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Superconductivity in Noble-Metal-Rich Hexagonal Close-Packed Phases*

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The superconductivity of phases rich in the noble metals (Cu, Ag, Au) was investigated. All face-centered cubic solid solutions (with Zn, Cd, Al, In) remained normal down to 0.014°K; and all hexagonal close-packed phases (with Si, Ge, Sn, Sb, Al, In) became superconducting in the range of 0.019–0.61°K. The results are interpreted as due to the Fermi-surface–Brillouin-zone interaction. The first superconductor with a DO_3 structure was found in the alloy Cu-15.5 at.% Sb.

I. INTRODUCTION

Attempts to search for a possible superconducting transition at low temperatures in the noble metals Cu, Ag, and Au have been made in the past.[1–3] In this investigation, the search has been extended to even lower temperatures and to the face-centered cubic (fcc) solid solutions of these metals and other related phases. Up to the present, the results of measurements on the pure metals and their fcc solid solutions with Zn, Cd, Al, and In are still negative. However, superconductivity has been found in the hexagonal close-packed (hcp) phases in the following systems: Cu-Si, Cu-Ge, Ag-Sn, Ag-Sb, Ag-Al, Au-In, and Au-Sn with electron concentration ($\mathfrak{z}$, the average number of valence electrons per atom) range of 1.3–1.8, which are the lowest values for metallic superconductors superconductors known to date.

It is well known that upon alloying these nontransition metals with the noble metals, hcp structures often result from the original fcc lattice by the simple change of atomic stacking once the electron concentration exceeds a value of about 1.4.[4] This phase change by which the free energy of the conduction electrons is lowered is believed to be due to the interaction of the Fermi surface and certain faces of the Brillouin zone[5] and the relative size factor between solute and solvent atoms.[6] The present results show that such a phase transition also induces superconductivity in the noble-metal base alloys. Throughout the homogeneity range of the hcp phases, the superconducting transition temperature (T_c) increases with increasing $\mathfrak{z}$ value.

An order cubic phase of DO_3 (BiF_3-type) structure in the Cu-Sb system has also been found superconducting. This is the first known superconductor which crystallizes in such a structure.

II. EXPERIMENTAL

A. Sample Preparation

Sources and purities of elements which were used in preparing alloys are listed in Table I. Weighed amounts of the elements were sealed into quartz tubes under reduced helium atmosphere and were melted at 1000°C for a few hours and then annealed. During melting, the alloys were shaken often to improve the mixing. Since Al reacted with quartz at high temperatures, its alloys were melted by induction in alumina crucibles under hydrogen and were subsequently annealed. The time and temperature of annealing are listed in Table II. After the heat treatment, alloys were quenched in water. The weight losses throughout the heat treatment are less than 0.2% for all alloys except those of Ag-Al whose losses are about 0.8%. The reported compositions are all nominal.

Table I. Sources and purities of starting materials.

Element	Source	Purity
Cu	a	99.999+%
	Jarrell-Ash	99.999%
Ag	a	99.999+%
	Engelhard Industries	99.999%
Au	a	99.999+%
Zn	a	99.999+%
Cd	b	99.9999%
Al	Semialloys	99.999%
In	a	99.999+%
	c	99.999%
Si	Du Pont	99.99999+%
Ge	A. D. McKay	99.999%
Sn	b	99.999%
	c	99.999+%
Sb	a	99.999+%

[a] American Smelting and Refining Co.
[b] Cominco Products.
[c] Indium Corp.

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The hcp phase in the Cu-Si system and the DO_3 ordered phase in the Cu-Sb system are only stable at high temperatures and were retained to room temperature by quenching from the molten state using a technique similar to that developed by Duwez and Willens,[7] but modified to adapt to an arc-furnace.[8]

Prior to the superconductivity measurements, x-ray diffraction patterns were taken for all alloys to assure their homogeneity and positive identification of the proper phases.

B. Apparatus

The T_c's were measured in a conventional adiabatic demagnetization cryostat. Chromium potassium alum [$CrK(SO_4)_2 \cdot 12H_2O$] was used as a cooling salt. Equal volume amounts of powdered salt and Epoxy resin were mixed to form a pill with some 500 evenly spaced No. 42 formex-coated copper wires running through it. Below the salt pill the wires were bundled together. The samples (some 10 mm^3 in volume) were then simply stuck into this wire bundle by means of Apiezon grease. The transitions were observed by measuring the low-frequency (80-cps) susceptibility of the samples with a mutual inductance bridge. It was observed that the superconductivity of these alloys could always be quenched in low fields of 5~30 Oe. This indicates that the superconductivity exhibited in the samples is a bulk phenomenon.

Temperatures were measured with a germanium thermometer, highly doped with arsenic which itself was calibrated against the susceptibility of a cerium-magnesium-nitrate single crystal. The lowest temperature reached was 0.012°K. Thermal equilibrium between thermometer and samples was assured by good thermal insulation (residual heat input into cooling salt being <2 ergs/min.)

III. RESULTS

(a) No transition was detected down to 0.014°K for specially purified Au (resistivity ratio ~10 000) and Ag (resistivity ratio ~10 000).

TABLE II. Heat treatment of the alloys.

	Alloy	Annealing temperature (°C)	Time (day)
(1) hcp phases	Cu-Ge	700	9
	Ag-Al	600	1
	Ag-Sn	550	$6\frac{1}{2}$
	Ag-Sb	550	3
	Au-In	550	4
	Au-Sn	275	85
(2) fcc phases	Cu-Zn	700	$1\frac{1}{2}$
	Ag-Cd	500	2
	Ag-In	700	3
	Au-Zn	700	2
	Au-Cd	700	2

TABLE III. Superconducting transition temperature of the hexagonal close-packed phases.

Alloy composition	Electron concentration ($\mathfrak{z}$)	T_c (°K)
Ag-30 at.%Al	1.60	0.110–127
33.3	1.667	0.126–135
35	1.70	0.100–127
37.5	1.75	0.106–115
40	1.80	0.088–98
Ag-15.5 at.%Sn	1.465	0.025–35
16.5	1.495	0.047–55
17.5	1.525	0.055–71
18.0	1.54	0.066–80
18.5	1.555	0.060–78
20.5	1.615	0.090–95
22.5	1.675	0.090–107
Ag-11.5 at.%Sb	1.46	0.019–?[a]
13.5	1.54	0.028–35
15.5	1.62	0.037–65
Au-16 at.%In	1.32	0.035–100
20	1.40	0.280–330
Cu-14 at.%Ge	1.42	0.025–?[a]
15	1.45	0.084–92
16	1.48	0.117–123
17	1.51	0.072–150
17.5	1.525	0.145–160
18	1.54	0.130–240
18.5	1.555	0.175–180
19	1.57	0.240–260
Cu-14 at.%Si	1.42	0.050–58
Au-11.5 at.%Sn	1.345	0.210–360
12.5	1.375	0.33 –44
13.5	1.405	0.435–460
14.5	1.435	0.430–510
15.5	1.465	0.53 –0.56
16.5	1.495	0.59 –0.61

[a] The superconducting transition could not be followed completely.

(b) fcc solid solutions: Alloys of the following compositions: Au-15 at.% Zn; Au-28–31 at.% Cd; Au-15 at.% Al; Au-12 at.% In; Ag-40 at.% Cd; Ag-15 at.% In; and Cu-34 at.% Zn remain normal down to 0.014°K.

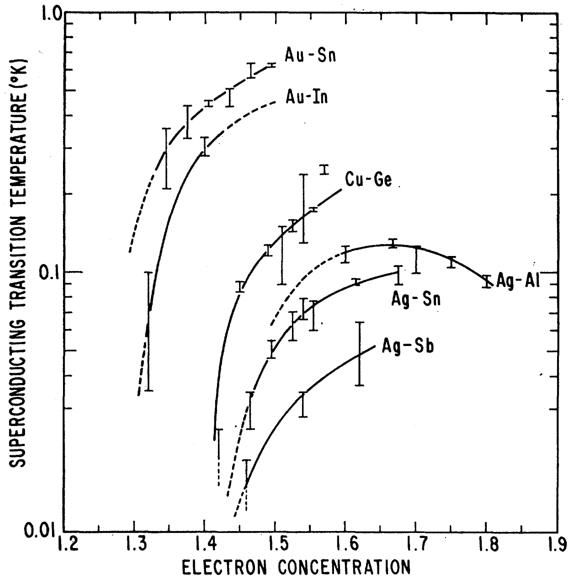

FIG. 1. Superconducting transition temperature of hcp noble-metal-based alloys versus electron concentration. The vertical bar shows the width of the transition.

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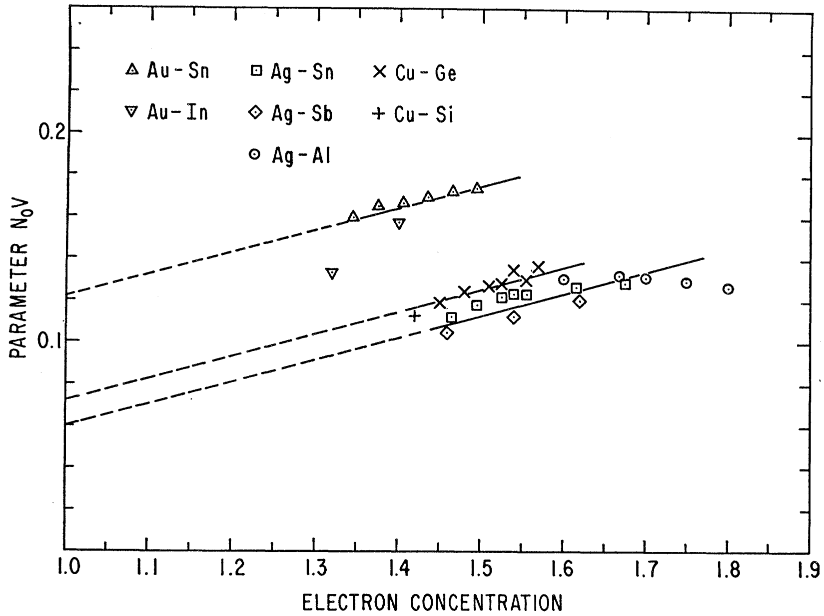

FIG. 2. BCS parameter N_0V as a function of electron concentration. In calculating the N_0V values, the onset temperatures of superconducting transitions were used.

(c) hcp phases: Data obtained from superconducting measurements are listed in Table III. T_c is also plotted as a function of electron concentration $\mathfrak{z}$ in Fig. 1. It is clear that T_c drops sharply as the composition approaches the hcp-fcc two-phase boundary.

(d) The ordered cubic phase of DO_3 structure was retained for the alloy Cu-15.5 at.% Sb. Its T_c was observed at 0.127–0.184°K and its lattice parameter was found to be 5.936±2 Å.

IV. DISCUSSION

While it is not possible to extrapolate from the present results to the superconducting transition temperature of the pure noble metals Cu, Ag, and Au, the present data may serve as a guide when trying to explain the absence of superconductivity in these monovalent metals. Superconductivity is usually not observed for $\mathfrak{z}$ values of less than 2, and the superconductors reported here are, to our knowledge, the ones with the lowest $\mathfrak{z}$ values. Theoretically, there is no reason why any diamagnetic metal should not become superconducting at some low temperature. The analysis which follows supports this, it suggests that the absence of superconductivity in Cu, Ag, and Au above the millidegree temperature range is simply due to a relatively weak electron-phonon interaction in these metals. In the BCS theory of superconductivity, T_c is given by

$$T_c = 1.14\Theta_D \exp(-1/N_0V),$$

where Θ_D is the Debye temperature, N_0 is the density of states at the Fermi surface, and V is an effective attractive electron-electron interaction. It is generally accepted that the electronic structure of the alloys investigated can be described with the model of nearly free electron, i.e., electrons moving in a pseudopotential with an amplitude of the order of only $\frac{1}{10}$ of the Fermi energy. The structure change from fcc to hcp at a $\mathfrak{z}$ value of around 1.4 is explained in this model to occur because the band gaps across the first hcp Brillouin-zone faces are larger than across the first fcc-zone faces and thus lead to a more effective lowering of the kinetic energy of the valence electrons.

The fcc and hcp phases in the noble-metal-base alloys are akin to each other, differing only in the stacking order of the closest-packed planes. Therefore, one may assume that the variation of any lattice-related property should be smooth and continuous across and through the two phases. Any specific deviation may be attributed to the change of lattice structure and hence to the change in the Brillouin zones and relatedly, to a change in the possible interactions between the Fermi surface and the respective Brillouin zones. Using this approach Massalski *et al.* were able to interpret rather successfully the lattice-parameter data of noble-metal-base alloys,[9] and concluded that the Fermi-surface–Brillouin-zone interaction was strongest in the Au-base alloys and weakest in Ag-base alloys.

From this point of view, one may expect that Θ_D does not vary strongly in alloys of the present composition range. The reported data in the literature[10–13] show that, indeed, Θ_D remains nearly constant. It is therefore reasonable to estimate the parameter N_0V of the different hcp phases by using the Θ_D values of the pure metals (e.g., 164, 229, and 343°K for Au, Ag, and Cu, respec-

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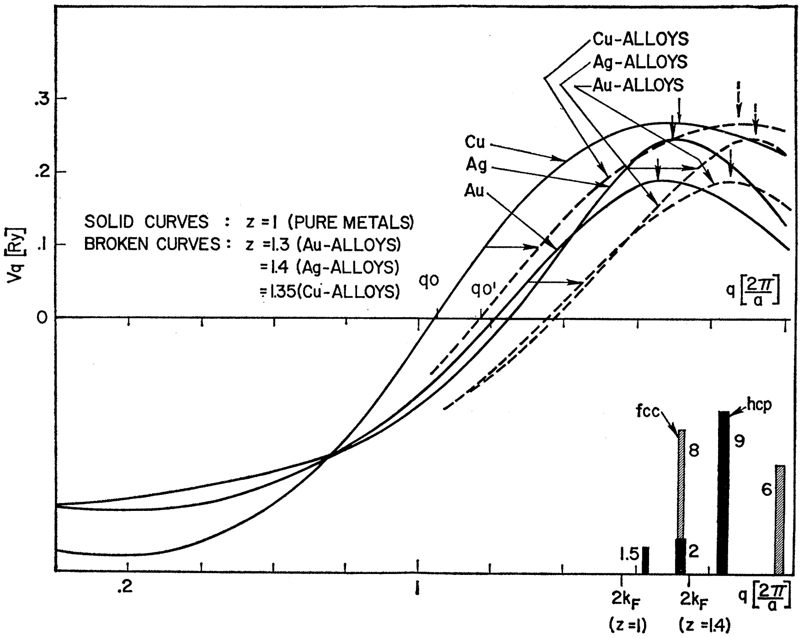

FIG. 3. Fourier expansion of the pseudopotential of Cu, Ag, and Au (data taken from a recent compilation of Cohen and Heine[19]), and extrapolated Fourier expansions of the pseudopotentials of Cu, Ag and Au based alloys at the beginning of the hcp phase ($z=1.35$ for Cu-alloys, 1.4 for Ag-alloys and 1.3 for Au-alloys). Also shown are the locations of the first few reciprocal-lattice vectors of the fcc and hcp structures with their structural weight, as well as twice the Fermi wave vector for free electrons for $z=1$ and $z=1.4$.

tively). In Fig. 2, the N_0V value is plotted against the electron concentration of the alloys. The plot shows that three linear relations between N_0V and $\mathfrak{z}$, with nearly the same slope and independent of solute elements can be approximated, one for each group of alloys of the same host metal. When such linear relations are extrapolated towards $\mathfrak{z}=1.0$, one would be tempted to predict that, should the pure Au, Ag, and Cu metals exist in the hcp structure, they would become superconducting at 0.57, 1.5×10^{-5}, 3.6×10^{-4}°K, respectively. It is particularly interesting to note that the predicted temperature for Au of 0.057°K is easily accessible, and the hcp modification of pure Au has been reported in thin-film work.[14]

From Fig. 2, the N_0V values of the Cu alloys are somewhat higher than those of the Ag alloys at the corresponding $\mathfrak{z}$ value, while those of the Au alloys are considerably higher yet. Qualitatively, this result correlates very well with Massalski's conclusion that the Fermi-surface–Brillouin-zone interaction is the strongest in the Au-base alloys. In addition, it is likely that Au contributes more than one conduction electron per atom in the alloys.

A general conclusion from the present investigation is that the noble-metal-base phases in the hcp structure are superconducting and those in the fcc structure are not. This conclusion is supported by the fact that the sharp decrease in T_c of the hcp phase corresponds to the drastic increase of stacking fault density[15,16] when the alloy composition approaches the two-phase boundary.

Recently, Massalski *et al.*[11–13] reported the data of electronic specific heats on the Ag-Sn and Cu-Ge alloy in the fcc and hcp phases. The coefficient (in mJ/mole °K^2) varies from 0.65 to 0.72 in the fcc phase and from 0.77 to 0.84 in the hcp phase of the Ag-Sn alloys. For the Cu-Ge alloys, the corresponding ranges of the γ value are 0.69–0.72 and 0.73–0.79, respectively. Using the free-electron approximation one may estimate that the density of states in the fcc phase is lower than that in the hcp phase by only 10–15% which is not sufficient to justify the total disappearance of superconductivity above 0.014°K in the fcc phases. Our preliminary measurements of the phonon part of the electrical resistivity in Ag-Sn and Cu-Ge alloys show that $\rho_{300°\mathrm{K}}-\rho_{4.2°\mathrm{K}}$ increases with increasing $\mathfrak{z}$ value. We thus believe that the absence of superconductivity in the fcc phases is not only due to a reduced density of states but also due to a strong decrease in the electron-phonon interaction.

In summary, the superconductivity reported here in the hcp phases of the noble-metal-base alloys is a structure-dependent effect. In the hcp structure, besides the electronic density of states being higher, a stronger electron-phonon interaction results from the proximity of the Fermi surface to the Brillouin-zone boundaries.

Note added in proof. Heine and Weaire[17] have shown that it is possible to calculate approximately the structure dependence of the kinetic energy of the valence electrons with the help of pseudopotential theory and explain the structure change from fcc to hcp with increasing electron concentration. It is more difficult to obtain a theoretical estimate of the average electron-phonon interaction of our alloys as a function of their

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electron concentration. In McMillan's theory,[18] the BCS parameter N_0V is replaced by

$$N_0V=\lambda-\mu^*(1+0.62\lambda)/1.04(1+\lambda)\,,$$

where λ is the electron-phonon coupling parameter and μ^* the Coulomb pseudopotential. McMillan shows that in the pseudopotential approximation λ is given by

$$\lambda=\tfrac{1}{2}\pi\frac{E_F}{k_Fe^2}\frac{\langle v_q^2\rangle}{\langle\omega^2\rangle/\Omega_p}\,,$$

with

$$\langle v_q^2\rangle=\int_0^{2k_F}v_q^2q^3dq\Big/\int_0^{2k_F}v_0^2q^3dq\,.$$

Here E_F is the Fermi energy, k_F is the Fermi wavevector, $\langle\omega^2\rangle$ is an average over phonon vibration frequencies, Ω_p is the unshielded ion plasma frequency, and v_q is the Fourier components of the pseudopotential. Plots of v_q versus q which are thought to apply for Cu, Ag, and Au are shown in Fig. 3 (data taken from Cohen and Heine[19]). We have extrapolated those plots to the hcp alloys with the indicated electron concentrations with the help of Heine's assumption that v_q should depend on $q/2k_F$ only. Also shown in Fig. 3 are the locations of the first reciprocal-lattice vectors of the fcc and hcp structures, indicating their structural weight (i.e., the number of equivalent vectors times the square of their structure factor). It can be seen that with increasing electron concentration the maximum of v_q moves from about the location of the first reciprocal-lattice vector of the fcc structure to the third reciprocal-lattice vector of the hcp structure. This would mean that the energy gaps across the 8 nearest fcc Brillouin-zone faces decrease with increasing $\mathfrak{z}$ ratio whereas those across the 12 third nearest hcp Brillouin-zone faces increase. That then is presumably the reason for the structure change from fcc to hcp around $z=1.35$. The parameter λ, however, remains unchanged in this approximation, since the assumption of v_q being dependent on $q/2k_F$ leaves $\langle v_q^2\rangle$ unchanged. Structure dependent effects have not been included in the expression of $\langle v_q^2\rangle$ and are corrections of higher order. It is therefore at this point difficult to say whether the experimentally observed structure dependence of λ, in the context of pseudopotential theory, is more due to a change in $\langle v_q^2\rangle$ or a change in $\langle\omega^2\rangle$. A change in $\langle\omega^2\rangle$ can of course be expected in going from the fcc to the hcp structure, in spite of the fact that the compressibility and the Debye temperature remain essentially unchanged. This is true because of the difference in elastic anisotropy in the two structures.

The added discussion here further supports our conclusion that the absence of superconductivity in the fcc phase (i.e., for $\mathfrak{z}<\sim1.3$) is most likely due to weaker electron-phonon interaction rather than due to the smaller density of states at the Fermi surface.

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