Alloy Concentration Limitations for Ideal Superconductivity Transitions

C. CHIOU, R. A. CONNELL, AND D. P. SERAPHIM
International Business Machines Corporation, Thomas J. Watson Research Center, Yorktown Heights, New York

(Received 11 September 1962)

For mean free paths less than 440±100 Å, the dc resistance, magnetic susceptibility, and low-frequency surface impedance data on a series of indium-base alloys (Bi, Pb, Sn, Cd, Tl, Hg) indicate negative interfacial energies between superconducting and normal material. The experiments demonstrate the presence of an intermediate state, normal and superconducting, at magnetic fields much less than H_c as well as the usual filamentary superconductivity at high magnetic fields. Thus, quantitatively, the mean-free-path effect and, qualitatively, the intermediate state effect at low fields are in agreement with the theory of Abrikosov and Gorkov. Data on severely cold-worked high-purity tantalum and on a cold-worked In alloy are compared to the effect of alloying alone. Cold work has only a minor effect in increasing the filamentary critical magnetic field in comparison to the mean-free-path effects in indium alloys. The implications for high-field superconductivity are discussed.

INTRODUCTION

THE superconducting transition characteristics of many dilute solid solutions are similar to those of pure metals. The transitions measured by flux, resistive, or other techniques, occur in a reversible manner at one well-defined magnetic field for all measurement techniques. The concentration of alloy for which this ideal behavior may be expected is limited. Beyond certain concentrations of solute in a given solvent, the interval of magnetic field, over which the transition from superconducting to normal state is evident, progressively increases with increasing solute concentrations. The critical current may decrease; the resistive transitions become abnormally sensitive to current density and occur at higher magnetic fields than the flux transition. Finally, the richer alloys may show "high-field" superconductivity, an imperfect Meissner effect, and a capacity to remain superconducting under conditions of high supercurrent density. The critical concentration of solute C_c below which the ideal characteristics associated with pure metal may be expected depends greatly on the specific solute.

A theoretical limitation for the critical concentration has been formulated by Abrikosov[1] and Gorkov[2] in terms of a critical residual normal state resistivity ρ_c which depends on the intrinsic properties of the solvent, influenced but slightly by the solute. They suggest that

$$\rho_c = 11k(ec)^{-1}\gamma^{-1/2}. \tag{1}$$

Here, k, e, and c are, respectively, the Boltzmann constant, electronic charge, and velocity of light, while γ is the normal-state temperature coefficient for the electronic specific heat. The value of γ is expected to have changed, but slightly, from the value for pure material at a concentration where ρ_c is critical. According to Abrikosov[1] and Gorkov,[2] the interfacial energy vanishes on the boundary between superconducting and normal regions at this critical resistivity ρ_c, while for $\rho > \rho_c$ the surface energy may become increasingly negative. Such a situation, where $\rho > \rho_c$, has been considered theoretically in some detail by Abrikosov, who showed that in terms of the Ginzburg–Landau[3] theory that a breakup into a stable network of "normal filaments" in a superconducting matrix would be expected for these "superconductors of the second kind" for fields where $H < H_c$. In a similar manner, Gorkov and others have explained the presence of superconducting filaments in a normal matrix for $H > H_c$. The magnitudes of ρ_c predicted by Eq. (1) and inferred from the experimental data of Doidge[4] for Sn with In solute are also in agreement, as shown by Gorkov.[2] The relative decrease of interfacial energy with solute concentration in In and Sn alloys as deduced by Davies[5] would eventually lead to negative surface energies for concentrations in the range used by Doidge.

We demonstrate this effect for six solutes in indium, test the prediction of Abrikosov for normal-state filaments at magnetic fields much less than critical with surface impedance measurements, and finally show that the onset of high-magnetic-field superconductivity is controlled by the resistivity.

Specimen Preparation

No doubt, there is significance to be placed on the preparation of alloys, as has been demonstrated by Stout and Guttman[6] for indium plus thallium, Doidge[4] for tin plus indium, Lynton, Serin, and Zucker[7] for tin-base alloys, Reeber[8] for indium plus mercury, and the present authors for indium alloys. In all these experiments the transitions improved with increased

[1] A. A. Abrikosov, J. Exptl. Theoret. Phys. (U.S.S.R.) **32**, 1442 (1957) [translation: Soviet Phys.—JETP **5**, 1174 (1957)].
[2] L. P. Gorkov, J. Exptl. Theoret. Phys. (U.S.S.R) **37**, 1407 (1959) [translation: Soviet Phys.—JETP **10**, 998 (1960)].
[3] V. L. Ginzburg and L. D. Landau, J. Exptl. Theoret. Phys. (U.S.S.R.) **20**, 1064 (1950).
[4] P. R. Doidge, Phil. Trans. Roy. Soc. (London) **A248**, 553 (1956).
[5] E. A. Davies, Proc. Roy. Soc. (London) **A255**, 407 (1960).
[6] J. W. Stout and L. Guttman, Phys. Rev. **88**, 703 (1952).
[7] E. A. Lynton, B. Serin, and M. Zucker, J. Phys. Chem. Solids **3**, 165 (1957).
[8] M. D. Reeber, Phys. Rev. **117**, 1476 (1960).

annealing time at the highest feasible temperatures. See, for example, the flux transitions in Fig. 1 for indium plus thallium after two successive annealing treatments. The interval in magnetic field over which the flux transition occurs in terms of percent of critical field has decreased from >25% to ~3% on extending the annealing treatment from 14 to 65 days. A similar effect was found for the resistive transitions. The broadening is, in general, increased by decreasing the temperature of measurement.

The following evaluation proceeds on material which has been improved by annealing to a limit dictated by economy in time (~2 months or more at 15 to 25°C below the melting point). The elements were thoroughly mixed in the molten state and then by extrusion in the solid state prior to annealing. Before any ac measurements, the specimens were electropolished to remove up to 0.002 in. of the original surface.

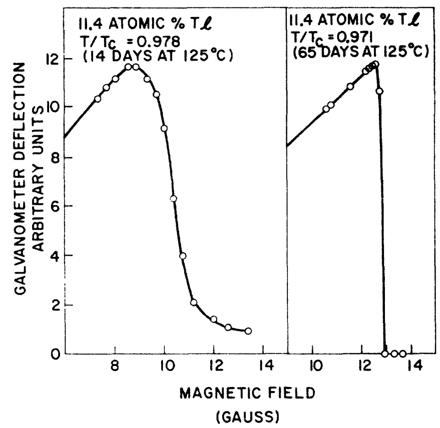


FIG. 1. Flux transitions for the In-11.4 at. % Tl alloy after two successive annealing treatments. The transition width in terms of percent of critical field has decreased from >25 to ~3% on extending the annealing treatment from 14 to 65 days.

Resistance Transitions

The transition to the normal state, measured by the resistance of a specimen, is greatly sensitive to small fractions of the specimen remaining superconductive above the critical magnetic field sufficient to switch the major portion of the specimen normal. In many cases, the flux penetrates 99% of the volume at H_c, while the specimen may still appear to be completely superconductive with zero resistance up to $H_n > H_c$ at small current density. This behavior is typical of all of the transition elements with extremely dilute concentrations of impurities and, to a lesser extent, is typical of lead. It is not typical of pure, well-annealed tin, indium, or aluminum, but appears at certain alloy concentrations, different for each solute in each solvent. In all cases for the lower impurity concentrations H_n depends greatly on current density when H_c is first exceeded. For this reason, we fix the current density at ~300 A/cm^2 and classify the concentration above which broad resistance transitions occur as critical, C_r. The temperature at which the transitions were compared does not affect the results very much since it was found that the interval of magnetic field covered by the transition is almost proportional to the magnitude of the critical field. Thus, for convenience, comparisons between the transitions for various compositions of alloy will normally be made near T_c, where H_c is between 10 and 30 G.

The data in Fig. 2 for lead (solute) in indium (solvent) are typical in showing the change in shape of resistance transitions when the alloy concentrations exceed C_r. The transitions for the specimen with 1.3 at. % Pb remain sharp like that in Fig. 2 even at very low temperatures, while the transitions progressively broaden with decreasing temperature for the other with 1.9 at. % Pb. The critical fields determined both from resistive and flux transitions for the two alloy specimens together with that of pure In are compared in Fig. 3, along with the interval in magnetic field covered by the resistive transitions. Clearly, C_r for In-Pb alloys is 1.6±0.3 at. % Pb. Similar data for other indium alloys fix C_r at 0.75±0.25 at. % for Bi, 4.0±0.25 at. % for Sn, 3.5±0.5 at. % for Cd, 6.8±0.6 at. % for Tl, and >6.6 at. % for Hg.

Flux Transitions

The critical concentration C_r above which the flux transition broadens is somewhat higher than the corresponding C_r found by resistive techniques. For example, although the resistive transitions for In-Tl are current sensitive and broad for 7.4 and 11.4% thallium, the flux transitions show only a hint of broadening at 11.4% in Fig. 1. Likewise, in the In-Pb system, the flux transition is sharp for 1.9 at. % Pb, shows a very slight broadening at 3.6 at. % Pb, and is definitely showing "high-field" characteristics only at 4.7 at. % Pb (see Fig. 4). The flux transitions show

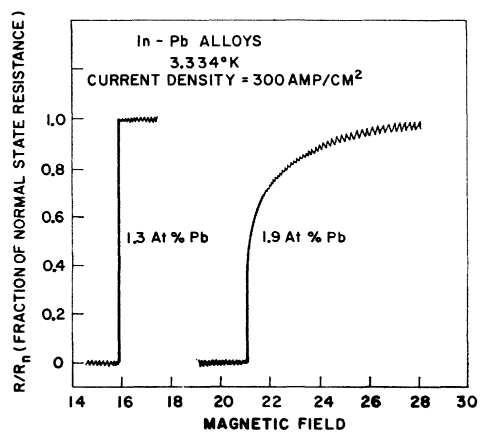


FIG. 2. Resistance transitions for two In-Pb alloys. The transitions broaden in the interval between 1.3 and 1.9 at. % Pb.

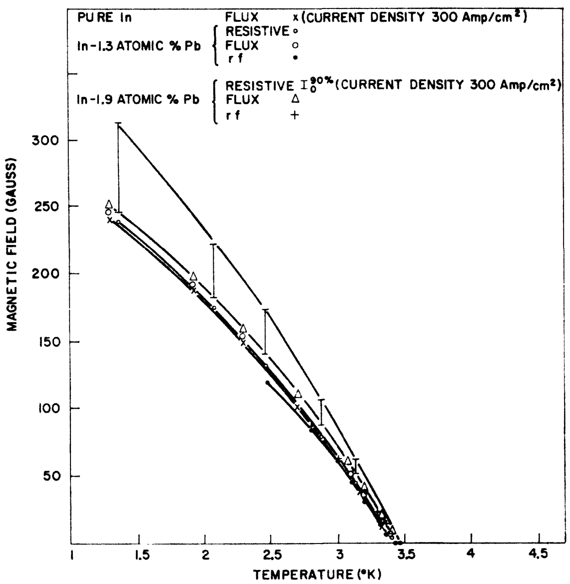


FIG. 3. Critical field curves for resistance, flux, and radio-frequency transitions for two In-Pb alloys. The curves for resistance and flux transitions for the 1.3 at. % alloy follows closely the curve for pure In, while the 1.9% alloy resistance transition covers an interval in magnetic field. However, the apparent field value for radio-frequency transitions appear to fall below the flux critical field curves.

qualitatively the same effects as the resistance transitions at a higher apparent critical alloy concentration ($\sim 2C_r$) for onset of "high-field" superconductivity effects. This is a matter of techniques, for sufficiently sensitive flux measurements show a small amount of superconducting material which could carry currents at high fields. (See, for instance, the flux transitions shown in Fig. 5 for 3.6% Pb, where the filamentary "tail" was examined in detail.)

Radio-Frequency Absorption

Measurements of Q of a superconducting LC circuit, with the specimen as the core of the inductance, should (see reference 1) disclose the complement to the dc resistance tail in giveng evidence of power dissipation in the specimen at small reduced fields ($H \ll H_c$), i.e., a normal-state tail at low fields.

The dissipation is most accurately determined by means of a transmission-type experiment as described by Chambers.[9] For the current series of measurements at $\nu \sim 1$ Mc/sec, the smallest detectable surface resistance which could be observed above background circuit losses was of the order of 10^{-6} Ω/square, as determined from an increase in half-width of the resonance peak.

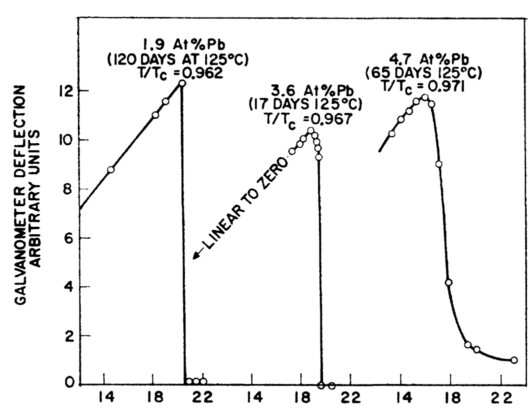
For a mixed state (i.e., normal and superconducting),

the rf field. In view of the exceeding complex situation, one can only predict qualitatively that the resultant values for Q and δ are roughly proportional to the ratio of the superconducting and normal surface areas.

Ideal behavior is illustrated in Fig. 6(a), where the dc resistance, resonance frequency, and half-width of the resonance curve ($\Delta\omega_{1/2} \propto R_s$) are plotted as a function of magnetic field. The superconducting material under investigation in this case was high-purity tantalum. It is to be noted that all three curves break at essentially the same point and show no signs of filamentary structures of any kind. Figure 6(b) shows a corresponding plot for a nitrogen-doped tantalum specimen. Characteristically, no discernible dissipation attributable to the specimen is evident on extrapolation to zero field (i.e., no flux trapping), but dissipation appears at the lowest fields, increasing monotonically with increasing field.

For speed and convenience, the technique employed by Schawlow and Devlin[10] was used in gathering most of the data on indium-base alloys. Here the superconducting LC circuit forms the tank circuit of an oscillator. As it is employed, the introduction of an equivalent shunt resistance of the order of $10^5 \Omega$ to the tank is sufficient to reduce the oscillator output to zero.

Typically, for pure metals and sufficiently dilute alloys, the dc external field H can be increased to the point at which $H + |H_{rf}| \simeq H_c$ ($H_{rf} \simeq 0.5$ Oe peak to peak for the oscillator, <0.1 Oe for transmission measurements) before the signal level drops. For alloys beyond the critical composition C_{rf}, the signal is damped at much lower fields. For instance, the specimen with 1.3% Pb provided reasonable bulk-penetration depth data[11] and exhibited a well-defined magnetic field cutoff throughout the temperature range investigated. The same may be said for an In+3.5 at. % Sn specimen, and an In+5.2 at. % Tl specimen.



In contrast, a specimen containing 1.9% Pb was somewhat history dependent, indicating some flux hysteresis. Apparent field cutoff values fell below the flux critical field curve, a discrepancy increasing as $T_c - T$ increased (see Fig. 3). This, no doubt, is an indication that the interphase surface energy is becoming very small, although it is most certainly positive close to T_c. In connection with this, it may be noted that deviation from dc magnetization data commences at higher temperatures for 1.9% Pb than for 1.3% Pb, as shown in Fig. 3. Likewise, a sample containing 6.2% Tl might be classified as marginal. The magnetic field cutoffs were still sharp, but the temperature transition showed considerable broadening.

The specimens containing 7.4 and 11.4% Tl and 3.6% Pb were almost completely nonideal, as we have defined it, behaving like the nitrogen-doped tantalum (Fig. 6(b). Figure 7 shows the oscillator cutoff as a function of applied field for In+6.2% Tl and In+3.6% Pb, illustrating the difference in character of the transitions in the two regions.

It is now apparent that when a weak magnetic field is applied to a nonideal suprconductor, there is a significant amount of normal material at magnetic fields much less than H_c which contributes to the rf absorption. Thus, the existence of normal metal filaments in weak fields as hypothesized by Abrikosov is apparently substantiated.

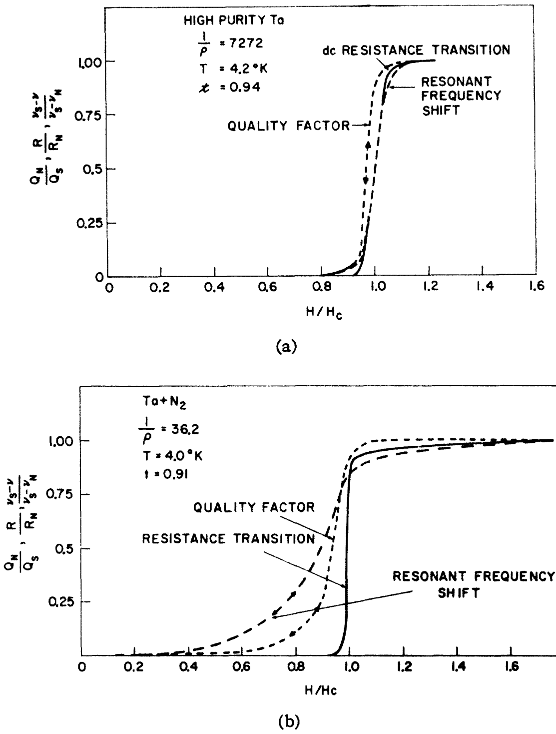


FIG. 6 (a) The dc resistance, resonance frequency, and half-width of the resonance curve plotted as a function of magnetic field for a high-purity Ta specimen. (b) A corresponding plot for a nitrogen-doped Ta specimen.

Concentration Limits

The critical concentration at which the superconducting transitions change behavior may be correlated directly with the resistivity. Indeed, for In alloys, as shown in Fig. 8, the critical concentration for each solute is roughly proportional to the reciprocal of the increase in resistivity for 1 at. % of the solute $(\partial\rho/\partial c)^{-1}$. In-Tl and In-Hg alloys, with extremely low resistivities per at. %, show ideal characteristics for resistive transitions up to 6.2 and ~7 at. %, respectively, and for flux transitions to even higher concentrations. On the other hand, we find In-Bi alloys with high resistivity per at. % exhibiting nonideal characteristics for concentrations less than 1 at. %. Qualitatively, the correlation is excellent, and we find a critical resistivity $1.3\pm0.2\ \mu\Omega$ cm for the onset of high-magnetic-field superconductivity in resistance transitions. From flux measurements with the sensitivity we used, it can be said to be $\sim 2.6\ \mu\Omega$ cm. The calculated magnitude from Eq. (1) is $2.8\ \mu\Omega$ cm. Hence, the quantitative agreement is reasonable for flux transitions and a factor of 2 low for resistive measurements. The rf data is essentially coincident with the resistance curve displayed in Fig. 8.

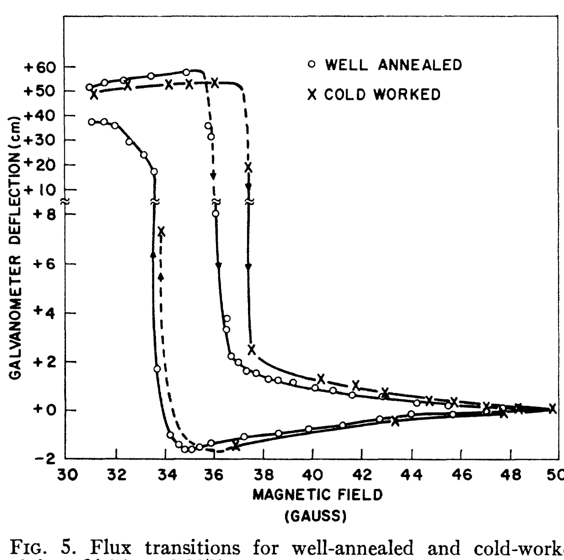


FIG. 5. Flux transitions for well-annealed and cold-worked In-3.6 at. % Pb at 3.337°K. Flux is expelled out of the specimen in increasing magnetic field and trapped in the specimen in decreasing magnetic field. There are two scales for the figure. A minor increase in the apparent fraction superconducting in the high-field range is observed for the cold-worked specimen.

There is also some roughly quantitative data for the transition elements and for aluminum-zinc alloys. Here, as above, we have neglected changes in γ with alloying. For tantalum the transitions are sharp (both flux and resistive transitions near T_c) up to resistivity values of at least $0.7\ \mu\Omega$ cm.[12] The broadening of transitions at low

[12] D. P. Seraphim, Solid-State Electron. 1, 368 (1960).

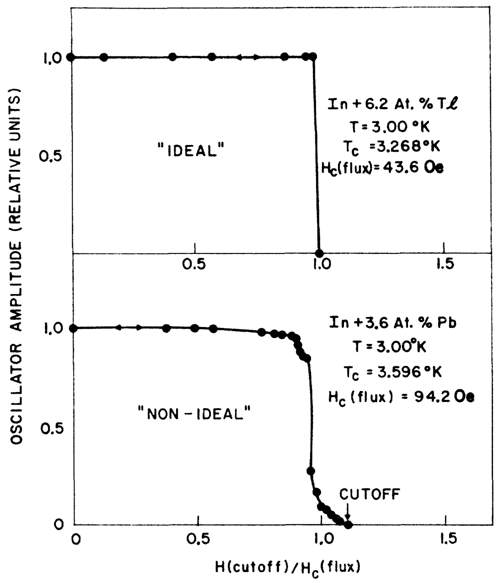


FIG. 7. A plot for the oscillator amplitude as a function of applied field for the In-6.2 at. % Tl and In-3.6 at. % Pb alloys. The difference in "ideal" and "nonideal" characteristics of the transitions is illustrated.

temperatures discussed in previous papers[13] is quite dissimilar in character, and occurs at impurity concentrations which are extremely dilute and also depend strongly on the thermal treatment of the specimens. Thus, ρ_c for tantalum is approximately 0.7 $\mu\Omega$ cm. Vanadium appears to have either an extremely low ρ_c or an extreme sensitivity to history.[14] In fact, vanadium has not been purified sufficiently to show sharp transitions in magnetic fields.[15] Therefore, vanadium may have a negative interfacial surface energy even in a relatively pure state. Lead is also changed in its characteristics by an extremely small amount of Ca and other impurities,[16] which apparently diffuse to grain boundaries and or dislocations. The phenomena in lead are strongly treatment sensitive and cannot be simply correlated with the above formalism. Aluminum-zinc alloys are ideal superconductors in the dilute range of concentration. However, 3 at. % zinc is sufficient for the onset of high-magnetic-field superconductivity.[17]

DISCUSSION

When $l<440\pm100$ Å, the resistance transitions for In with solutes Bi, Pb, Sn, Cd, Tl, or Hg are broad due to superconducting filaments existing at magnetic fields greater than H_c. The rf transitions show the complement to this effect with normal state evident at magnetic fields approaching zero. Thus, we may infer that in indium alloys the surface energy is decreased to zero for $l\sim440$ Å as it is with In solute ($l\sim800$ Å, see Doidge[4]), in qualitative agreement with the behavior of interfacial energies (superconducting to normal) deduced by Davies[5] for several dilute alloys, and in qualitative agreement with theoretical calculations by Abrikosov[1] and Gorkov.[2] The flux transitions, although less sensitive to the effect, indicate a qualitative change in behavior by transition broadening. Concurrently (as has previously been observed by Pippard[18] for Sn-base alloys), the transitions become hysteretic. The flux is shielded from the specimen by the filaments for increasing magnetic field and kept within the specimen by the filaments for decreasing magnetic fields at fields well above H_c. The filaments are, therefore, multiply connected, unlike the model of Abrikosov and Gorkov. Therefore, one must look elsewhere to complete the picture. Dislocations and often grain boundaries are multiply connected, continuous in network, and create strain and perhaps compositional fluctuations in the lattice; they may be remnant superconducting filaments at high magnetic fields. However, the stress fields around dislocations are probably not sufficient to increase the critical magnetic field by a factor of 2, even very near the core (see Cottrell[19]) for the stresses near

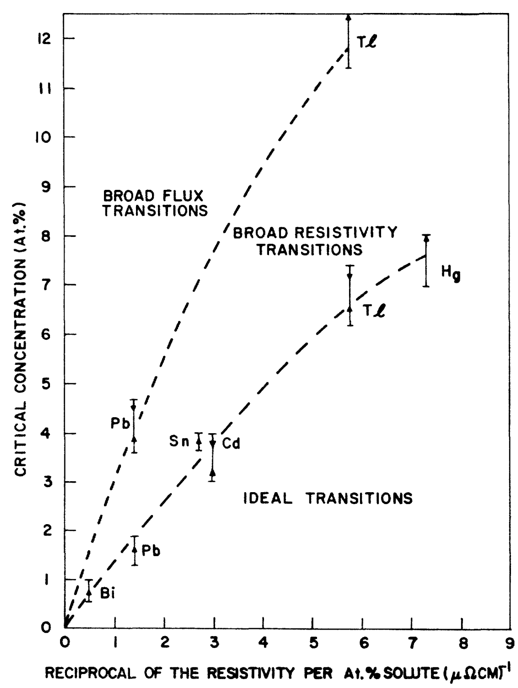


FIG. 8. Critical concentrations of In alloys for ideal superconducting transitions as a function of the reciprocal of the resistivity per at. % solute. The transitions measured by flux and resistive techniques are shown. The extremes indicate the alloys studied on either side of the critical concentration; the arrows indicate which alloy the critical concentration is nearest.

[13] D. P. Seraphim and R. A. Connell, Phys. Rev. **116**, 606 (1959).
[14] A. Wexler and W. S. Corak, Phys. Rev. **85**, 85 (1952).
[15] D. P. Seraphim (unpublished data).
[16] R. W. Shaw and D. E. Mapother, Phys. Rev. **118**, 1474 (1960).
[17] C. Chiou and D. P. Seraphim, Trans. Am. Inst. Mining, Met., Petrol. Engrs. (to be published).
[18] A. B. Pippard, Phil. Trans. Roy. Soc. (London) **A248**, 97 (1955).
[19] A. H. Cottrell, *Dislocations and Plastic Flow in Crystals* (Clarendon Press, Oxford, 1958), p. 36.

TABLE I. Comparison of reduced effective critical fields and residual resistivity.

Material	T_c (°K)	$H_0{}^a(R)$ (kOe)	H_0/T_c	ρ_{res} ($\mu\Omega$ cm)	$1/\Gamma^b$	Source	Comments
In	3.4	0.3	0.09	1.0	0.135	IBM	dilute alloy
Ta	4.4	1.0	0.23	0.5	0.033	Fansteel	0.010-in. diam degassed and aged[c]
Nb	9.5	7.0	0.74	2.3	0.175	Fansteel	0.003-in. diam
Mo-50% Re	12.6	27	2.14	10.5	0.95	Chase Brass	0.003-in. diam
Nb-25% Zr	11.7	93.7	8.09	24.4	1.85	Wah-Chang	0.010-in. diam
Nb_3Sn	18.4	100	5.4	9.4	0.43	IBM (McGuire)	stoichiometric, sintered
Nb_3Sn	18.4	238	12.9	...	...	Oak Ridge	0.006-in. diam sintered and drawn, in 0.015-in. diam Nb sheath

[a] Estimated from resistance measurements.
[b] $1/\Gamma \equiv \rho_{res}/(\rho_{300}-\rho_{res})$. The residual resistivity of the high-temperature superconductors ($T_c>5$°K) was estimated from the resistivity values at 300 and 77°K.
[c] See reference 13.

dislocations and, for example, Seraphim and Marcus[20] for hydrostatic and shear stress effects on the critical magnetic field. Thus, high-magnetic-field superconductivity in bulk metals would seem primarily a size effect similar in mechanism to superconductivity in extremely thin films.

It is now believed that thin films in close proximity with normal material lose their superconductivity.[21] It may be inferred that remnant superconductivity around structural and compositional defects in a bulk metal is affected similarly unless the filaments are isolated in some manner.

A possible mechanism of isolation is to decrease the superconducting coherence length. This may be accomplished by decreasing the normal-state mean free path[22] as we have done in the present investigation for single-phase alloys. A second mechanism is to create a structure with sufficient boundaries so that the range of coherence will be limited. This may be the result in the martensiticly transformed Ti-base alloys or in the ω phase-type structure reported by Seraphim *et al.*[23] (Also see Kneip *et al.*[24] on heat-treated Nb-Zr alloys.) It must be remembered that in these materials the scattering from point defects may also be significant. Yet another mechanism of isolation is to create local distributions of point imperfections at, for example, dislocations or grain boundaries (i.e., strain aging).

Thus, the dislocations and other structural defects can act as filaments only when the mean free path is capable of: (a) creating a negative surface energy, (b) decreasing the coherence length and, consequently, the size of the filaments, or (c) stated in another way, decreasing the range over which the proximity effect occurs. The finer filaments are assumed to be associated with shorter mean free paths. To check this conjecture, we have investigated some of the effects of structure. For high-purity tantalum, the introduction of dislocations by severe cold work produced only a fractional increase in critical magnetic field.[25] For In+3.6 at. % Pb, cold worked at ambient and immediately tested, there was a minor increase in the apparent fraction superconducting in the high-field range (see Fig. 5). It may be noted that cold-worked Nb and cold-worked Re also show only fractional increases in filamentary critical field.[26] This is also the result for cold-worked[27] Nb-Zr which, however, showed a *profound* increase in current carrying capacity for fields less than the filamentary critical field, in contrast to the relatively minor effects observed for pure metals.

Clearly, the effect of cold work is to increase the current-carrying ability at fields less than the filament critical field and the filamentary critical field itself is an intrinsic property not much affected by the structure in single-phase alloys. The structure has a large effect on the current carrying capacity only under the special condition of a short mean free path.

In support of these arguments we report the critical magnetic fields and normal-state temperature-independent resistivity of some high-magnetic-field superconductors in Table I. The correlation between high normal-state resistivity and high critical magnetic field is most apparent for drawn Nb-Zr and Nb_3Sn.[28] The rather low critical field for[29] the Mo-Re is to be associated with the exceptionally low electronic specific

[20] D. P. Seraphim and P. M. Marcus, Phys. Rev. Letters **6**, 680 (1961).
[21] P. H. Smith, S. Shapiro, J. L. Maks, and J. Nicol, Phys. Rev. Letters **6**, 686 (1961).
[22] A. B. Pippard, Proc. Roy. Soc. (London) **A216**, 547 (1953).
[23] D. P. Seraphim, N. R. Stemple, and D. T. Novick, J. Appl. Phys. **33**, 136 (1962).
[24] G. D. Kneip, Jr., J. O. Betterton, Jr., D. S. Easton, and S. O. Scarbrough, J. Appl. Phys. **33**, 754 (1962).
[25] D. P. Seraphim, D. T. Novick, and J. I. Budnick, Acta Met. **9**, 446 (1961).
[26] J. J. Hauser and E. Buehler, Phys. Rev. **125**, 142 (1962).
[27] T. G. Berlincourt, R. R. Hake, and D. H. Leslie, Phys. Rev. Letters **6**, 671 (1961).
[28] J. Babiskin and P. G. Siebenmann, Post-Deadline Paper, Baltimore Meeting of The American Physical Society, March, 1962 (unpublished).
[29] J. E. Kunzler, E. Buehler, F. S. L. Hsu, B. T. Matthias, and C. Wahl, J. Appl. Phys. **32**, 325 (1961).

heat for that alloy, deduced from the single-crystal critical field data of Blaugher and Hulm.[30] On the other hand, Nb_3Sn undoubtedly has an unusually large electronic specific heat, comparable to V_3Ga.[31]

[30] R. D. Blaugher and J. K. Hulm, Phys. Rev. **125**, 474 (1962).
[31] F. J. Morin, J. P. Maita, H. J. Williams, R. Sherwood, J. H. Wernick, and J. E. Kunzler, Bull. Am. Phys. Soc. **7**, 190 (1962).

ACKNOWLEDGMENTS

The authors wish to express their appreciation to W. E. Beck, A. C. Burgess, and P. A. Roland for their assistance in making the necessary measurements, and to D. J. Quinn for the use of his susceptibility apparatus. We would also like to thank Dr. T. R. McGuire for providing a Nb_3Sn specimen for us to test.

PHYSICAL REVIEW VOLUME 129, NUMBER 3 1 FEBRUARY 1963

Direct Measurement of the Vacancies Produced in Sodium Chloride by Fast Reactor Neutrons*

PAUL W. LEVY
Brookhaven National Laboratory, Upton, New York
(Received 16 August 1962)

When unstrained NaCl single crystals are irradiated with gamma rays, reproducible curves of color-center, especially *F*-center, concentration vs dose can be obtained. At doses of approximately 10^7 R it appears that all of the negative-ion vacancies in the crystal have been converted into *F* centers and that they are stable at room temperature. When crystals which have been previously colored with gamma rays to this extent are bombarded with fast neutrons, and then the gamma-ray irradiations are resumed, there is an increase in *F* center, i.e., vacancy concentration, which is proportional to the total fast neutron flux. The number of vacancies induced by the fast neutron bombardment, determined in this way, is in agreement with the theoretical treatments of Kinchin and Pease, and Seitz and Koehler.

INTRODUCTION

ONE of the fundamental problems in "radiation damage" is the determination of the number of defects, e.g., vacancies, interstitials, and complex imperfections consisting of more than one vacancy or interstitial, or both, formed in a substance by a specified bombarding particle such as a 1-MeV neutron. Ideally, one would like to count the defects in a crystal before and after bombardment. This can be accomplished in many indirect ways, e.g., by measuring electrical resistivity. A direct way of determining the concentration of a specific type of defect in a crystal is by measurement of the number of color centers associated with it, providing, however, that a known fraction, or all, of the defects have been converted to color centers. Specifically, in NaCl the negative-ion vacancy concentration can be determined if a known fraction of these vacancies have been converted to *F* centers by electron capture. This paper will describe a direct determination of the number of vacancies produced in single-crystal NaCl by fast neutron reactor bombardment by measuring the saturation *F*-center coloring.

EXPERIMENTAL

All of the NaCl crystals used were cleaved from large crystals obtained from the Harshaw Chemical Company. The crystals for any single experiment were always taken from the same piece. None of the samples were annealed before irradiation since it was found that coloring curves obtained from untreated materials were the most reproducible. It is entirely possible that when the crystals are received they contain less strain than any of the crystals we subjected to thermal annealing. All crystals were kept in desiccators as much as possible.

For irradiation and absorption spectrum measurements, the crystals were mounted in slightly oversized plastic or aluminum frames to prevent their being strained in any way. Once optical absorption measurements and irradiations were started, the crystals were

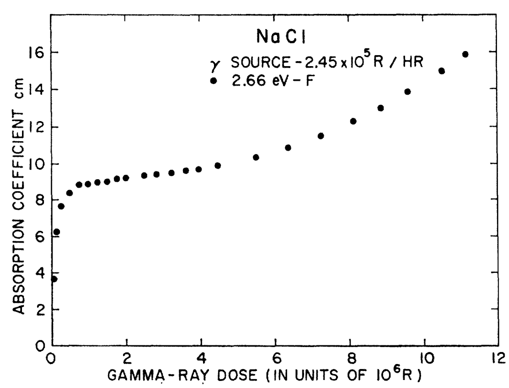


FIG. 1. The absorption coefficient at the peak of the NaCl *F*-center absorption band vs gamma-ray dose. Usually these curves are referred to as growth or coloring curves.

* Work performed under the auspices of the U. S. Atomic Energy Commission. Presented at the 1959 International Symposium on Color Centers in Alkali Halides, Corvallis, Oregon, September 1959 (unpublished); see also Bull. Am. Phys. Soc. **5**, 184 (1960).