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## SUPERCONDUCTIVITY OF CERIUM UNDER PRESSURE\*

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Superconductivity has been detected in a high-pressure phase of cerium at pressures higher than 50 kbar. This is the first example of a pure metal which, in different crystallographic phases, shows both magnetic ordering and superconductivity. The important question again arises whether the "collapsed"  $\alpha$  phase will become superconducting at a certain pressure.

The peculiarities of many physical properties of cerium under pressure are related to a shift of the  $4f$  electron into an  $sd$  conduction band as was successfully proposed previously.<sup>1</sup> From this simple description one can expect properties in the tetravalent state which resemble those of thorium, which is below cerium in the periodic table. Two recent attempts to search for superconductivity in the so-called "collapsed"  $\alpha$  phase of Ce at about 10 kbar by Smith<sup>2</sup> and by Phillips, Ho, and Smith<sup>3</sup> showed the absence of superconductivity down to 0.3°K. As the approach to the tetravalent state to all present knowledge<sup>4</sup> takes place continuously with pressure, it was not clear whether the pressure of 10 kbar was high enough.

In the present investigation the pressure range is extended to about 100 kbar, using an opposed-anvil press designed for work at low temperatures.<sup>5</sup> The electrical resistance of the sample is measured by the four-probe method. Occasionally a six-lead technique is used for simultaneous measurement on two samples, one of those serving as a superconducting manometer.<sup>6</sup> Figure 1 shows the well-known dependence of the resistance of cerium on pressure at room tem-

perature. The large drop at 7 kbar belongs to the formation of the "collapsed"  $\alpha$  phase. At about 50 kbar an increase indicates another

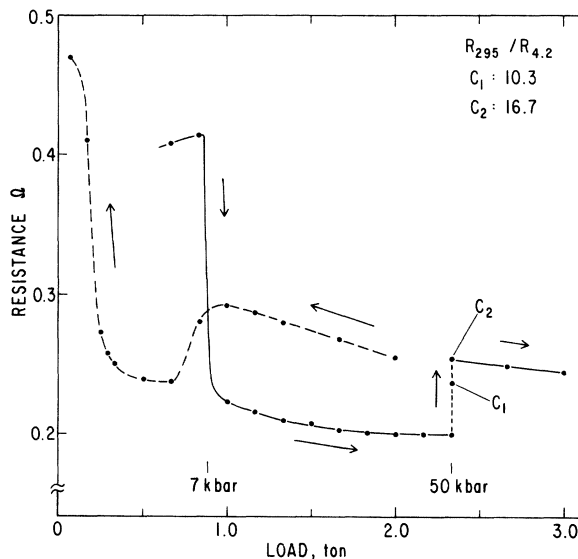


FIG. 1. Resistance of Ce at room temperature versus press load. At the 50-kbar transformation the resistance drifts upwards with time:  $C_1$  after 5,  $C_2$  after 22 h.

phase change. It is this latter phase of unknown structure which is found to be superconducting under pressure in the available temperature range (1.3°K).

The 50-kbar transformation is very sluggish at room temperature as can be seen from the drift of the resistance with time at constant pressure. After 5 h the transformation was not accomplished (resistance value labeled  $C_1$  in Fig. 1). The superconducting transition of the sample in this partially transformed state shows a normal conducting tail ( $C_1$ , Fig. 2). After an additional anneal of 17 h at room temperature, the transformation ran to completion ( $C_2$ , Fig. 1). In this state the sample exhibited a full superconducting transition ( $C_2$ , Fig. 2). At 1.5°K the resistivity was smaller than  $10^{-5}$  of the residual resistivity. Complete superconducting transitions have been repeatedly observed with samples which after the onset of the phase transformation have been held at room temperature for at least 15 h. A drastic improvement of the residual resistivity ratio  $R_{295^\circ\text{K}}/R_{4.2^\circ\text{K}}$  was observed after the completion of the transformation.

Five different lots of Ce, each of a stated purity of 99.9 wt%, have been tested for superconductivity in the high-pressure phase down to 1.3°K. Only one of these<sup>7</sup> becomes superconducting. The following is a brief summary of the results of 30 measurements on ten different samples which prove that superconductivity must be the intrinsic property of cerium.

Taking the residual resistivity ratios (of the samples under pressure) as one criterion for the purity of the lots, the superconducting one is the purest.

Appearance or disappearance (measurements on the pressure-releasing branch) of superconductivity in the sample down to 1.3°K unambiguously corresponds to the presence or absence of the high-pressure phase which is stable above 50 kbar.

One may argue that the formation of a superconducting alloy between Ce and impurities takes place in the course of the high-pressure lattice transformation which results in superconducting filaments, as for example has been observed for very small La concentrations in Rh.<sup>8</sup> This seems to be very unlikely. The observed superconducting transitions were always sharp (Fig. 2); the width slightly broadened due to the inhomogeneity of the pressure along the sample. A pressure increase to about 100 kbar shifts the critical temperature below 1.3°K. This shift of  $T_c$  with pres-

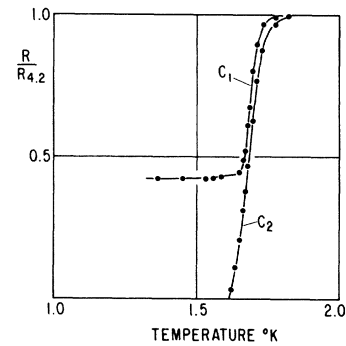


FIG. 2. Superconducting transition curves of Ce. The labels refer to resistance values before cooling (see Fig. 1).

sure is completely reversible. The transition appears again above 1.3°K on successive release of pressure by an appropriate amount. One would not expect such simple behavior in a pressure cycling experiment with filaments in a nonsuperconducting matrix. In addition, after complete release of pressure from 60 kbar to zero pressure at 1.5°K, no sign of superconductivity could be detected. Apparently no minor traces of the superconducting high-pressure phase can be quenched to zero pressure. This would presumably not be the case for a superconducting alloy at this very low temperature.

To make a proposal for the failure of the other lots to show superconductivity above 1.3°K a dilute Ce:Gd alloy (argon-arc melted from the superconducting Ce lot, containing 0.22 at.% Gd) was investigated. The sample seemed to be completely in the high-pressure phase after standing 20 h under a pressure of 50 kbar at room temperature. No sign of superconductivity could be detected down to 1.30°K. Thus  $T_c$  is depressed at least 0.4°K by this small magnetic impurity concentration. Apparently rare-earth additions, and perhaps other magnetic impurities, have the same effect in lowering  $T_c$  by pair-breaking as is well known in the case of lanthanum<sup>9</sup> and thorium.<sup>10</sup> It is very likely that in the case of the other lots magnetic impurities depress  $T_c$  below the temperature limit of this apparatus. For the same reason the transition temperature reported here for cerium (cf. Fig. 2) may be somewhat depressed by unknown contamination with magnetic impurities still present in this particular sample.

The detection of superconductivity in cerium once more confirms the idea of the unstable 4f electron being pushed into the conduction band

with decreasing lattice parameter. Apparently in the superconducting high-pressure phase the bound-state character of the  $4f$  electron at zero pressure (which gives rise to antiferromagnetism in the  $\beta$  phase) is completely removed. From the results the fascinating question again arises whether the nonmagnetic "collapsed"  $\alpha$  phase of very high-purity cerium will become superconducting also at a certain pressure. Experiments down to  $0.3^\circ\text{K}$  will be done in the near future. Furthermore, a determination of the structure of the superconducting high-pressure phase will be helpful for an understanding with regard to the superconductivity of thorium.

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## NEW MODEL FOR INTERFACE CHARGE-CARRIER MOBILITY: THE ROLE OF MISFIT DISLOCATIONS

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It is suggested that consideration of misfit dislocations is essential for analysis of mobility in metal-oxide-semiconductor inversion layers. Occurrence of such dislocations is generally expected for interfaces. Also, aspects of "surface" state behavior fit well with the dislocation model.

Study of inversion layers at the Si-SiO<sub>2</sub> interface over the past several years has provided extensive experimental information on carrier mobilities in such layers.<sup>1-6</sup> However, a satisfactory theoretical understanding of these data is still lacking. Early interpretations were generally based on the assumption of diffuse or partially diffuse surface scattering, but deficiencies of this theory have already been pointed out.<sup>3,4,7</sup> As an alternative, scattering by surface charges has recently been proposed in a number of papers, both in nonquantum<sup>4,8</sup> and also in quantum<sup>9</sup> formulations. However, this approach also presents difficulties: (1) One of the nonquantum approaches<sup>8</sup> assumes the surface charge to be localized strictly at the surface, and concludes that the resultant mobility will always be equal to or higher than that resulting from completely diffuse scattering; experimentally, at least some

mobility values are lower.<sup>10</sup> (2) The other non-quantum approach<sup>4</sup> gives better agreement with the data, but assumes a conversion of surface charge into equivalent volume charge; this is arbitrary, and moreover implies "surface" charge extending up to  $\sim 300 \text{ \AA}$  into the material. (3) As to the quantum formulation, no agreement is obtained between the theoretical<sup>9</sup> and the experimental<sup>6</sup> variation of mobility with gate bias.

In the present paper, we propose that so-called misfit or interfacial dislocations fulfill a crucial role in determining interface properties in general, and mobility behavior in particular. In fact, consideration of such dislocations for interface properties appears not only reasonable but essential: Their occurrence is expected on energetic grounds in cases of lattice mismatch,<sup>11</sup> and moreover, they have been observed even in systems with much less lattice mismatch than Si-