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Superconductivity in metal-semiconductor eutectic alloys*

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In an eutectic alloy obtained by melting the constituents, alternating domains of metal and semiconductor can exist in a well-defined microscopic array. The possibility of superconductivity arising from an interface interaction between the metal and semiconductor has been investigated. Superconductivity has been observed as a *bulk* property of some eutectic alloys (e.g., Al-Si and Al-Ge). Transition temperatures well in excess of those for the pure metal were found. The effect of rapid cooling the alloys from the liquid state on the microstructure and on the superconducting properties has been studied. It was found that a decrease in the characteristic domain sizes of the metal and semiconductor was accompained by an increase of the superconducting transition temperature of the alloy. The results suggest that the enhancement of T_c depends on the Fermi energy of the metal. In metal-metal eutectic systems with comparable microstructure, no increase of T_c was observed. Several explanations of the experimental findings are considered. The exciton mechanism discussed by Ginzburg and by Allender, Bray, and Bardeen is considered as a possible means to account for the enhancements of the metal T_c's.

I. INTRODUCTION

Superconductivity in metal-dielectric systems is a subject of much current interest. Various mechanisms leading to superconductivity at the interface regions of such binary systems have been proposed.[1–5] A number of experimental efforts have been devoted to demonstrating the existence of the suggested mechanisms.[6,7] Most of these studies involved thin films obtained by vapor deposition. Experiments with thin films are invariably accompanied by problems such as gaseous contamination and nonuniformity of the samples. Furthermore, the small sample size precludes many measurements. Intimate contact between metal and dielectric layers is usually difficult to achieve. In an eutectic alloy obtained by melting the constituents, alternating domains of metal and semiconductor can exist in a well-defined microscopic array. For this reason, superconductivity resulting from an interface interaction could be realized in this type of alloy. This possibility provided the motivation for the present investigation. The microstructure of these alloys was studied by optical microscopy and by scanning electron microscopy. Measurements included resistivity, magnetoresistivity, and magnetization as a function of temperature.

II. EXPERIMENTAL PROCEDURES

The alloys studied contained x at.% of a metal A and $100-x$ at.% of a semiconductor B. Their compositions are given in Table I.

Alloys were prepared by induction melting of the appropriate quantities of the constituents in a glassy carbon crucible under an argon atmosphere. The purity of Ge and Si was 99.999% and that of metals was 99.99% except Be which contained an undetermined amount of oxide and Sb which was 99.9%. The as-cast samples were drawn into 2-mm rods from the melt. The quenched alloys were obtained by rapid cooling from the liquid state following a technique described in Ref. 8. The cooling rate is estimated to be 10^6 °C/sec.

To determine the crystal structure and the microstructure of the alloys, techniques of x-ray diffraction and scanning electron microscopy (SEM) were used. Energy dispersive analysis of the secondary-x-ray-emission spectrum (EDAX) was used in conjunction with SEM to identify phases. The lattice parameters of each phase were determined from Debye-Scherrer films and were computed by using the Nelson-Riley extrapolation function.

Electrical resistivity was measured by the standard four-probe technique. Magnetoresistivity was obtained in fields up to 10 kG. The superconducting transitions were observed by a standard ac bridge technique, using a frequency of 1 kHz. The esti-

TABLE I. Compositions of alloys.

Constituents A	B	at.% of A in A_xB_{100-x}
Al	Ge	1, 2, 5, 10, 25, 50, 70
	Si	99, 97.5, 95, 90, 85
		80, 75, 70, 60, 50, 10
Ga	Ge	10, 50
	Si	10, 50
Sn	Ge	10, 20, 70
Pb	Ge	2, 5, 10, 70
In	Ge	10, 70
Be	Si	62
Tl	Ge	10, 70

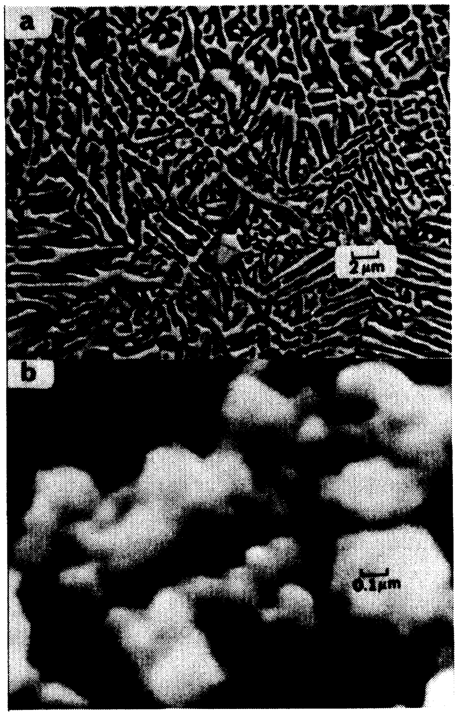

FIG. 1. Scanning electron micrographs of (a) $Al_{70}Ge_{30}$ as cast; (b) $Al_{70}Si_{30}$ liquid quenched. The Al in both samples has been leached out during etching.

mated ac magnetic field at the specimen location was of the order of a few gauss. The temperature was measured with a germanium resistance thermometer with an accuracy of 0.05 °K. Magnetization as a function of field was obtained with a standard Faraday magnetometer.

III. RESULTS

Alloys were studied both in the as-cast form and in the rapidly quenched form. Most of the results reported here are for Al alloys.

A. As-cast alloys

1. Microstructure analysis

The x-ray diffraction analysis indicates that all the as-cast alloys consist of two phases as expected from the phase diagrams.[9] The lattice parameters were found to be independent of compositions. For example, the alloy $Al_{70}Si_{30}$ gives a lattice parameter of 4.048 ± 0.005 Å for Al and 5.432 ± 0.005 Å for Si. This indicates that there is no significant mutual solid solubility of the two phases. The SEM studies further reveal the micromorphology of the alloys. The general features of the Al-Si and Al-Ge microstructure resemble those reported in previous metallographic studies.[10,11] For as-cast Al-Ge samples used in this study, typical Al domains are lamellar in form and have a characteristic thickness ranging from 400 to 3500 Å. The adjacent Ge domains range from 400 to 2500 Å. A scanning electron micrograph is shown in Fig. 1(a). The beginning formation of lamellar colonies is noticeable. The Al-Si eutectic exhibits a less regular structure. Protruding fan-shaped Si spikes are surrounded by Al.

2. Electrical resistivity

Superconducting transitions in the as-cast alloys were observed as a function of temperature, magnetic field, composition, and heat treatment. Electrical resistivity as a function of temperature for $Al_{70}Ge_{30}$ and $Al_{70}Si_{30}$ is shown in Fig. 2. The resistivity begins to drop at a temperature defined as T_c' and falls sharply to a value less than 10^{-9} Ω cm at a temperature defined as T_c. For $Al_{70}Ge_{30}$, $T_c' \cong 2$ °K and $T_c \cong 1.8$ °K. For $Al_{70}Si_{30}$, $T_c' \cong 1.9$ °K and $T_c \cong 1.5$ °K. For these alloys, annealing at 600 °C for 8 days produced no observable effect on T_c. Critical-current-density (J_c) measurements at 1.3 °K in zero magnetic field give values on the order of 10^3 A/cm^2 for both alloys. The annealing reduces J_c by at least one order of magnitude.

The effect of magnetic field on the resistive transitions for these two alloys at 1.3 °K is shown in Figs. 3 and 4. For $Al_{70}Ge_{30}$, a sharp resistive transition occurs at a field of 85 G, and for $Al_{70}Si_{30}$ a similar transition occurs at 40 G. However, a small amount of superconductivity appears to persist in much higher fields (approximately 3 kG for $Al_{70}Ge_{30}$). The resistive transition was nearly independent of the field orientation with respect to current direction.

The resistive transitions were also found to be nearly independent of composition. For low Al concentrations (e.g., Al_5Ge_{95}) T_c remains unchanged while T_c' is somewhat higher. The critical current density is of the order of 10 A/cm^2 for

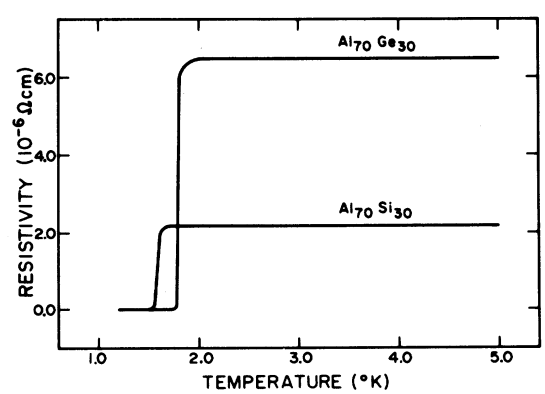

FIG. 2. Electrical resistivity as a function of temperature for $Al_{70}Ge_{30}$ and $Al_{70}Si_{30}$ as cast.

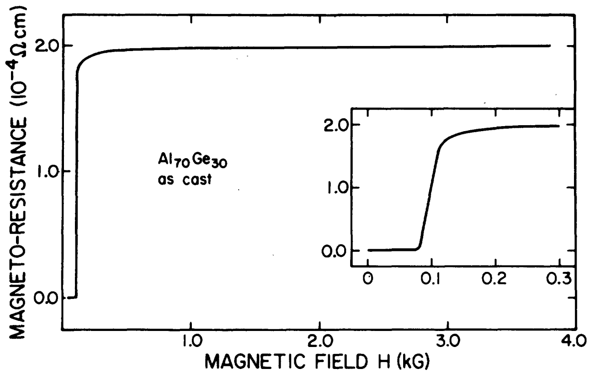

FIG. 3. Longitudinal magnetoresistance at 1.3 °K as a function of magnetic field for $Al_{70}Ge_{30}$ as cast. The insert shows low-field data.

Al_5Ge_{95}. Two examples of resistive transitions of alloys containing lower Al concentrations are shown in Fig. 5.

3. *Magnetic measurements*

Relative inductance change as a function of temperature using a standard ac bridge for $Al_{70}Ge_{30}$ and $Al_{70}Si_{30}$ is shown in Fig. 6. A large inductive transition occurs at a slightly lower temperature (~ 0.1 °K lower) than that of the resistive transition shown in Fig. 2.

Typical results of magnetization measurements at 1.3 °K for $Al_{70}Ge_{30}$ are presented in Fig. 7. As a function of field, a constant diamagnetic susceptibility up to a field of 25 G was observed. With increasing fields above 25 G, the negative magnetization falls abruptly. For fields exceeding 200 G, it decreases more slowly. Complete vanishing of superconductivity occurs at a field of about 7 kG. The magnetization as a function of field for $Al_{70}Si_{30}$ is similar to that for $Al_{70}Ge_{30}$.

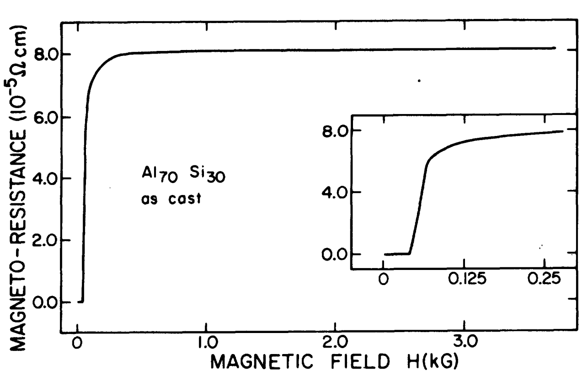

FIG. 4. Longitudinal magnetoresistance at 1.3 °K as a function of magnetic field for $Al_{70}Si_{30}$ as cast. The insert shows the low-field data.

B. Liquid-quenched Al-Ge and Al-Si alloys

1. *Crystal structure and microstructure*

For Al-Si alloys, x-ray diffraction studies indicate that liquid-quenched alloys consist of two phases, Al and Si, in agreement with previous work.[12] A lattice parameter of 5.434 ± 0.003 Å was found for the Si phase and was independent of Si concentration. The lattice parameter of the Al phase was found to vary slightly with increasing Si concentration in the alloy. A graph is shown in Fig. 8. It should be noted that a Si phase is observed in Debye-Scherrer films for alloys containing more than 5-at.% Si, however, the Al lattice parameter decreases with increasing Si concentration for alloys with somewhat higher Si content. The behavior is in general agreement with previous studies.[13]

Since it has been previously established that the microstructure of the Al-Si eutectic is very sensitive to the cooling rate from the melt,[11] it is expected that rapid quenching from the melt can drastically alter it. The SEM studies on rapidly quenched Al-Si alloys substantiate this expectation. In the quenched samples, there is a spatial distribution of cooling rates. In the regions where the cooling rate is greatest (near the substrate), the eutectic composition is seen to be shifted to higher Si concentrations. In Fig. 1(b), a scanning electronmicrograph of a region near the substrate is shown. In these regions, Al domains ranging in size from less than 100 Å to several hundred angstroms can be seen interpenetrating a network of Si crystals typically 500–3000 Å in size. The Al here is apparently rejected from the Si during rapid cooling. X-ray analysis of Al-Ge alloys gives similar results except for the presence of a

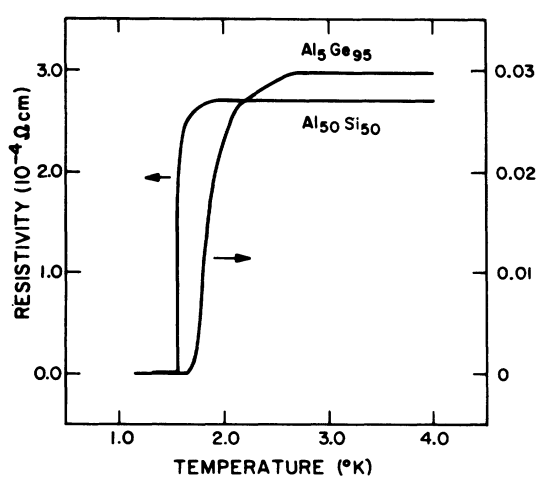

FIG. 5. Electrical resistivity as a function of temperature for Al_5Ge_{95} and $Al_{50}Si_{50}$ as cast.

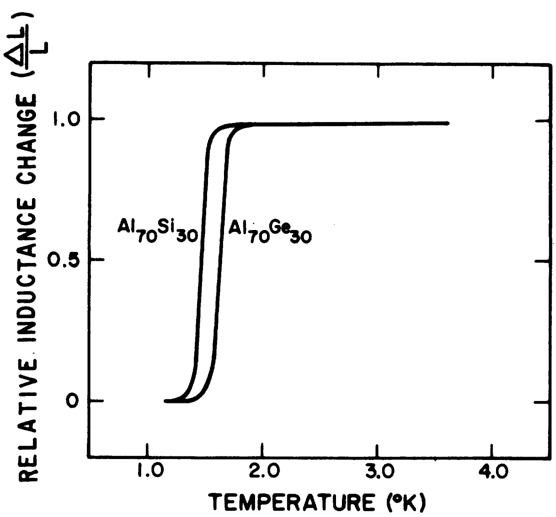

FIG. 6. Relative inductance change as a function of temperature for cast $Al_{70}Ge_{30}$ and $Al_{70}Si_{30}$.

tetragonal Al_2Ge phase and another phase the crystal structure of which has not been determined.[14,15]

2. *Electrical resistivity*

Electrical resistance as a function of temperature for several liquid quenched Al-Si alloys is shown in Fig. 9. The superconducting transition temperature T_c increases with increasing Si content of the alloy reaching a maximum of ~5.5 °K for the alloy $Al_{70}Si_{30}$. T'_c, the onset temperature, reaches 7.5 °K in some samples containing 40–50-at.% Si. However, significant broadening of the transition accompanies additions of Si in excess of 40 at.%. For example, samples containing 50-at.% Si have transition widths as large as 3 °K. Similar results were found for Al-Ge alloys. The onset temperature T'_c reaches a maximum of ~6.0 °K for the alloy $Al_{70}Ge_{30}$.

The magnetoresistance of rapidly quenched $Al_{70}Si_{30}$ was measured for both the transverse and longitudinal orientations of field with respect to current. The magnetoresistance was nearly independent of field orientation. A typical graph is shown in Fig. 10. A broad magnetoresistive transition beginning at 3.5 kG and ending at about 10 kG is observed.

3. *Magnetic measurements*

Results of the ac inductance bridge measurements for two quenched $Al_{70}Si_{30}$ samples are shown in Fig. 11. The onset of the transition is somewhat lower than those indicated by the resistance measurements (Fig. 7). Most of the transition occurs between 1.5 and 3.0 °K. Magnetization as a function of applied field at 1.4 °K for $Al_{70}Si_{30}$ quenched from the melt is illustrated in Fig. 12.

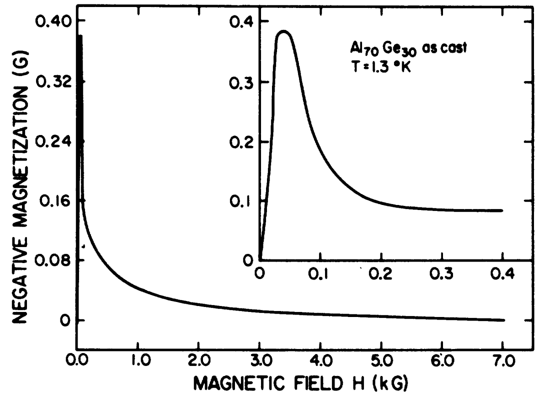

FIG. 7. Magnetization as a function of magnetic field for cast $Al_{70}Ge_{30}$ at 1.3 °K. The insert shows the low-field data.

The phenomenon of irreversible magnetization is observed. The sample shows linearly increasing negative magnetization up to 100 G. A sharply decreasing magnetization is observed for fields greater than 200 G. Superconductivity persists to fields up to between 6 and 7 kG.

C. Results for other alloys

In Table II a summary of some results for other alloy systems is presented. In the table ΔT_c refers to the maximum observed enhancement $(T'_c - T_{c0})$, where T_{c0} is the bulk superconducting transition temperature of the metal included in each system. To define T'_c, electrical resistivity measurements were used.

The rapidly quenched alloys $Sn_{70}Ge_{30}$ and $Pb_{70}Ge_{30}$ were studied by x-ray diffraction and found to contain only Sn and Ge, and Pb and Ge, respectively. Relative inductance measurements as a function of temperature for as-cast $Ga_{10}Ge_{90}$ showed a large,

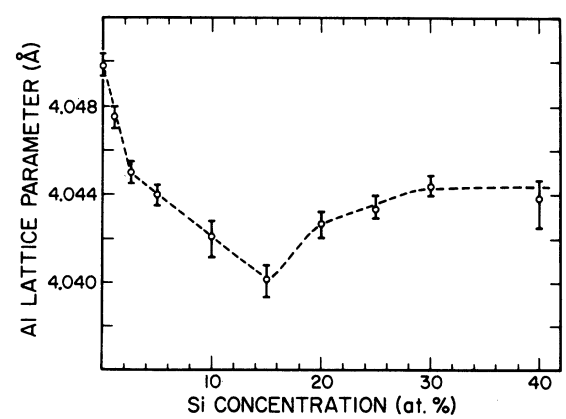

FIG. 8. Lattice parameter of Al, in liquid quenched Al-Si alloys, as a function of Si content of alloy.

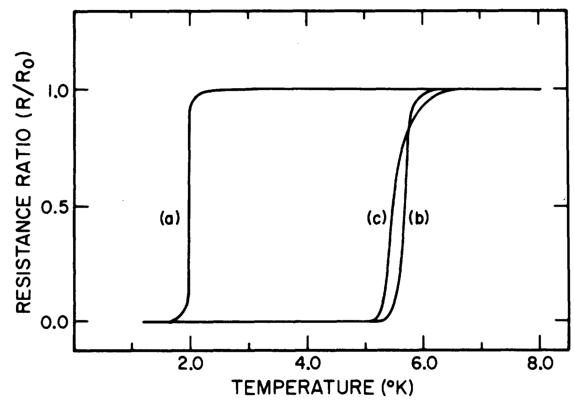

FIG. 9. Resistance ratio (R/R_0) (R_0 is the residual resistivity at 8 °K) as a function of temperature for (a) $Al_{95}Si_5$, (b) $Al_{70}Si_{30}$, (c) $Al_{60}Si_{40}$ quenched from the liquid state.

broad transition with an onset temperature $T_c' = 3.5$ °K. A very sharp transition at 6.4 °K was also found, but was only a few percent in magnitude of the dominant transition. The T_c of this smaller transition can presumably be identified as that of β-Ga.[16] For the rapidly quenched $Ga_{10}Ge_{90}$ alloy, inductance measurements showed a very similar result. Resistivity measurements for $Be_{62}Si_{38}$ showed a broad, often incomplete, transition with an onset temperature $T_c' \cong 9.0$ °K. A few samples are completely superconducting with $T_c \cong 6.0$ °K.

To clarify the role of the semiconducting phase in the observed superconductivity of alloys so far reported, a study of the eutectic system between two metallic phases Al–Al_2 Cu was conducted. X-ray analysis of the as-cast alloy $Al_{48.1}$ $(Al_2Cu)_{51.9}$ (eutectic composition) indicated that two phases Al and Al_2Cu are present. A metallographic study shows a lamellar eutectic structure similar to that of Al-Ge. However, in many regions, the Al and Al_2Cu domain sizes are noticeably smaller than those of the Al-Ge eutectic. The electrical resistivity of $Al_{48.1}(Al_2Cu)_{51.9}$ in the as-cast form showed no evidence of a superconducting transition down to a temperature of 1.25 °K. Finally, pure Al, Sn, and Pb were quenched to determine the effect of rapid cooling on the superconducting transition of the pure metals. Resistivity measurements on these samples showed no enhancement of their respective superconducing transition temperatures.

IV. ANALYSIS AND DISCUSSION

All alloy systems studied in this investigation have one feature in common. The equilibrium phase diagrams indicate that only two phases are present in a given alloy. One of these phases is semiconducting, the other is metallic. It was found that the as-cast alloys of Al-Ge and Al-Si had superconducting transition temperatures significantly enhanced from those of pure Al. In all as-cast alloys showing an enhancement of the T_c of the metallic phase, rapid quenching the alloys was observed to increase T_c further. Parallel microstructure studies indicated that the size of the metal domains decreased significantly as a result of rapid quenching.

Of the metals studied, enhancement of T_c was observed for Al, Be, Ga, Sn, and Pb. No significant enhancement was found for the metals In, Tl, Cd, and Zn. A simple method of presenting these results is shown in Fig. 13. The maximum observed enhancement $(\Delta T_c)_{max}$ for each metal is plotted as a function of the Fermi energy, calculated from the free-electron model. For Al, $(\Delta T_c)_{max}$ is nearly the same for both the Al-Ge and Al-Si alloys. However, since the presence of metastable phases in quenched Al-Ge alloys plays

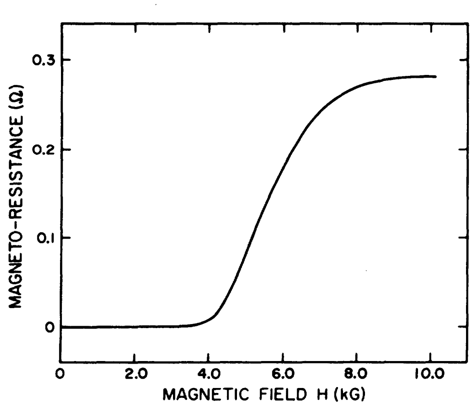

FIG. 10. Longitudinal magnetoresistance at 1.3 °K as a function of magnetic field for $Al_{70}Si_{30}$ as quenched from the liquid state.

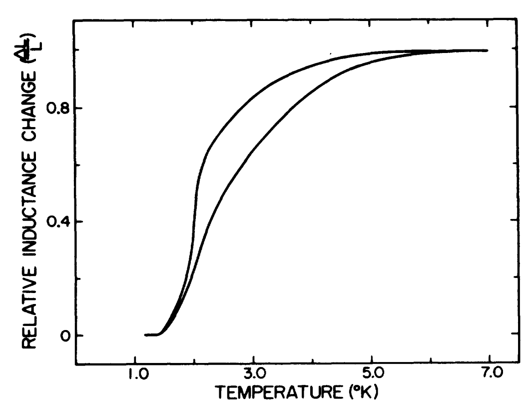

FIG. 11. Relative inductance as a function of temperature for two samples of $Al_{70}Si_{30}$ quenched from the liquid state.

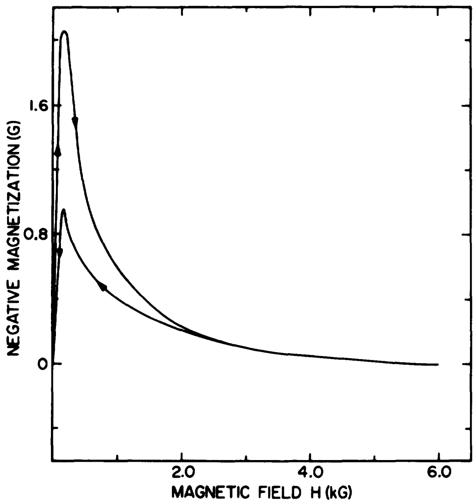

FIG. 12. Magnetization as a function of applied field at 1.4 °K for $Al_{70}Si_{30}$ quenched from the liquid state. The arrows indicate the direction of field change.

a role in the superconductivity,[14] the maximum enhancement obtained for Al-Si alloys is plotted. Since Be and Ge do not form a eutectic system, the result for Be-Si is used. For all other metals, the $(\Delta T_c)_{max}$ plotted is that obtained in a Ge matrix. Only the result for the dominant transition at 3.5 °K is plotted for the Ga-Ge system since the presence of the β phase of Ga is likely to be responsible for the small transition at 6.4 °K. A systematic dependence of $(\Delta T_c)_{max}$ on the Fermi energy is observed.

Consideration is now given to explaining the observed enhancements of T_c. The following possibilities exist.

(i) The presence of dissolved Si or Ge in the metal domains, disorder in the metal lattice, strain, or surface effects can all result in the softening of the phonon modes of the metal. This in turn could increase T_c.

(ii) The existence of surface-phonon modes (Rayleigh waves) and electronic surface states at the metal-semiconductor interface resulting in some kind of surface superconductivity as suggested by Ginzburg[1] and others might be considered.

(iii) The presence of a third metastable superconducting phase in the alloys could explain the enhanced T_c.

(iv) The high onset temperature T_c' observed in some alloys (e.g., 7.5 °K in Al-Si alloys and 9.0 °K in Be-Si alloys) may arise as a result of superconducting fluctuations of a "Curie-Weiss" nature rather than a true superconducting state.

(v) If the metal electrons can tunnel a significant distance into the Ge or Si and interact with the valence electrons of the semiconductor, then the exciton mechanism originally proposed by Ginzburg[1] and modeled by Allender, Bray, and Bardeen (ABB)[2] could be effective.

The following can be said regarding the first possibility. For Al-Si alloys, the highest transition temperature is obtained for alloys containing 30 at.% Si, whereas the solubility limit of Si in Al is no more that 12 at.%.[13] A rapid increase of T_c with increasing Si content of the alloy is associated with the appearance of Si lines in the x-ray pattern (i.e., the precipitation of Si crystals out of the matrix). Thus, the presence of dissolved Si in Al does not explain the observed enhancement of T_c. Rather, the enhancement effect seems to be associated with the formation of Al-Si interface area. Since the rapidly quenched pure-Al samples showed no enhancement of T_c, it is clear that disorder arising from rapid cooling alone will not increase the T_c of Al. Although strain effects have been observed to increase the T_c of Al,[17] the magnitude of this effect (an increase of about 0.2 °K for a tensile strain of 3%) is small. Accounting for the enhancements of this investigation in terms of strain effects seems very unlikely.

TABLE II. Maximum observed enhancement of T_{c0} for various alloys.

Alloy	$T_c' - T_{c0} = \Delta T_c$(°K)	Remarks
$Sn_{70}Ge_{30}$	7.0° − 3.7° = 3.3°	r.q.[a]
$Pb_{70}Ge_{30}$	7.5° − 7.2° = 0.3°	r.q.
$Ga_{10}Ge_{90}$	6.4° − 1.1° = 5.3° 3.5° − 1.1° = 2.4°	r.q. and as cast. Two transitions are observed. Low-temperature transition is dominant. The β and γ phases of Ga are present.
$In_{70}Ge_{30}$	0	No enhancement of T_c in as-cast or r.q. alloys
$Tl_{70}Ge_{30}$	0	
$Zn_{70}Ge_{30}$	0	
$Be_{62}Si_{38}$	~(9.0° − 0.0°) = 9.0°	r.q. Broad resistive transition

[a] Rapidly quenched.

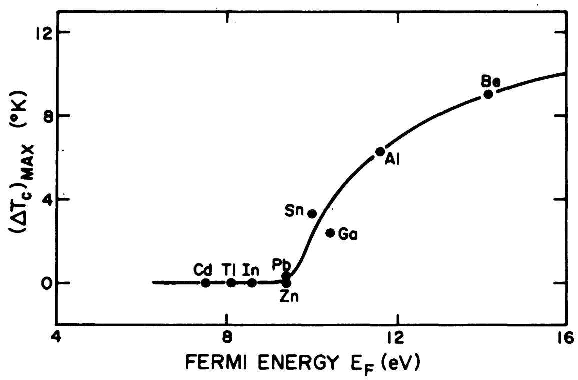

FIG. 13. Enhancement of T_c vs Fermi energy of the metal.

Dickey and Paskin[18] have performed molecular dynamical calculations to determine how the phonon spectrum of small metal grains differs from the bulk phonon spectrum of a metal. Substantial softening of the phonon modes occurs when a metal grain is a few atomic layers thick and has at least one free surface. The bulk phonon spectrum is quickly approached as the grain becomes larger or the free surface is eliminated. Hauser,[19] for example, has used this approach to explain enhancement of T_c in cosputtered Al-Ge films.[20] However, a large density decrease was observed in these films compared to the bulk Al-Ge alloy indicating the presence of voids and internal free surfaces. No comparable density change occurs in the alloys of this study. Furthermore, the size of the Al domains here is larger than the grain size obtained in the coevaporated films containing Al. It is doubtful that the softening of the phonon spectrum can account for the enhancement of T_c.

The second possibility, that of surface superconductivity, cannot be readily ruled out. However, it is not clear that the observed T_c enhancement as a function of the Fermi level of the metal can be explained in terms of surface electronic levels. Also, there is the objection that long-range order cannot exist in a two dimensional system discussed by Ginzburg.[1]

The possibility that a third undetected metastable phase exists in the as-cast alloys is remote. Furthermore, that such a phase could remain after annealing at 600 °C for 8 days is very unlikely. For the rapidly quenched Al-Si alloys, magnetization measurements, and resistivity measurements all indicate that the superconductivity is a bulk property of the alloy. That a third metastable phase undetected in the x-ray analysis could account for this is unreasonable.

Regarding the fourth possibility, Strongin[21] has pointed out that "Curie-Weiss" behavior and fluctuation phenomenon can occur in thin films where the electronic mean free path is small. The high onset temperature T_c' of liquid-quenched Al-Si and Be-Si alloys may be associated with such behavior. Examination of Fig. 9(b) suggests for example that the portion of the resistive transition above ~ 5.7 °K has the general characteristics of fluctuation superconductivity. The electronic mean free path in this alloy ($Al_{70}Si_{30}$) is difficult to estimate due to the irregular shape and nonuniform thickness of the liquid-quenched sample. Using the rough value of 10^{-4} Ω cm (based on an average sample thickness of order 1 μ) for the resistivity, we find an electronic mean free path of order 5 Å. Superconducting fluctuations can be expected to be observable in this case. Thus, care must be exercised when defining the highest temperature for which a stable superconducting state exists.

The curve in Fig. 13 suggests that the Fermi energy of the metal plays an important role in the observed superconductivity. In the ABB model for excitonic superconductivity such a dependence is predicted. The results of this investigation are now discussed in terms of the ABB model for excitonic superconductivity.

We take a simple model for the Al-Si and Al-Ge microstructure consisting of alternating layered domains of Al and Si (Ge) of thickness t_{Al} and t_{Si}, respectively. We consider a single domain of Al sandwiched between two Si layers. ABB give the superconducting transition temperature of such a sandwich by the following approximate formula:

$$T_c \cong (\Theta_0/1.45)\, e^{-1/g_{eff}} \quad , \tag{1}$$

$$g_{eff} = \lambda^*_{ph} + (\lambda^*_{ex} - \mu')/[1 - (\lambda^*_{ex} - \mu')\ln(\omega_g/\omega_{p0})] \ , \tag{2}$$

$$\mu' = \mu/[1 + \mu \ln(\omega_F/\omega_g)] \quad .$$

The parameters λ^*_{ph} and λ^*_{ex} are the renormalized phonon and exciton interaction constants, μ is the Coulomb interaction constant, $\hbar\omega_g$ and $\hbar\omega_F$ are the energy gap of the semiconductor and the Fermi energy of the metal, respectively, and Θ_0 and $\hbar\omega_{p0}$ are the Debye temperature and Debye energy of the metal. Requiring that $T_c = 1.18$ °K (the transition temperature of pure Al) when $\lambda^*_{ex} = 0$, and taking $\hbar\omega_F = 11.6$ eV, $\hbar\omega_g = 1$ eV, $\Theta_0 = 428$ °K, and a reasonable estimate of $\mu = 0.3$ (for Al), it is found that $\lambda^*_{ph} \cong 0.29$. Then for a given enhanced T_c, an estimate can be made of the corresponding value of λ^*_{ex}. Choosing $T_c = 1.8$ °K (as-cast $Al_{70}Ge_{30}$) and $T_c = 5.5$ °K (T_c of rapidly quenched $Al_{70}Si_{30}$) the results are $\lambda^*_{ex} = 0.034$ and $\lambda^*_{ex} = 0.127$, respectively. We ignore the high-temperature tail of quenched $Al_{70}Si_{30}$ which may be due to superconducting fluctuations. The corresponding unrenormalized values of the exciton interaction constant ($\lambda_{ex} = \lambda^*_{ex}/[1 - \lambda^*_{ex}]$) are $\lambda_{ex} = 0.035$ and $\lambda_{ex} = 0.161$. Using the ABB approximate expression for λ_{ex} in terms of the characteristic parameters of the sandwich

$$\lambda_{ex} \cong s\gamma b\mu\,(\omega_p^2/\omega_g^2) \quad , \tag{3}$$

a rough idea of the value of these parameters is obtained. In the formula, $\hbar\omega_p$ is the plasma frequency of valence electrons in the semiconductor, s is a screening factor which approximates the effect of the dielectric tensor ($s \sim \langle 1/\epsilon \rangle$), γ is a factor which accounts for the reduced amplitude of the wave function of metal electrons which tunnel into the semiconductor regions, and b is a factor which represents the fraction of time which metal electrons spend in the semiconductor regions. With the favorable estimates $s \sim \frac{1}{3}$, $\gamma \sim \frac{1}{3}$, $\hbar\omega_g = 1$ eV, and $\hbar\omega_p = 10$ eV, it is found that $\lambda_{ex} = 0.035$ gives $b \cong 0.012$ and $\lambda_{ex} = 0.161$ gives $b \cong 0.048$. Less favorable values of the parameters imply a larger b. Since b must be of the order of $(\gamma(2D)/t_{Al})$ (with D being the characteristic tunneling depth of metallic electrons into the semiconductor and the factor of 2 arising from the semiconductor being on both sides) we can estimate D. Table III is a summary of these results. The values of D/t_{Al} are probably only a lower bound for this parameter. Thus in as-cast $Al_{70}Ge_{30}$, we find letting $\langle t_{Al} \rangle \sim 1000$ Å, $D > 17$ Å and for rapidly quenched $Al_{70}Si_{30}$, with $\langle t_{Al} \rangle \sim 200$ Å, $D > 14$ Å.

The above calculation should be taken only as a very rough estimate of D. However, one fact emerges from it. To account for the observed enhancement of T_c, a somewhat larger tunneling depth D than that indicated by ABB probably should be assumed. Concerning this fact, it may be noteworthy that the presence of Al impurities in Si or Ge could enhance the tunneling depth. In the alloy systems studied here, in particular the rapidly quenched alloys, the Si and Ge are probably heavily doped. The presence of large quantities of p-type impurities may be essential for obtaining a large value of D and consequently for enhancing T_c. Strongin *et al.* have recently reported results for ultrathin Al films expitaxially deposited on a single Si crystal.[5] No significant enhancement of T_c was found. The lack of impurities in the Si may be significant in these experiments. In addition, for ultrathin Al films, the effect of extremely small dimensions (~10–50 Å) on the electronic structure of Al plays an unclear role in the exciton mechanism.

TABLE III. Approximate values for λ_{ex}, b, t_{Al}, and D for an Al transition temperature T_c. Values of $\gamma \sim \frac{1}{3}$, $s \sim \frac{1}{3}$, $\hbar\omega_p = 10$ eV, and $\hbar\omega_g = 1$ eV and $\mu = 0.3$ are assumed.

T_c (°K)	λ_{ex}	b	t_{Al} (approx.) (Å)	D (≳) (Å)
1.8	0.035	0.012	1000	17
5.5	0.161	0.048	200	14

The results shown in Fig. 13 suggest a relationship between the maximum observed enhancement of T_c and the Fermi energy of the metal. Numerical calculations by ABB predict the functional dependence of T_c on E_F (Fig. 7 of Ref. 2). In particular, the ABB results show that no significant enhancement of T_c will occur below a certain value of the Fermi energy. This "threshold" Fermi energy depends on the width (in energy units) of the exciton spectrum. For the case of the quenched alloys of this study, the exciton spectrum will have a larger width than that expected from a single crystal of Si or Ge. This implies that the "threshold" Fermi energy will be large. A rough estimate of 10 eV for the threshold energy is consistent with the results of ABB and with the experimental findings presented in Fig. 13. Finally, the dependence of T_c on E_F predicted by ABB is very similar to that observed in Fig. 13.

The magnetic behavior expected from an alternating metal-semiconductor structure such as that of as-cast $Al_{70}Ge_{30}$ will be complex. Clearly, an intrinsic Meissner effect will not be observed for the semiconductor domains. However, if the semiconductor layers are sandwiched between superconducting metal layers within a lamellar colony, then a weak magnetic field normal to the layers can be expelled from the entire lamellar colony. A weak magnetic field parallel to the interfaces will selectively penetrate the semiconducting layers of the colony. Since the lamellar colonies in the microstructure have essentially random orientations with respect to each other, the behavior of the bulk alloy must reflect both orientations of the field with respect to the lamellar colonies. In particular, a penetrating magnetic flux line will necessarily cross some lamellar colonies in the direction normal to the interfaces. Thus the magnetic field will penetrate the sample significantly only when the critical field for the normal orientation is exceeded. This field can be estimated if we make the rather crude assumption that the entire Al domains are superconducting with a single transition temperature, and that flux is completely excluded from the sample. Then letting $T_c = 1.8$ °K for the Al domains, this gives $\Delta(T=0\,°\mathrm{K}) \cong 1.6 K_B T_c = 2.48\times10^{-4}$ eV, and $\Delta(T=1.3\,°\mathrm{K}) \cong \Delta(0)(1 - T/T_c)^{1/2} = 1.32\times10^{-4}$ eV. Noting that the field must be screened from the semiconductor domains as well as from the Al itself, and using a simple thermodynamic argument gives

$$d_{Al}[(\tfrac{1}{2}) N_{E_F} \Delta^2(1.3\,°\mathrm{K})] = (H_c^2/8\pi)(d_{Al} + d_{Ge}) \quad . \tag{4}$$

In the formula, d_{Al} and d_{Ge} are the characteristic thicknesses of the Al and Ge layers, respectively.

With $d_{Al} = 2d_{Ge}$, and $N_{E_F} \cong 1.7\times 10^{22}$ (states/eV cm^3), the resulting field is $H_c \cong 60$ G. Thus for a field of roughly this value or somewhat less (demagnetization effects are not included) magnetic flux will penetrate the sample. This rough estimate based on the simple assumptions above is at least consistent with the magnetization curve shown in Fig. 7 and the magnetoresistivity curve shown in Fig. 3. The small magnetization which persists to much higher fields can be explained by considering the behavior of the lamellar layers in the presence of a field parallel to the interfaces. Very weak fields can penetrate the Ge layers in this case. However, due to the small size of the Al domains[22] and, more importantly, due to the fact that the order parameter may vary significantly as a function of distance from the interface within an Al domain, a much larger upper critical field may be expected in the case of parallel field orientation. Spatial variation of the order parameter may come about as a result of the increased attractive interaction at the interface regions. Since the Al domains are ~1000 Å thick, the order parameter may be significantly smaller in the center of an Al domain than at the Al-Ge interface.[23] This can result in a departure from type-I magnetic behavior and consequently increase the upper critical field in the direction parallel to the interface.

At this point, it is worthwhile to comment that the "size effect" for the metals Al, Be, and Sn could have its origin in the excitonic mechanism. It has been shown that thickness in itself is not sufficient for the enhancement of ultrathin Al and Sn films.[6] On the other hand, Al and Al_2O_3 form an eutectic system. In addition, relatively thick granular Al-Al_2O_3 films codeposited at room temperature have a bulk transition at 2 °K.[24] The element Be readily forms a highly stable oxide BeO. The Be-BeO eutectic system is established.[9] Be films with organic inclusions have been found to have values of T_c as high as 11 °K along with T_c ~9 °K for thin Be films.[25] Unless an extremely high vacuum is used ($<10^{-8}$ torr), the presence of significant amounts of the dielectric oxide BeO is unavoidable in vapor-deposited Be films. As a consequence, a favorable setting for the exciton mechanism exists.

V. SUMMARY

Superconductivity has been observed as a *bulk* property in eutectic alloys consisting of alternating metal and semiconductor domains (e.g., Al-Si, Al-Ge). Transition temperatures well in excess of those for the pure metals were found in some cases. Quenching the alloys from the liquid state was found to increase the superconducting transition temperature and critical field, and decrease the characteristic size of the microstructure. A correlation between the Fermi energy of the metal and the enhancement of T_c was noticed. In metal-metal eutectic systems (e.g., Al-Al_2Cu) with comparable microstructure no enhancement of T_c was observed. Various explanations of these results have been discussed. The exciton mechanism, originally proposed by Ginzburg, and modeled by Allender, Bray, and Bardeen for a metal-semiconductor interface is considered as a possible means to account for the enhancement effect.

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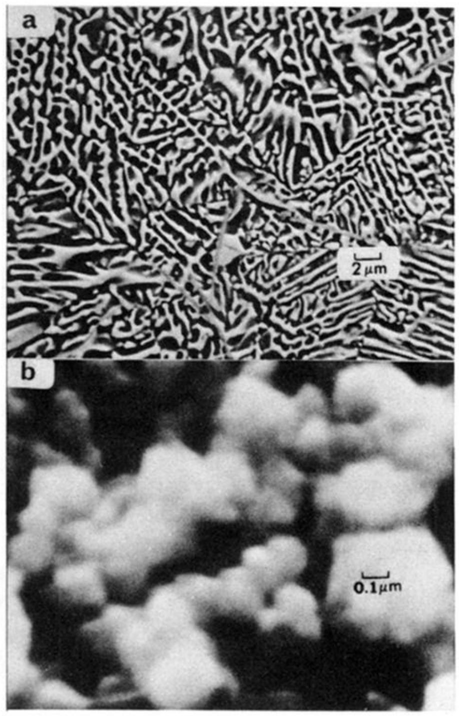

FIG. 1. Scanning electron micrographs of (a) $Al_{70}Ge_{30}$ as cast; (b) $Al_{70}Si_{30}$ liquid quenched. The Al in both samples has been leached out during etching.