that for $\Delta(r) < kT$ the metal behaves as if it were normal and that the contribution to the relaxation rate from regions where $\Delta(r) > kT$ is negligible. However, it does yield the correct order for the relaxation rate for the values of ξ and d which are known and gives the appropriate field dependence as well as the approximate temperature dependence to be expected from the predicted forms of $\Delta(r)$.

We have made T_1 measurements on other type-II superconductors with large Landau-Ginzburg parameters (V_3Ga and V_3Ge) and in each case the deviation of T_1 from the BCS value is observed to begin at $T \sim T_c/4$, which indicates that this low-temperature relaxation process may be a general property of this class of type-II superconductor.[9]

We would like to thank W. G. Clark, G. Feher, P. Pincus, A. G. Redfield, and S. Schultz for useful comments regarding this work.

*Work supported by the National Science Foundation.
†Alfred P. Sloan Foundation Fellow.

[1]C. Caroli and J. Matricon, Physik Kondensierte Materie 3, 380 (1965).
[2]J. Korringa, Physica 16, 601 (1950).
[3]J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).
[4]L. C. Hebel and C. P. Slichter, Phys. Rev. 113, 1504 (1959).
[5]C. Caroli, P. G. de Gennes, and J. Matricon, Phys. Letters 9, 307 (1964).
[6]M. Weger, B. G. Silbernagel, and J. H. Wernick, Bull. Am. Phys. Soc. 11, 241 (1966).
[7]B. G. Silbernagel, M. Weger, W. G. Clark, and J. H. Wernick, to be published.
[8]T. J. Greytak and J. H. Wernick, J. Phys. Chem. Solids 25, 535 (1964).
[9]Recent measurements in type-II superconductors with small Landau-Ginzburg parameter also indicate the presence of a core-relaxation process: Warner Fite, II, and Alfred G. Redfield, preceding Letter [Phys. Rev. Letters 17, 381 (1966)].

EFFECT OF RARE-EARTH ADDITIONS ON THE PRESSURE DEPENDENCE OF THE SUPERCONDUCTING TRANSITION TEMPERATURE OF LANTHANUM†

T. F. Smith
Department of Physics and the Institute for the Study of Matter,
University of California, San Diego, La Jolla, California
(Received 24 June 1966)

The superconducting transition temperature for solid solutions of Gd, Pr, Yb, and Ce in lanthanum has been measured as a function of pressure up to ~10 kbar. The transition temperatures for La + Gd with 0.6, 0.8, 1.0, and 1.2 at.% Gd, La + 1 at.% Yb, and La + at.% Pr, while depressed from that of pure lanthanum, exhibit positive pressure dependences similar to that observed for the double hexagonal close-packed (dhcp) phase of pure La,[1] the values for the La + Pr and La + Yb being essentially the same. However, for the La + Gd alloys, $\partial T_c/\partial P$ is enhanced, the increment in slope being proportional to the Gd concentration. This enhancement of $\partial T_c/\partial P$ is consistent with the Abrikosov-Gor'kov[2] (A-G) theory for the effect of paramagnetic impurities upon T_c. A value for $2\partial \ln J/\partial \ln V + \partial \ln N(0)/\partial \ln V$, where J is the effective conduction-electron–localized-spin exchange parameter, and $N(0)$ is the density of electron states per atom at the Fermi surface, has been estimated for Gd dissolved in La and is compared with the value obtained from the pressure dependence of the Curie temperature of pure Gd. Small percentage additions of cerium, however, rapidly decrease the positive pressure dependence of La and eventually result in a strong negative pressure dependence of T_c for alloys containing more than 1 at.% Ce. This behavior for the solid solutions with Ce is attributed to the instability of the $4f$ electron of this element.

The solid-solution samples were prepared by melting the constituents in a water-cooled copper-hearth arc furnace. The weight losses were small, and the compositions quoted are those calculated from the relative proportions of the constituents, no attempt being made to chemically analyze the samples. The alloys containing less than 1 at.% of the rare-earth addition were made by diluting a portion of the 1 at.% alloy by addition of lanthanum. No attempt was made to attain single-phase solid solutions (either dhcp or fcc) by annealing the alloys following preparation. In fact, such an annealing is undesirable because it causes the precipitation of rare-earth solutes heavier than Pr.[3,4]

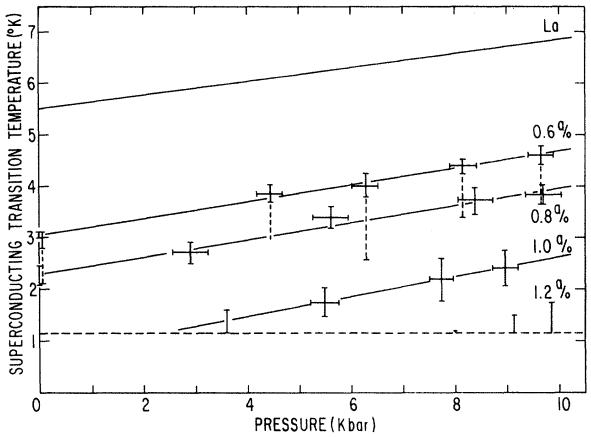

FIG. 1. The superconducting transition temperature for a range of La+Gd alloys as a function of pressure. The appropriate Gd compositions are indicated by each curve. The vertical lines indicate the width of the transition.

Sugawara and Eguchi report,[4] on the basis of an x-ray examination, that "as cast" alloys of La with rare-earth additions are predominently in the fcc phase. In contrast to this, the specific-heat data of Finnemore et al.[5] for La+Gd alloys indicate that these alloys are predominently in the dhcp phase. While the samples in the present investigation undoubtedly contained both the dhcp and fcc phases, the superconducting transitions at zero pressure were, in general, relatively sharp, and none showed structure representative of two superimposed transitions. The zero-pressure T_c's for all the alloys examined were in close agreement with those of other workers.[3-7]

The pressure dependence of T_c was determined in the same apparatus as that used[1] for the measurements on pure La. Pressures at the low temperature were determined relative to the transition temperature of tin,[8] a small piece of which was incorporated in the sample assembly.

The superconducting transition temperatures, as a function of pressure, for the full range of La+Gd and La+Ce solid solutions examined are shown in Figs. 1 and 2, respectively. The

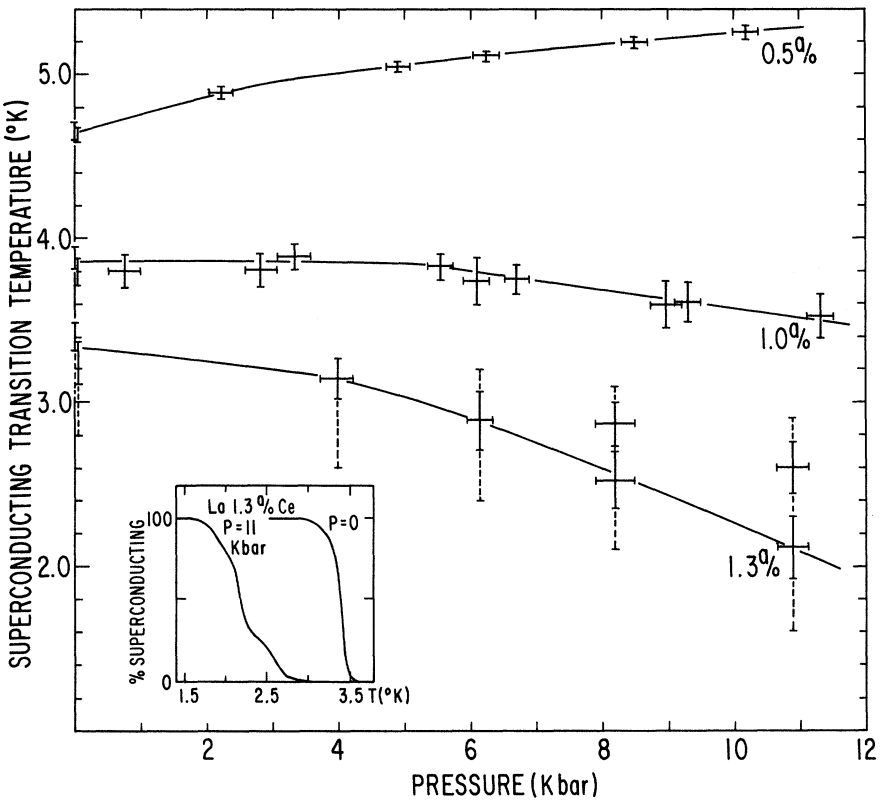

FIG. 2. The superconducting transition temperature for a range of La+Ce alloys as a function of pressure. The appropriate Ce compositions are indicated by each curve. The vertical lines indicate the width of the transition. Insert: transition curves for the La-1.3 at.% Ce alloy at 0 and 11 kbar illustrating the appearance of a second transition at the high pressure.

vertical lines indicate the width of the superconducting transition, determined by extrapolation of the linear portion of the transition curve to the fully normal and fully superconducting state. For alloys where there was considerable rounding at the ends of the transition, the extent of the "tail" is indicated by the broken-line extension of the vertical line. The majority of the alloys, however, had relatively well-defined transitions.

It is evident from Fig. 1 that the linear, positive pressure dependence of T_c observed for La is retained in the La+Gd alloys over the range of compositions investigated. Moreover, $\partial T_c/\partial P$ is enhanced from that of pure La by an amount which is directly proportional to the Gd concentration. This increase of $\partial T_c/\partial P$ is quite appreciable and amounts to $(5.0 \pm 0.5)\times 10^{-5}$ °K bar^{-1} per at.% Gd. No significant change from the value of $\partial T_c/\partial P$ for pure La could be distinguished for the La+1 at.% Pr and La+1 at.% Yb alloys.

The pressure-dependence data for La+Ce, shown in Fig. 2, contrast sharply with that of Fig. 1 and exhibit a marked dependence upon the Ce concentration. The addition of 0.5 at.% Ce is sufficient to reduce drastically the positive pressure dependence of T_c associated with pure La and cause a departure from linearity. With 1 at.% Ce the positive pressure dependence is totally depressed, and T_c is essentially independent of pressure below ~5 kbar. Increasing the pressure beyond ~5 kbar results in a decrease of T_c. The alloy containing 1.3 at.% Ce exhibits a nonlinear decrease of T_c with applied pressure, the slope increasing with pressure. An interesting feature of the data for the 1.3 at.% alloy is the partial resolution of a second superconducting transition, preceding the main transition, for pressures in excess of ~6 kbar. Transition curves for this alloy at zero pressure and 11 kbar, illustrating this second transition, are reproduced in the insert of Fig. 2. This second transition may possibly arise from the separation of transitions related to the dhcp and fcc phases due to an increased difference in pressure dependence for the two phases. However, such an explanation does not seem likely as there is already an appreciable difference between the transition temperatures for the two phases at zero pressure.[4,7] In addition, no such separation was observed for any of the other alloys, including the lower concentration Ce alloys. This separation is reversible, the second transition disappearing upon the release of the pressure. It would appear, therefore, that there is the possibility of a further superconducting phase forming above ~6 kbar. Further measurements to higher pressures are planned in an attempt to clarify this situation.

Following the cycle of pressure application, the zero-pressure T_c, for all of the samples, was slightly displaced to a lower temperature. This effect, which was small relative to the reversible pressure-induced change in T_c, may possibly be a consequence of slight changes in the relative proportions of the dhcp and fcc phases in the sample.

For low concentrations of paramagnetic additions to a superconductor the A-G theory predicts the relationship

$$T_{cp} = T_c - \tfrac{1}{4}\pi\tau_s, \qquad (1)$$

where T_c is the transition temperature of the pure superconductor and τ_s is a magnetic scattering relaxation time. This linear dependence of T_{cp} on concentration has been observed experimentally for a number of systems and, in particular, for the range of rare-earth concentrations in La considered in the present investigation.[3-7] We shall, therefore, adopt (1) to describe the superconducting behavior for these alloys. Differentiating (1) with respect to pressure, we find

$$\frac{\partial T_{cp}}{\partial P} = \frac{\partial T_c}{\partial P} + \Delta T_c \kappa \frac{\partial \ln N(0)}{\partial \ln V} + \frac{2\partial \ln J}{\partial \ln V}, \qquad (2)$$

where $\Delta T_c = T_c - T_{cp}$, $\kappa = -V^{-1}(\partial V/\partial P)$, and $N(0)$ and J are, respectively, the density of states per atom at the Fermi level and the exchange interaction between conduction electrons and localized spins. Thus $\Delta(\partial T_c/\partial P)$ is expected to vary linearly with concentration, in agreement with the observations on the La+Gd alloys. Substituting the observed values of $\Delta(\partial T_c/\partial P)/\Delta C$, $\Delta T_c/\Delta C$, where C is the concentration in at.%, into (2), and assuming κ is little changed from the value of -42×10^{-7} bar^{-1} for pure La, we find

$$[\partial \ln N(0)/\partial \ln V] + 2(\partial \ln J/\partial \ln V) = 2.5 \pm 0.3. \qquad (3)$$

We may compare this value directly with that obtained from measurements of the volume dependence of the Curie temperature of Gd,

which may be written as[9]

$$\frac{\partial \ln\Theta}{\partial \ln V} = \frac{\partial \ln N(0)}{\partial \ln V} + \frac{2\partial \ln J}{\partial \ln V}. \quad (4)$$

Using the value for $\partial\Theta/\partial P$ given by Bloch and Pauthenet,[10] we calculate $\partial \ln\Theta/\partial \ln V = 2.03 \pm 0.06$, which is in relatively reasonable agreement with the value calculated from (2). The higher value of $\partial \ln N(0)/\partial \ln V + 2\partial \ln J/\partial \ln V$ calculated from (2) may be a consequence of a somewhat larger volume dependence of the density of states of La than that for Gd. If we assume that (3) is the same for the La + Pr and La + Yb alloys we calculate $\Delta(\partial T_C/\partial P) \sim 0.5 \times 10^{-5}$ °K bar^{-1}, a change which would be too small to resolve in the present measurements and is, therefore, consistent with the value of $\Delta(\partial T_C/\partial P) \sim 0$ observed for these alloys.

The pressure dependence of T_C for the La + Ce alloys indicates that in this system the term in brackets in (2) is not a constant, as is the case for the La + Gd alloys, but is strongly sensitive to pressure and becomes the dominant contribution to the pressure dependence of T_C for alloys containing more than 1 at.% Ce. To arrive at such a strong pressure dependence, we require a model in which the state of the $4f$ electron, associated with the cerium-impurity atom, is sensitive to pressure. Such a model would be one in which the $4f$ electron occupies a virtual bound state,[11] rather than being localized in a $4f$ orbital state situated at the Ce atom.[12] Considerable interband mixing will be associated with such a virtual bound state,[11,13] particularly in view of the considerable $4f$ character that is undoubtedly present in the conduction band of La. It is probable, in fact, that for cerium the interband mixing provided the dominant contribution to J.[4,14] It may then be argued that reduction of the atomic separation will have the tendency to increase the overlap of $4f$ wave functions and produce a broadening of the virtual bound state, with an associated increase in the interband mixing. Experimental evidence to support this approach is found in the well-known instability of the $4f$ electron in cerium.[15]

This virtual bound-state model is essentially the same as that proposed by Rocher for cerium.[12] In effect, as there will be little change in the character of the conduction band along the length of the lanthanide series, we may consider the $4f$ electrons associated with the solute atoms in La as occupying states which will differ in energy only to a small extent from those in the solute element. The relatively reasonable agreement between the values of $\partial \ln N(0)/\partial \ln V + 2\partial \ln J/\partial \ln V$ for pure Gd and Gd dissolved in La provides strong support for this approach. The $4f$ electrons of Pr, Yb, and Gd additions are therefore considered to be situated in truly bound or very narrow virtual bound states well removed from the Fermi level, and in such they will be relatively unaffected by volume changes of the magnitude considered here.

The virtual bound-state approach adopted here for La + Ce alloys could also account for the anomalously high depression[3] of T_C and the large residual resistivity of these alloys[4] when compared with the values for other La + rare-earth alloys.

Further work is in progress to extend the pressure range of the present measurements and to cover a wider variety of La + rare-earth solid solutions. A detailed report of this work will be presented in due course.

Discussions with P. A. Griffin, S. Gygax, B. T. Matthias, and, in particular, D. B. McWhan are gratefully acknowledged.

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*Supported by the U. S. Air Force Office of Scientific Research.

[1]W. E. Gardner and T. F. Smith, Phys. Rev. 138, 484 (1965).

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

[3]B. T. Matthias, H. Suhl, and E. Corenzwit, J. Phys. Chem. Solids 13, 156 (1960).

[4]T. Sugawara and H. Eguchi, J. Phys. Soc. Japan 21, 725 (1966).

[5]D. K. Finnemore, D. L. Johnson, J. E. Ostenson, F. H. Spedding, and B. J. Beaudry, Phys. Rev. 137, A550 (1965).

[6]B. T. Matthias, H. Suhl, and E. Corenzwit, Phys. Rev. Letters 1, 92 (1958).

[7]R. Schwidtal, Z. Physik 169, 564 (1962).

[8]L. D. Jennings and C. A. Swenson, Phys. Rev. 112, 31 (1958).

[9]S. H. Liu, Phys. Rev. 127, 1889 (1962).

[10]D. Bloch and R. Pauthenet, in Proceedings of the International Conference on Magnetism, Nottingham, England, 1964 (The Institute of Physics and the Physical Society, London, 1965).

[11]J. Friedel, J. Phys. Radium 23, 692 (1962); P. W. Anderson, Phys. Rev. 124, 41 (1961); P. A. Wolff, Phys. Rev. 124, 1030 (1961).

[12]Y. A. Rocher, Advan. Phys. 11, 233 (1962).

[13]R. E. Watson, S. Koide, M. Peter, and A. J. Freeman, Phys. Rev. 139, A167 (1965).

[14]T. Sugawara, J. Phys. Soc. Japan 20, 2252 (1965).

[15]A review of the relevant experimental data on the electronic state of cerium is given by K. A. Gschneidner, Jr., and R. Smoluchowski, J. Less-Common Metals 5, 374 (1964).

COMMENTS ON "DIRECT EVIDENCE OF FLUX MOTION"

P. P. M. Meincke
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received 7 July 1966)

Pearl[1] has suggested two experiments to demonstrate that potential differences in superconductors are due to moving vortices. One of these experiments employing magnetically coupled films had already been done independently by Giaever[2] and Solomon.[3] Pearl chose the experiment of moving a region of magnetic field in a superconductor in such a way as to produce a net flow of vortices across the sample with no net change in magnetic flux linking the voltmeter circuit. The purpose of this note is to point out that the voltage which Pearl observes is not necessarily due to the motion of vortices and that exactly the same result can be achieved using any magnetoresistive material. Volger and co-workers[4] have pointed out that many effects in superconductors such as their superconducting homopolar dynamo are observable in magnetoresistive materials. There is little doubt that the resistivity of the magnetic field region is due to the motion of vortices when that region is in the mixed state, but unfortunately, Pearl's experiment cannot distinguish this situation from the one in which the region is entirely normal.

If we connect a voltmeter to two points on a sample in which completely general current patterns may be flowing, and if the only source of emf is a time-varying magnetic field, then Kirchhoff's rule may be written

$$\oint \frac{-d\vec{A}}{dt}\cdot d\vec{l} - \oint \frac{\vec{j}_{\text{sample}}}{\sigma}\cdot d\vec{l} = I_m R_m = V, \qquad (1)$$

where $-dA/dt$ describes the time variation of the magnetic field ($\vec{B} = \text{curl}\,\vec{A}$), $\vec{j}_{\text{sample}}$ is the current density at each point along the path integration (not including the current flowing through the voltmeter), and σ is the conductivity (assumed isotropic) of the sample at each point along the path of integration. It is assumed that the resistance of the meter, R_m, is much greater than the resistance of the sample and leads. I_m is the current through the meter, and V is the voltage.

Consider the two-dimensional analog of Pearl's experiment shown in Fig. 1. For simplicity, we will not consider the boundaries of the sample but it can be shown that these do not affect the nature of the result. The induction will be canceled by simply bringing the voltmeter lead back along the surface of the samples from b to a. The simplest field A which gives the desired magnetic field is shown in Fig. 1. When the region in which the field exists is moved to the right with the velocity v, the magnitude of $-dA/dt$ is given by

$$-dA/dt = Bv\cos\theta. \qquad (2)$$

The charge carriers in the sample in region 2 will respond to this dA/dt field by flowing in the direction of $-dA/dt$, giving rise to a current density $j = -\sigma_2 dA/dt$. There will be a backflow of current outside region 2, so that current continuity is preserved and

$$\int_x^{x+l/\cos\theta} \vec{j}\cdot d\vec{l} = -\left[\int_a^{x} \vec{j}\cdot d\vec{l} + \int_{x+l/\cos\theta}^{b} \vec{j}\cdot d\vec{l}\right].$$

The $-dA/dt$ terms cancel out, corresponding to the fact that we have no net flux change in the circuit, and the voltmeter reading is given

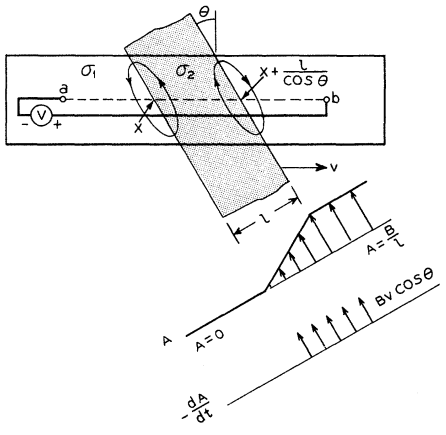

FIG. 1. $\vec{B}$, $\vec{A}$, and $d\vec{A}/dt$ fields in the sample. The induced current patterns are indicated by the loops.