PRESSURE-DEPENDENT PAIR BREAKING IN SUPERCONDUCTING $La_{3-x}Ce_xIn$ ALLOYS*

M. B. Maple and Kang-Soo Kim
Institute for Pure and Applied Physical Sciences, University of California, San Diego, La Jolla, California 92037

(Received 7 May 1969)

A minimum has been observed in the variation of the superconducting transition temperature of $La_{3-x}Ce_xIn$ alloys with pressure. From this it is inferred that the pair-breaking parameter initially increases with pressure and then goes through a maximum associated with a transition of the Ce impurity from a magnetic to nonmagnetic state.

We have observed an extraordinary dependence of the superconducting transition temperature (T_c) of $La_{3-x}Ce_xIn$ alloys on pressure (P). In the pressure range investigated (0-23 kbar), dT_c/dP is positive for pure La_3In.[1] Upon addition of Ce ($x \geqslant 0.0421$), dT_c/dP is initially negative until a critical pressure is reached at which dT_c/dP changes sign. The critical pressure and the initial slopes $(dT_c/dP)_{P=0}$ depend on the concentration. These results may be interpreted in terms of a virtual Ce $4f$ impurity level slightly below the Fermi level such that the $4f$ level moves nearer the Fermi level with increasing pressure. At sufficiently high pressures, corresponding to the minimum in $T_c(P)$, the Ce impurity appears to be involved in a transition from a magnetic to nonmagnetic state.

The $La_{3-x}Ce_xIn$ and $La_{3-x}Gd_xIn$ alloys were prepared by melting the constituents under argon in a conventional arc furnace. Pressure, applied at room temperature and retained to low temperature by means of a standard Be-Cu clamp, was transmitted to the sample through a 1:1 mixture of isoamyl alcohol and n-pentane, and determined from the critical temperature of a superconducting Pb manometer placed in the Teflon sample cell. Superconducting transitions were detected by a standard ac (140-cps) mutual-inductance technique, and T_c was defined as the midpoint of the susceptibility-versus-temperature curve associated with the normal-superconducting transition. The widths of the transitions were $\lesssim 0.1$°K, except for the sample of highest Ce concentration (0.35°K), and were nearly independent of pressure. Transition temperatures were reversible with respect to pressure.

Our results for the dependence of T_c on concentration at normal pressure are in reasonable agreement with previous investigations,[2] except that we find a T_c of 9.45°K rather than 9.2°K for pure La_3In. Shown in Fig. 1 are the results of the dependence of T_c on pressure for five $La_{3-x}Ce_xIn$ alloys and one $La_{3-x}Gd_xIn$ alloy, as well as for pure La_3In. The increased negative dependence of dT_c/dP on Ce concentration at low pressures is apparent and qualitatively the same as observed in the previously studied $La_{1-x}Ce_x$ [3] and $La_{1-x}Ce_xAl_2$ [4] systems. However, the saturation of $T_c(P)$ at higher pressures which develops into a minimum for the more concentrated samples is a new behavior which, to our knowledge, has not heretofore been observed. For the $La_{3-x}Gd_xIn$ sample ($x = 0.0398$), dT_c/dP behaves qualitatively like pure La_3In.

The depression of T_c of a superconductor by magnetic impurities is a function of a pair-breaking parameter α. In the first Born approximation of magnetic scattering of conduction electrons by magnetic-impurity spins,[5]

$$\alpha \sim nN(E_F)J_{eff}^2(P)S(S+1) \equiv nI(P). \qquad (1)$$

$N(E_F)$ is the density of states at the Fermi level

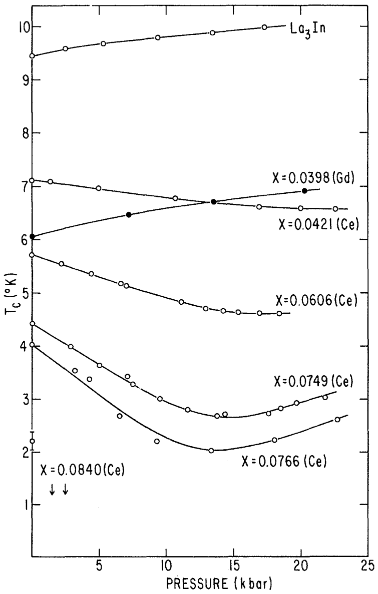

FIG. 1. The superconducting transition temperature (T_c) of a series of $La_{3-x}Ce_xIn$ alloys and one $La_{3-x}Gd_x$-In alloy as a function of pressure. The appropriate Ce and Gd nominal compositions are indicated for each curve. Transition widths are smaller than or of the order of the diameter of the circles except for the highest concentration sample for which the width is indicated by a vertical bar.

(which we have assumed does not change appreciably with pressure[6]) and J_{eff} is an effective s-f exchange-coupling parameter defined by the interaction Hamiltonian $\mathcal{H}_{\text{int}} = -2J_{\text{eff}}\vec{S}\cdot\vec{s}$, where $\vec{S}$ is the magnetic-impurity spin and $\vec{s}$ is the conduction-electron spin. Ordinarily we vary α by changing the magnetic-impurity concentration n; however, for a given concentration n, α may be varied with pressure through $|J_{\text{eff}}(P)|$. From the negative value of the initial slopes $(dT_c/dP)_{P=0}$, we infer that α, and therefore $|J_{\text{eff}}|$, initially increases with pressure. The concentration dependence of $(dT_c/dP)_{P=0}$ may then be qualitatively explained since a given initial increase of $|J_{\text{eff}}|$ with pressure leads to a greater increase of α for larger concentrations, and in turn, to a greater decrease of T_c. From the minimum observed in $T_c(P)$ at higher pressures it may be inferred that α goes through a maximum.

In order to explain the apparent increase of $|J_{\text{eff}}|$ with pressure in previously studied systems, it has been suggested that the Ce $4f$ electron lies in a virtual impurity level a small energy E below the Fermi level.[3,4,6] This results in an important hybridization of Ce $4f$ with conduction-band states and a large antiferromagnetic coupling of conduction-electron and magnetic-impurity spins (characterized by J_{eff}).[7] In the approximation of the Schrieffer-Wolff transformation,[8] $|J_{\text{eff}}|$ is proportional to the square of a matrix element mixing $4f$ with conduction-band states and inversely proportional to E. Therefore $|J_{\text{eff}}|$, and accordingly α, is expected to increase as E decreases with pressure.[6,9]

Upon further application of pressure, the Ce $4f$ level should eventually begin to overlap the Fermi level. This should initiate a transition of the Ce $4f$ electron from a magnetic to nonmagnetic impurity state, and consequently, a decrease in the pair-breaking parameter α. Although it is difficult to anticipate how such a transition will take place in detail, it seems reasonable that it would occur gradually, as suggested by Fig. 1, since the f level, originally broadeded by interactions with conduction electrons, should experience stronger interactions and greater broadening as it comes into coincidence with the Fermi level.

Another feature which is evident from Fig. 1 is that the minimum in $T_c(P)$ shifts to lower pressures for higher concentrations. It appears, therefore, that the Ce $4f$ level moves toward the Fermi level with increasing concentration of Ce. This is consistent with the apparent increase of $|J_{\text{eff}}|$ with concentration inferred from the concentration dependence of T_c at normal pressure which falls below that expected from the Abrikosov-Gor'kov theory for $|J_{\text{eff}}|$ independent of concentration.

The low-pressure results may be related to the pair-breaking theory in the following manner. According to the Abrikosov-Gor'kov theory,[5] T_c is given by the equation

$$\ln(T_c/T_{c0}) = \Psi(\tfrac{1}{2}) - \Psi(\tfrac{1}{2} + 0.140\alpha T_{c0}/\alpha_{cr}T_c); \qquad (2)$$

T_{c0} corresponds to $\alpha = 0$, α_{cr} to $T_c = 0$ (complete destruction of superconductivity), and Ψ is the digamma function.

Thus

$$t \equiv T_c/T_{c0} = f(\alpha(n,P)/\alpha_{cr}(P)), \qquad (3)$$

where $\alpha_{cr}(P) = \pi T_{c0}(P)/2\gamma$ ($\ln\gamma$ is Euler's constant).

Differentiating expression (3) with respect to P yields

$$\left|\frac{\partial t}{\partial P}\right|_{P=0} = \left[f'\left(\frac{\alpha}{\alpha_{cr}}\right)\frac{\alpha}{\alpha_{cr}}\frac{\partial}{\partial P}\ln\frac{I(P)}{T_{c0}(P)}\right]_{P=0} = C[f'(\alpha/\alpha_{cr})(\alpha/\alpha_{cr})]_{P=0}, \qquad (4)$$

where

$$C \equiv \left[\frac{\partial}{\partial P}\ln\frac{I(P)}{T_{c0}(P)}\right]_{P=0}$$

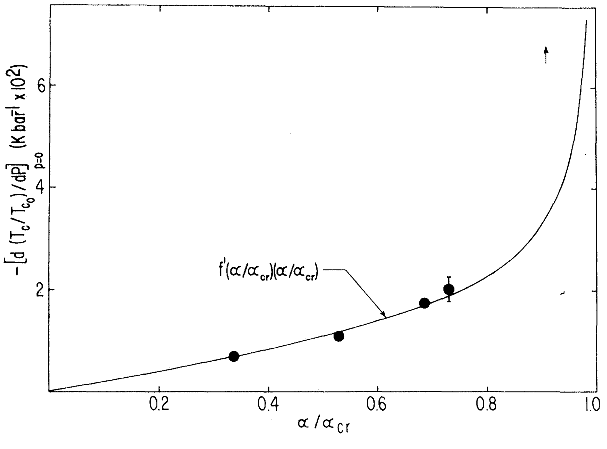

FIG. 2. Experimental values of $-[d(T_c/T_{c0})/dP]_{P=0}$ versus the reduced pair-breaking parameter α/α_{cr}. The curve represents the function $f'(\alpha/\alpha_{cr})(\alpha/\alpha_{cr})$ discussed in the text. The arrow indicates the lower limit of $-[d(T_c/T_{c0})/dP]_{P=0}$ (assuming a linear variation with P for $P \lesssim 2$ kbar) for the sample of highest concentration investigated.

is assumed to be independent of n.

The function $f'(\alpha/\alpha_{cr})(\alpha/\alpha_{cr})$ is shown in Fig. 2, where the constant C has been evaluated for the sample of lowest concentration. Experimental values of α/α_{cr} are determined uniquely from Eq. (2). The data are in good quantitative agreement with this relationship at low concentrations, and in qualitative agreement for the highest concentration point for which only the lower limit of $-(\partial t/\partial P)_{P=0}$ could be determined in our He^4 cryostat.

The discussion given here does not include the complications of the Kondo effect which may be expected in this system because of the large antiferromagnetic s-f exchange interaction; the magnetic-nonmagnetic transition which we infer from the minimum in the curves of T_c vs P may arise from the development of the quasi bound state at higher temperatures with increasing pressure due to a continued increase of $|J_{\text{eff}}|$ with pressure.[10] Alternatively, the minimum in T_c vs P may reflect a gradual onset of magnetic order with increasing pressure. This would also lead to a decrease in pair breaking, and in turn, to an enhancement of T_c.[11] An extension of the $T_c(P)$ measurements to higher pressures, and low-temperature normal-state resistivity measurements at normal and high pressures, will be carried out to examine these possibilities.

Informative discussions with Dr. D. K. Wohlleben, Dr. J. Wittig, Dr. B. W. Howlett and, in particular, Professor B. T. Matthias, are gratefully acknowledged.

---

*Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, under Grant No. AF-AFOSR-631-67.

[1] Our measurements of $T_c(P)$ of pure La$_3$In are in reasonable agreement with those of T. F. Smith and H. L. Luo, J. Phys. Chem. Solids 28, 569 (1967).

[2] J. E. Crow and R. D. Parks, Phys. Letters 21, 378 (1966); J. E. Crow, thesis, University of Rochester, 1967 (unpublished).

[3] T. F. Smith, Phys. Rev. Letters 17, 386 (1966).

[4] M. B. Maple and T. F. Smith, Solid State Commun. 7, 515 (1969).

[5] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. 39, 1781 (1960) [translation: Soviet Phys.—JETP 12, 1243 (1961)].

[6] B. Coqblin and C. F. Ratto, Phys. Rev. Letters 21, 1065 (1968); the expression for J_{eff} given by the Schrieffer-Wolff transformation was first applied to the pressure dependence of the superconducting transition temperature of La$_{1-x}$Ce$_x$ alloys by these authors.

[7] P. W. Anderson and A. M. Clogston, Bull. Am. Phys. Soc. 6, 124 (1961); J. Kondo, Progr. Theoret. Phys. (Kyoto) 28, 846 (1962); P. G. de Gennes, J. Phys. (Paris) 23, 630 (1962).

[8] J. R. Schrieffer and P. A. Wolff, Phys. Rev. 149, 491 (1966).

[9] M. B. Maple and Z. Fisk, in Proceedings of the Eleventh International Conference on Low Temperature Physics, St. Andrews, Scotland, 1968, edited by D. M. Findlayson and D. M. McCall (St. Andrews University Press, St. Andrews, Scotland, 1968).

[10] For example, M. J. Zuckermann, Phys. Rev. 168, 390 (1968).

[11] K. H. Bennemann, Phys. Rev. Letters 17, 438 (1966).

SURFACE NUCLEATION AND BOUNDARY CONDITIONS IN SUPERCONDUCTORS

H. J. Fink*
Atomics International, A Division of North American Rockwell Corporation, Canoga Park, California 91304

and

W. C. H. Joiner†
Department of Physics, University of Cincinnati, Cincinnati, Ohio 45221

(Received 4 June 1969)

We have calculated the surface nucleation field as a function of the slope of the superconducting order parameter at the surface of a semi-infinite superconducting half-space. When the order parameter increases on approaching the surface, as would be the case in the presence of a surface region of enhanced transition temperature, nucleation fields larger than those expected for a uniform sample are predicted. Cold working the surface on an InBi foil produces this condition and qualitatively confirms the prediction.

It has been shown that for an ideal superconducting surface adjacent to a vacuum interface in a parallel applied magnetic field, superconductivity persists in the surface region to a field[1]

$$H_{c3} = 2.38\kappa H_c, \qquad (1)$$