ting the SF_6 data with the cubic model.[5] We found no significant change in the resulting exponents. We suspect that the small difference we do observe among the critical exponents of different fluids arises from the effects of nonuniversal corrections to scaling. A test of this conjecture will require a very lengthy analysis of the data because of the complexity of the expressions for $\rho - K_T\mu$ which are suitably parametrized and which contain both scaling and correction-to-scaling terms.

The exponents and coefficient ratios for these quite different pure fluids tend towards the Ising values close to the critical point. We interpret this result to imply that asymptotically the thermodynamic anomalies will be those of the Ising model.

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Unexplained Superconductivity in the Metallic-Semiconducting $NbGe_2$-Ge System*

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We have observed superconductivity to 16°K in mixtures of metallic $NbGe_2$ and semiconducting Ge, and we show that both constituents are necessary. We show that the superconductivity is associated with the $NbGe_2$, although by itself, it is not a superconductor above 2.5°K. Various explanations are considered.

Anomalously high superconducting critical temperatures are observed for rf-sputtered samples of niobium-germanium in the 95–65 at.% germanium concentration range; the samples consist of a mixture of metallic $NbGe_2$ and semiconducting Ge. In this paper we present our results on these

Ge-NbGe$_2$ samples. The transition temperature behavior versus germanium concentration is complemented by critical-current measurements, and by x-ray analysis. Conclusions based on these experiments are presented. These conclusions are discussed and compared with the predictions of existing theoretical models.

The samples for this study were prepared by the dual-target rf-sputtering technique. Arc-melted targets of high-purity germanium and niobium were cosputtered onto heated sapphire substrates, and a special mask placed over the substrate permitted the rapid survey of the sample properties with respect to compositional variation. The sputtering apparatus and procedures used to sputter alloy samples have been described in previous publications.[1-3] Specifically, during the deposition process, the sputtering voltage was kept at ~2000 V, the substrate temperature in the range 650–850°C, and the sputtering gas (high-purity argon) pressure ~50–100 mTorr. Deposition rates under these conditions were ~50 Å/min and sputtering times were such as to produce sample thickness ranging from 0.2 to 1.0 μm. In the latter part of the study, samples were made in a new sputtering chamber which enabled the preparation of several (typically four) samples under different sputtering conditions without breaking vacuum, thereby minimizing changes in sputtering conditions which frequently occur from run to run.

Resistance measurements were carried out with a special probe utilizing the four-probe technique. Temperatures were determined by measurements using germanium thermometers calibrated in the range of 2–40°K. The structural properties of the sample were obtained by x-ray-diffractometer techniques scanned at room temperature. The nominal compositions of the samples were calculated from a knowledge of the sputtering radiation pattern as has been demonstrated by Johnson.[4] Sample thickness was estimated from the sputtering times and weight loss of targets used during the sputtering process. It is to be noted that the film thickness is not uniform across the substrate.

Figure 1 shows resistivity measurements of a sample spanning the range 95 to 19 at.% Ge prepared on a single-crystal sapphire substrate maintained at a temperature of ~810°C. Curves representing a number of different concentrations are shown. The sample and target geometry is schematically shown along with the Mo mask defining the various sample strips, numbered as indicated.

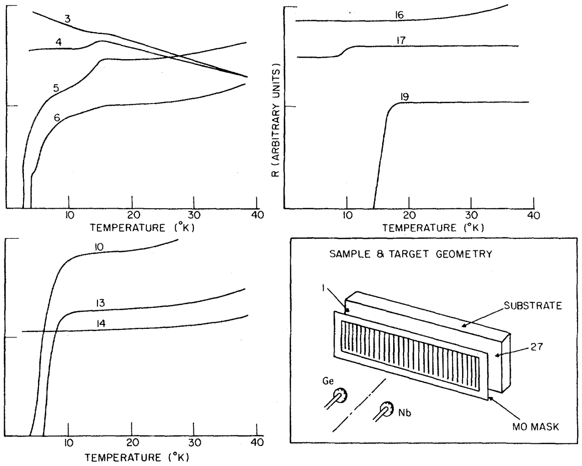

FIG. 1. Resistance versus temperature plots of several strips of a Ge-Nb sample prepared at T_s ~810°C. The numbers of the curves indicate the sample strips of different composition, with low numbers corresponding to high Ge concentration. The fourth figure is a schematic of the two-electrode sputtering, mask, and substrate geometry.

Beginning at the Ge-rich end of the sample, strips 1 and 2 (not indicated) show a negative temperature derivative of the resistance indicating a predominant semiconducting behavior down to 4°K with no evidence of superconductivity. In strip 3 we see an abrupt decrease in the resistance curve at 16.0°K. This abrupt drop becomes more pronounced for subsequent strips. We interpret this abrupt drop in resistance as the onset of a superconducting phase. The onset temperature T_{co} is defined as the temperature at which the deviation from the normal-state resistance is observed. Strip 5 is the first to show a complete superconducting transition. The temperature at which the sample becomes completely superconducting is denoted by T_{cl}. As the germanium concentration is reduced (i.e., going to higher strip numbers), T_{co} begins to drop while T_{cl} rises to ~6°K at strip 13. At this point there is a dramatic change in behavior with strips 14 to 16 showing no evidence of superconductivity down to 2°K. Starting with strip 17, a superconducting transition (incomplete) is observed; T_{co} rises with strip 19 showing values of T_{co} of 18.5°K and $T_{cl} \simeq 14$°K. These critical temperatures are shown in the top diagram of Fig. 2. The range from T_{co} to T_{cl} is indicated.

Two things are to be noted from the T_c diagram: (1) Two separate regions of superconducting behavior are observed and (2) these are sep-

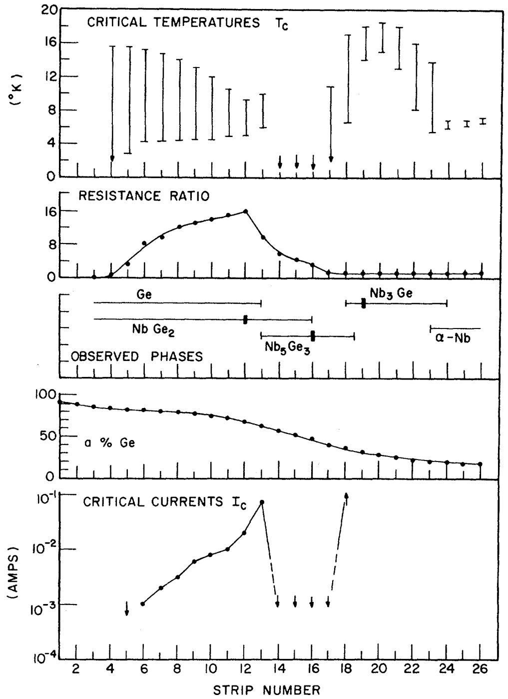

FIG. 2. Diagrams from top to bottom: superconducting transition temperature, resistance ratio $R_{300°K}/R_{20°K}$, phases present, Ge concentration, and critical currents. The abscissa (sample number) is the same for all curves.

arated by a region of no apparent superconductivity.

The resistance ratio Γ defined as $R_{300°K}/R_{20°K}$ is shown in the next diagram of Fig. 2. A peak in the Γ curve is observed at strip 12. Critical-current measurements (defined as the onset of an observable resistance) in zero field made at 4.2°K are also shown in the lowest diagram of Fig. 2. The main features are the peak at strip 13 and also $I_c > 1$ A for strips 18 to 26.

X-ray measurements were carried out to identify the various phases in each strip. The line-intensity measurements were used to estimate the phase boundaries, and are shown in the third diagram of Fig. 2. The thick bar indicates the peak of the diffraction line intensity of the respective phases. Linewidth measurements indicate an average crystallite size > 500 Å for both Ge and $NbGe_2$. The x-ray analysis helps us to determine that (1) the T_c observed in the low-number strips is in the Ge-$NbGe_2$ part of the phase diagram, with superconductivity being depressed below 2°K after the Ge-$NbGe_2$ phase boundary is crossed; (2) the T_c peak in the high-number strips is due to A-15 Nb_3Ge; and (3) the sharp T_c, ~7°K, observed for strips 23-26 is due to "dirty" α-Nb. In the rest of this paper we will only be concerned with the superconducting region in the Ge-rich end of the phase diagram unless stated otherwise.

Samples were prepared at various substrate temperatures T_s ranging from 700°–870°C. It was noted that the higher T_{co} were obtained for $T_s > 800°C$, the highest T_{co}, 16.0°K, being observed for a sample made at 870°C. This sample also showed the highest T_{cl}, >10°K, and the largest I_c, ~0.5 A. The A-15 region always had an $I_c > 1.0$ A at 4.2°K (1.0 A is the maximum current that can be put through the electrical leads). The essential features of all of the samples are the same as the one described above.

One sample made at room temperature showed a maximum T_{co} of ~4°K and had an "amorphous" structure with $\Gamma < 1.0$ (the behavior of "dirty amorphous" Nb). On subsequent annealing at 750°C, the A-15 phase formed at ~25-at.% Ge with $T_c = 15.6°K$, while a weak peak with $T_c = 2.7°K$ was observed at ~67-at.% Ge. We note that the behavior of this sample is quite similar to that reported by Hanak *et al.*[5] who also studied the Nb-Ge system by sputtering. However, they cooled their substrates (77°K) rather than heating them. They show a T_{co} ~6°K in the Ge-rich region but did not comment on this.

To eliminate any possible effect of the mask on our results, two samples, one with the mask and one without, were made under identical sputtering conditions in a multisubstrate holder. It was found that the T_c behavior of both these samples was identical, eliminating any possible "mask" effect. In addition, the edges of the sample strips of one of the high-T_c samples was ground off and its T_c was remeasured and found to be unchanged. However, the critical current I_c was reduced by ~20% which is almost proportional to the decrease in the width of the sample strip; this indicates that the superconducting phase is homogeneous through the sample strip. To show whether germanium is necessary to observe the high T_c, a sample was prepared under essentially similar conditions as the two-sample experiments but using a single alloy target of composition $Nb_{0.35}Ge_{0.65}$ (bulk measured T_c of 1.85°K). No T_c above 2°K was observed and x-ray analysis shows almost single phase $NbGe_2$ with no observable Ge.

We have observed the anomalous superconductivity in the Ge-rich end of the Ge-Nb phase diagram on a total of seventeen samples involving a total of thirteen separate sputtering runs. We find considerable variation in the magnitude of the maximum T_c; it ranges from 6.0 to 16°K. We do not yet know what causes this although there is some correlation of large T_c with large resistance ratio.

Based on the experimental results obtained so far, we arrive at the following conclusions concerning anomalous superconductivity in the Ge-rich end of the Ge-Nb system: (1) Both Ge and $NbGe_2$ are present and both appear to be necessary in order to observe a high T_c. (2) Since the critical-current and resistance-ratio curves have a similar shape for low-numbered strips and since both reach a maximum near strip 12 where the $NbGe_2$ x-ray intensity is a maximum, we conclude that the enhanced superconductivity is associated with the metallic $NbGe_2$ phase. (A curve of $NbGe_2$ x-ray intensity is not shown but it is similar to the critical-current and resistance-ratio curves.) (3) High substrate temperatures (700–850°C) are necessary to obtain the high T_c. (4) The maximum I_c is observed at the concentration showing the highest T_{ci}.

We now consider a number of possible explanations for the occurrence of this anomalous superconductivity in Ge-rich Ge-Nb system.

(i) If a third phase is present, then its volume must be less than 10% since x-ray analysis showed only Ge and $NbGe_2$ and there were no extra lines. From the I_c measurements we infer that the amount of this third phase would have to be proportional to the quantity of $NbGe_2$ present. Furthermore, since both Ge and $NbGe_2$ are necessary the most likely location would be in the grain boundaries between the two phases. If this phase were a metastable phase of $NbGe_2$ its most likely crystal structure would be related to either the $MoSi_2$ or $TiSi_2$, a class of crystal structure in which superconductivity above 2.5°K has not been observed.

The only candidates among known compounds that could account for the high T_c must be the Nb compounds. Although free Nb is ruled out, the reactive formation of NbN is possible. Gavaler *et al.*[6] have extensively studied the reactive sputter formation of NbN and have shown that high-T_c NbN (~15.5°K) depends strongly on the N_2 partial pressure. Since in our system the N_2 partial pressure was ~10^{-9} Torr, which may rise somewhat during the sputtering process, we believe the formation of stochiometric NbN is quite remote under these conditions. In support of this inference, one of the high-T_c samples was analyzed for nitrogen by the spark-source mass-spectrographic method; nitrogen was found at a concentration level of 0.2 ± 0.1 at.%. This value is consistent with zero, since an unrelated niobium specimen measured at the same time gave the same reading.[7] Nb_3Ge is not likely because the A-15 peak is observed in the region of the phase diagram where it should be.

(ii) The surface-plasmon enhancement of Economou and Ngai[8] is ruled out because the particle size is too large and the carrier concentration in the semiconductor is too low.

(iii) The alternate layer scheme of Cohen and Douglass[9] seems a remote possibility as the barrier thickness (in our case the crystallite size) is too large.

(iv) Many of the experimental facts seem to agree with the features of the exciton mechanism originally proposed by Ginzburg[10] and developed by Allender, Bray, and Bardeen[11] (ABB theory). We observe large T_c enhancement in the region of metal-semiconductor mixtures of $NbGe_2$-Ge, both being necessary constituents. Using Eq. (4.10) of ABB, and using reasonable parameters, we calculated that a T_c increase from 2.5 to 16°K would require λ_{ex} (the electron-exciton interaction constant) to be $\simeq 0.37$, which is not unreasonable. However, an estimate of the tunneling depth D into the semiconductor yields values to ~300 Å for metal films ~500 Å thick. This value is ~30 times larger than that required by the ABB theory. However, we note that the ABB theory is for a single interface and assumes a "clean" semiconductor, a feature not satisfied in our samples. We think that it would be worthwhile if the ABB theory were extended and modified to include metal granules in a semiconductor matrix or vice versa, and to also allow the semiconductor to have impurity states in the gap.

(v) Phillips[12] has suggested that the observed T_c behavior could be due to the presence of a NbGe metastable phase in a narrow metastable interfacial region.[13] Presumably such an interfacial phase is quasicubic with the NbN structure.

In conclusion, we have found anomalous superconductivity in the metal-semiconductor $NbGe_2$-Ge system. At present we have no satisfactory explanation.

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Organic Linear Conductors as Systems for the Study of Electron-Phonon Interactions in the Organic Solid State

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A model calculation shows that each phonon band which couples to the electron density in an organic linear-chain semiconductor effectively develops an infrared activity along the chain axis. The origin of the effect lies in *phase* oscillations of additional charge-density-wave distortions which inevitably arise in the presence of electron-phonon interactions. This suggests that organic linear conductors may constitute unique systems for the study of electron-phonon interactions in the organic solid state.

I have calculated the frequency-dependent conductivity, $\sigma(\omega)$, of an organic linear-chain semiconductor on the basis of a model which attempts to allow for all the possible (i.e., symmetry allowed) conduction-electron-phonon couplings that can be expected to be present in such a semiconductor.[1] The result is remarkable in that it suggests that organic linear conductors, for example, triethyl ammonium tetracyanoquinodimethane [TEA(TCNQ)$_2$], tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ), and related charge-transfer salts,[2] may constitute rather unique systems for the experimental and theoretical study of electron-phonon (e-p) interactions in the organic solid state.

The model is a linear-chain system defined by the Hamiltonian ($\hbar = 1$)

$$H = \sum_k \epsilon_k \theta(\epsilon_B - |\epsilon_k|) a_k^\dagger a_k + V(\rho_{q_0} + \rho_{-q_0}) + \sum_n \sum_q [b_n^\dagger(q) b_n(q) + \tfrac{1}{2}] \omega_n(q) + N^{-1/2} \sum_n \sum_q g_n Q_n(q) \rho_{-q}. \tag{1}$$

The first two terms describe a system of n conduction electrons per unit length with energies $\epsilon_k = (|k| - k_F) v_F$ lying within the range $|\epsilon_k| < \epsilon_B$ (relative to their Fermi energy) moving in a periodic potential V ($|V|/\epsilon_B$ assumed small) of wave vector $q_0 = 2k_F$. They represent a simple model of the semiconductor in the absence of e-p coupling. k_F, v_F, and $a_k^\dagger$ denote, respectively, the conduction-electron Fermi wave vector, velocity, and creation operator. The operator $\rho_q = \sum_k a_k^\dagger a_{k+q}$ creates an electronic density fluctuation of wave vector q. The fourth term describes a coupling of the conduction electrons to a set of G distinct phonon bands labeled by the index n ($n = 1, 2, \ldots, G$). I do not specify the precise nature of these bands; in general they will be determined by the group symmetry of the underlying molecular and electronic structure. Note, however, that in organic systems many of them will be associated with those *intra*molecular vibrations which induce modulation of the local conduction-electron, molecular-orbital (MO) energy, i.e., with the totally symmetric (a_g) molecular vibrational modes which, in the isolated molecule, are infrared-*non*active.[1] $Q_n(q) = b_n(q) + b_n^\dagger(-q)$ denotes the di-