

The quality of the resistive transition in the mixed "Au_5Si_2" improves markedly with increasing ion-beam fluences. Interestingly, the "Au_5Si_2" mixed with a high fluence has a T_c and resistive transition width similar to those of the high-dose-mixed "AuSi." Finally, the "$AuSi_4$" samples have a substantially lower T_c and a broader transition width which are less sensitive to the mixing fluence. We will now turn to a discussion of the potential character of the Au-Si bonding and of how XAS measurements can be used to evidence such bonding.

Au BONDING

Theoretical discussions of noble-metal bonding to less electronegative atoms have emphasized the important role of the *d* orbitals of the noble metal.[9,10] The striking violet-metallic compound $AuAl_2$ provides an excellent example of this type of bonding. As the most electronegative metal, Au in compounds tends to demand a charge transfer to the Au sites. In $AuAl_2$ Watson *et al.* have calculated that this charge transfer to the Au is of *non-d character* and is roughly one electron per Au atom.[11] They emphasized, however, that roughly one electron of *5d character* is backtransferred *away* from the Au sites in order to maintain charge neutrality. This compensating flow of *d* and *non-d* charge density is effected through Au-Al hybridization (or covalent mixing).[10–13] Here the creation of mixed (Au 5*d*)–(Al *sp*) antibonding states above the Fermi level ε_F leads to the effective decrease in net Au-5*d* orbital occupancy.

XAS AS A BONDING PROBE

Recent work has indicated that L_2- and L_3-edge XAS measurements can provide valuable insight into the effective 5*d*-orbital electron (or hole) count.[4] The $L_{2,3}$ near-edge spectrum of a 5*d* transition metal is dominated by a strong white line (WL) feature caused by atomiclike $2p\rightarrow5d$ transitions.[15] This broadened solid-state vestige of the atomic $2p\rightarrow5d$ transition has a Lorentzian-like line shape.[16–18] Within the single-particle picture the integrated area of this WL feature should scale with n_d, the number of holes in the 5*d* orbital (i.e., the number of available final states).[16] In view of the central importance of changes of n_d induced by bond formation in Au compounds in general and in the $AuAl_2$ example in particular, $L_{2,3}$ near-edge spectroscopy appears to be ideally suited for such studies.

In the solid, the onset of transitions from 2*p* to the continuum moves down to ε_F (below the WL peak) and hence this step-function feature (conventionally represented by an arctangent) must be subtracted from the $L_{2,3}$ spectra to extract the WL feature. Since pure Au has almost no WL feature, indicating almost no 5*d*-band holes, we use the elemental Au $L_{2,3}$-edge spectrum to approximate the continuum background. A quantitative measure of the WL feature is obtained by first normalizing both the elemental Au and the Au-compound spectra at high energies to unity. The elemental Au $L_{2,3}$ spectrum is then shifted so that it superimposes on the Au-compound spectrum in the initial 10 eV of the rise. The two are subtracted to yield a difference spectrum. The area ΔA under the graph of the difference spectrum between its initial rise and its first zero crossing then provides a measure of the strength of the WL feature of the compound.

As an illustration of this analysis method we show in Fig. 3 results for $AuAl_2$. The substantial WL feature arises from an increase in the effective Au *d*-hole count due to the chemical bonding in the compound. Previous

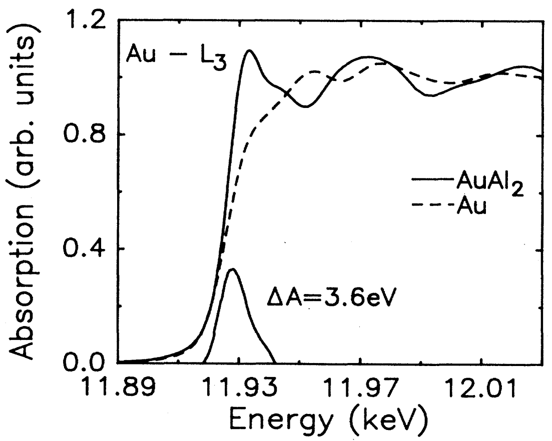

FIG. 3. The Au L_3 absorption edge spectra of $AuAl_2$ and elemental Au. Each spectra is normalized to unity step height at energies well above the edge. The translated Au spectrum is subtracted from the $AuAl_2$ spectrum to provide a rough estimate of the white line (WL) area at the compound edge.

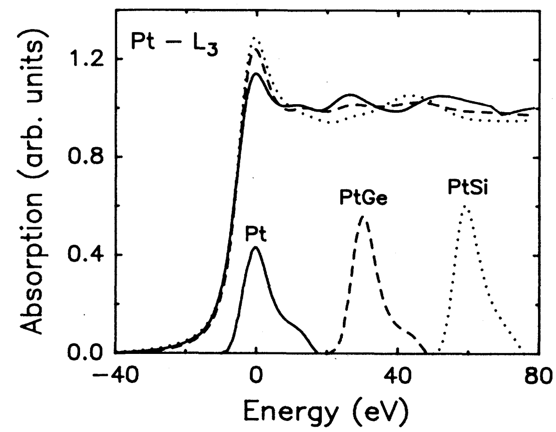

FIG. 4. The Pt L_3 absorption edge spectra of PtGe, PtSi, and elemental Pt. The difference spectra obtained by subtracting the elemental Au spectrum (as illustrated in Fig. 3) are also shown. The difference spectra provide an approximation of the white line near-edge feature.

work on the 5*d* elements indicates that an increase of one in the 5*d*-hole count is roughly equivalent to an increase in WL strength (measured by the area ΔA) of 3 eV.[14] Actually the area units are eV × (step height) where the step height is the continuum step in the absorption coefficient across the edge. Thus a value of $\Delta A = 3.6$ eV for $AuAl_2$ corresponds to roughly 1.2 Au 5*d* electrons transferred away from the Au because of Au-Al bonding. Taking into account the somewhat smaller L_2-edge area change and the precision of both WL area estimation and electron count per WL area calibration, our results are consistent with between 1 and 1.2 Au 5*d* holes being created by bonding in $AuAl_2$.[14] This result agrees well with Pauling's estimate for the electron transfer of $1.19e^-$ as well as with Watson's estimate of about $1e^-$.[11,19]

We have studied many other Au, Pt, Ir, and Re compounds with Al, Si, Ge, Ga, In, and Sn and have found similar results.[20] We find this same type of increase in the $L_{2,3}$ near-edge area in all cases and associate it with compound formation. We therefore believe that such an area increase can be used as a measure of the strength of chemical bonding upon compound formation. In particular, we show in Fig. 4 the L_3 spectra of the MnP structure compounds PtSi and PtGe along with the spectrum of elemental Pt for comparison. The clear increase in the WL areas of these compounds provides evidence for the creation of bonding-induced 5*d*-hole states. The somewhat stronger WL in PtSi than in PtGe indicates that Si is chemically more aggressive in bond formation (Pt 5*d*-hole creation) than Ge. It is interesting to note that the PtSi and PtGe compound formation is accompanied by the occurrence of superconductivity with $T_c = 0.88$ and 0.4 K, respectively.[21,22]

XAS RESULTS ON MIXED Au-Si MATERIALS

With the above background in mind we now turn to our XAS results on Au-Si *ion-beam-mixed* materials. In Fig. 5 we show the Au L_3 spectra of several of these materials superimposed in each case on the elemental Au spectrum. Also shown is the Au L_3 spectrum of a layered Au-Si film which was not ion mixed.

We note a number of points regarding the near-edge spectra of these materials. First the layered material which was not mixed manifests a near-edge spectrum identical to elemental Au. (See Fig. 5 bottom.) Second, the ion-beam-mixed materials show small but distinct increases in the WL strength over that in elemental Au. The WL location is indicated in Fig. 5. Third, the WL strength increases noticeably between the mixed "Au_5Si_2" and "AuSi" but remains relatively constant between the mixed "AuSi" and "$AuSi_4$" materials.

As emphasized above, this increase in WL area is precisely the behavior one would expect from Au-Si bonding in a compound. Since Au and Si form no equilibrium compounds or alloys, the local bonding and associated compound formation induced in these materials must be metastable. The increasing strength of the WL feature in mixed "Au_5Si_2" relative to mixed "AuSi" can be attributed to the increased Au-Si bonding upon increased average Si coordination to the Au. We have observed this effect in numerous Au and Pt compounds where the bonding induced an increase of the 5*d*-hole count with coordination.[20] The saturation of the WL strength with the increase of silicon concentration in going from mixed "AuSi" to "$AuSi_4$" on the other hand, would appear to indicate that the optimum Au-Si coordination is obtained for mixed "AuSi." Further addition of Si in these materials (above the "AuSi" composition) would therefore appear not to coordinate with Au but segregate between the fully coordinated AuSi complexes. We will see additional support for this idea in the near-edge fine-structure oscillations discussed in the next section.

The mixed "AuSi" compound not only exhibits the maximum (or saturated) "Au-Si" bonding but also the sharpest superconducting transition and highest T_c of the three Au-Si samples. It is therefore useful to consider

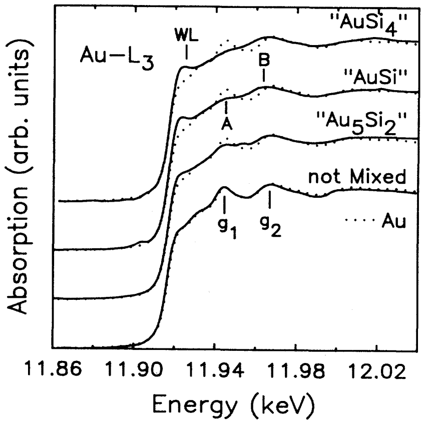

FIG. 5. The Au L_3 absorption spectra of selected Au-Si ion-beam-mixed materials (solid line) superimposed in each case on the elemental Au spectrum (dotted line). The doses of the displayed spectra were "$AuSi_4$," 4.0×10^{15} ions/cm^2; "AuSi," 0.5×10^{15} ions/cm^2; and "Au_5Si_2," 4.0×10^{15} ions/cm^2. Also Au-L_3 spectrum of a layered Au-Si film which was not mixed is shown (see bottom of figure).

how this material fits into the extensive XAS studies of Jeon *et al.* on $T=$Au and Pt bonding with $X=$Al, Si, and Ge in equilibrium compounds.[20] Although Jeon *et al.* have developed a quantitative scale for estimating the degree of 5d orbital charge loss due to bonding (Δn_d) in these compounds, a few observations regarding these results will suffice to provide an estimate of Δn_d expected for a hypothetical AuSi compound. First, it was observed[20] that in a series of compounds $T_{1-x}X_x$ (T and X being constant) the number of T 5d holes that were created scaled roughly linearly with the concentration x. For example, since Δn_d is in the $1-1.2e^-$ range for AuAl_2, then one might expect Δn_d to be $0.75-0.9e^-$ for the AuAl compound. Second, it was observed[20] that there was very little difference between bonding-induced 5d-hole creation in T-Al and T-Si compounds. In view of this second observation the above estimate of Δn_d for AuAl should hold roughly for hypothetical AuSi also (i.e., Δn_d in the $0.75-0.9e^-$ range). A third observation provides another estimate for the Δn_d value for hypothetical AuSi. The third observation is that Au and Pt compounds (with the same stoichiometry and ligands) have very comparable Δn_d values. In view of this last point the $\Delta n_d \approx 0.8e^-$ that we have estimated from the $L_{2,3}$ XAS spectrum of PtSi provides an immediate estimate for AuSi. Thus by two means one deduces that the Δn_d value for the compound AuSi, if it can be formed, should be about $0.8\pm0.1e^-$.

We have analyzed the area of the L_3 WL of our mixed "AuSi" material and have found it to be equivalent to roughly a Δn_d value of $0.6e^-$. Although we have not measured the L_2 WL area for these mixed films one might expect from our bulk-compound studies[20] that it lies roughly 30% below the L_3 WL value, i.e., at a Δn_d value of $0.4e^-$. Thus we estimate the Δn_d value of about $0.5\pm0.1e^-$ for our mixed "AuSi" films. This estimate of Δn_d derived from our experiments is roughly 40% lower than the value expected for a pure AuSi compound from the comparison noted above to other related compounds. Such a reduction would follow if 40% of the Au sites in the mixed material remained in a Au-like local environment whereas 60% were in a AuSi-like local environment. As we will see below, the fine-structure oscillations in the near-edge spectra support a similar proposal.

XAS NEAR-EDGE FINE-STRUCTURE DISCUSSION

We turn now to a discussion of the fine-structure oscillations in the absorption coefficient in the range 60 eV above the edge. These oscillations are caused by interference of photoelectron backscattering from the near-neighbor atoms.[23] The details of this process can involve both single and multiple scattering and can be quite complicated.[23] Empirically, however, changes in local atomic environment are known to lead to changes in these fine structure (FS) features.

Inspection of the spectra in Fig. 5 clearly shows changes in the FS features of the ion-beam-mixed materials relative to pure Au. Focusing on the mixed "AuSi" FS features first, we note in Fig. 5 that feature A in the mixed film is substantially broadened and degraded relative to the g_1 feature in elemental Au occurring near the same energy. The B feature of the mixed AuSi material is also broadened and strongly shifted to lower energy relative to the g_2 feature of elemental Au. Thus the FS features in mixed "AuSi" clearly reflect a local geometrical structure different from elemental Au. That is the Au and Si must be mixed on a local atomic scale and not simply phase segregated on a larger scale.

It should be noted that additional FS features develop in mixed "AuSi" with the higher ion-beam fluence of 4.0×10^{15} ions/cm^2. The resistive superconducting transition temperatures of these higher-dose materials are substantially lowered. We believe therefore that the "AuSi" with a mixing dose of 4.0×10^{15} ions/cm^2 (the Au L_3 spectrum of which is shown in Fig. 5) represents the optimally mixed and locally ordered material.

The FS of the mixed "Au_5Si_2" spectrum deviates from the FS of elemental Au in some ways that are analogous to the mixed "AuSi" material. Specifically the mixed "Au_5Si_2" feature near the Au g_1 feature is broadened and the mixed "Au_5Si_2" feature near the Au g_2 feature is both broadened and shifted to lower energy. However, these two spectral changes are not as pronounced as in the mixed "AuSi" spectrum. Also, the spectrum of the mixed "Au_5Si_2" has a small additional peak between the g_1 and g_2 features. This same feature (along with another at a higher energy) was observed in high-dose-mixed "AuSi" and was accompanied by a lowering of the transition temperature to coincide with that of the mixed "Au_5Si_2." Interestingly, the mixed "Au_5Si_2" achieves its optimum superconducting transition temperature and transition width at the higher mixing fluence of 4.0×10^{15} ion/cm^2.

Comparing the mixed "AuSi_4" FS features to those of mixed "AuSi" we note that they are essentially the same. Thus, we infer that the local environment of the Au in the mixed AuSi and mixed "AuSi_4" is essentially the same. This is consistent with the observation noted above concerning the equality of the WL feature strengths in the mixed "AuSi" and "AuSi_4." Indeed, a more specific tentative conclusion can be reached by a comparison between the FS of the equilibrium MnP structure compound PtSi and the FS of mixed "AuSi" (or "AuSi_4"). This comparison is done in more detail in Fig. 6 where we show an expanded view of the near-edge region of PtSi, of our mixed "AuSi," and of elemental Au. We note that the FS of the PtSi spectrum has much in common with the mixed "AuSi" spectrum. However, we note that relative to the PtSi spectrum the "AuSi" spectrum manifests a large energy broadening on the main FS feature (labeled B) and a sharpening of the weak FS feature (labeled A). Such spectral modifications are consistent with some of the Au sites in the mixed material remaining in a Au-like local environment. Accordingly we have constructed a model spectrum from the elemental Au and PtSi spectra with the respective weights of 0.4 and 0.6. The model spectrum is shown as a dashed-dotted line overlaying the mixed "AuSi" spectrum. The large WL feature of PtSi causes the model spectrum (the dashed-dotted line) to lie above the mixed "AuSi" spectrum as one approaches the edge from high energy. (The

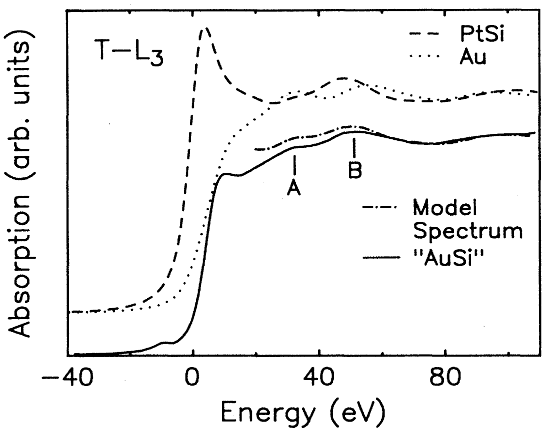

FIG. 6. Au L_3 and Pt L_3 absorption edges for PtSi, mixed "AuSi," and elemental Au. A model spectrum (dashed-dotted line) constructed from the elemental Au and PtSi spectra with respective weights of 0.4 and 0.6 is also shown to compare with mixed "AuSi" spectrum.

model spectrum has been cut off to avoid displaying a spurious intense WL feature.) Otherwise agreement in the spectral features is sufficiently good to support the ideas that about 60% of the Au sites in the mixed "AuSi" have a local environment which is structurally similar to that of PtSi and that about 40% of the Au sites are structurally the same as in elemental Au.

SUMMARY AND CONCLUSIONS

Generally our Au L_3 XAS measurements on ion-beam-mixed Au-Si materials have shown evidence of both Au-to-Si bonding typical of compound formation and local atomic arrangements (about the Au sites) dramatically different than in elemental Au. These two observations support the notion that, at least on a local scale, new metastable compound formation occurs in these materials. Moreover, our results suggest that the superconductivity in these materials is associated with electronic structure changes which accompany such metastable compound formation.

More specially our work supports a number of proposals regarding ion-beam-mixed Au-Si materials.

(1) A metastable "AuSi" compound is formed with a sharp superconducting transition ($T_c = 1.26$ K). The local structure of this compound is of the MnP type like that of PtSi.

(2) Roughly 60% of the Au sites in the mixed "AuSi" material have this PtSi-like local environment while 40% of the sites are Au-like.

(3) Mixed "$AuSi_4$" has a local structure about the Au sites which is similar to the mixed "AuSi." The additional Si in this material presumably resides between mixed "AuSi" sites or between segregated mixed "AuSi" regions. The low T_c of "$AuSi_4$" is presumably because the compounded clusters are small and more dispersed than in AuSi.

(4) A metastable compound also forms in mixed "Au_5Si_2" with a T_c of about 1.15 K.

(5) The highest-T_c material in this group "AuSi" is stabilized by mixing fluences of 0.5×10^{15} ions/cm^2. However, a higher fluence of 4.0×10^{15} ions/cm^2 causes destabilization of "AuSi" to a lower T_c compound which occurs in the "Au_5Si_2."

(6) Providing that one postulates that a fraction of the Au sites remain the same as they are in elemental Au (e.g., 40% in mixed "AuSi") then the degree of Au 5*d*-hole formation (due to bonding with Si) in these metastable compounds is consistent with trends in Au and Pt bonding in equilibrium Si, Al, and Ge compounds.

ACKNOWLEDGMENTS

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