tion calibration to an estimated factor of five.

The first suggestion that nitrogen was involved in the centers was actually obtained from the fluorescent phonon wings of the more tightly bound NN lines. All the lines display phonon wings corresponding to lattice phonons, but the deep lines give distinct phonon replicas which correspond to energies greater than that of the LO lattice phonon. These must represent local modes and have been labeled in Fig. 1 for NN_1 and NN_3. It is found that $\hbar\omega_{loc} = 0.061$ eV. If $\hbar\bar{\omega}$ (= 0.048 eV) is the average of the lattice TO and LO phonons,[1] a crude model gives for the local mode frequency

$$\omega_{loc} \approx \bar{\omega}\left\{\frac{1/4M_{Ga} + 1/M_N}{1/M_{Ga} + 1/M_P}\right\}^{1/2} = 1.27\bar{\omega},$$

where M_N is the atomic weight of nitrogen, etc. Experimentally, $\omega_{loc} = 1.27\bar{\omega}$ in coincidentally good agreement with the expected value. The local modes are more important for the deeper bound excitons because these more tightly bound states have wave functions more concentrated at the central nitrogen atoms.

Several other series of lines have been observed which are generically related to the NN lines, and which probably involve elements other than nitrogen. This type of binding to neutral centers may therefore be quite common and may lead to a wide variety of states within the forbidden gap of semiconductors. It seems likely that at least some of these centers will bind not only excitons but also either holes or electrons. They may therefore influence not only optical but also electrical properties of semiconductors.

Thanks are due to R. T. Lynch for growing the crystals from gallium solution, and to H. C. Montgomery for electrical measurements. Part of this work was performed by one of us (J.J.H.) during a stay at the Bell Telephone Laboratories.

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SUPERCONDUCTIVITY OF PROTACTINIUM*

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We have observed superconductivity in protactinium metal below 1.4°K and thus filled the last vacant spot in the center of the periodic system, the region in which every element becomes either superconducting, ferromagnetic, or antiferromagnetic. We show in the following table the position of Pa in relation to its surrounding elements with their superconducting transition temperatures.

Hf 0.1	Ta 4.4	W 0.011
Th 1.4	Pa 1.4	U 0.7(o), 1.8(c)[a]

[a]The two polymorphic modifications of uranium are orthorhombic and cubic. They have different transition temperatures. See B. S. Chandrasekhar and J. K. Hulm, J. Phys. Chem. Solids 7, 259 (1958).

Pa has five valence electrons and hence would be expected to have the highest transition temperature in the series Th, Pa, U. All surrounding elements are superconductors, and by analogy with the Hf, Ta, W series, Pa would be expected to have a very high transition temperature, certainly far above 18°K. This reasoning would hold, however, only if Pa were to crystallize in one of the simple elemental structures. It is therefore of interest that Zachariasen found an entirely different crystal structure for Pa,[1] namely, that it is tetragonal with a tenfold coordination, a structure observed to date only for Pa. The fact that Pa metal has a more complicated structure than most metals is in agreement with the empirical observation that, whenever a metal could be expected to have a very high transition temperature, it was found instead to have a lower crystal symmetry and therefore also a lower transition temperature.

While these arguments, based on analogies to superconductors in other parts of the peri-

odic system, might explain the apparent low value of the transition temperature of protactinium, we shall show below that another explanation, which accounts for the transition in more detail, is more likely to be true.

In Fig. 1 we show the superconducting transition of protactinium measured in a liquid He^3 cryostat using the ac method of Schawlow and Devlin,[2] with the sample and detection coil immersed in the bath. Curves of thorium and uranium, measured in an identical manner, are also shown for comparison.

While the incomplete curves of Pa and U cannot be normalized, it is readily apparent that they are considerably broader than that of Th. Furthermore, it is noteworthy that if we assume that proper normalization of the Pa and U curves would involve scaling down the absolute height (in cycles per second) of the uranium curve by a factor of two relative to the protactinium curve, we find that the two curves are almost identical! [See Fig. 1(c).] (Such adjustment, to correct for differences in sample size and ac "skin effect," is quite reasonable.) The superconductivity of Pa and that of U are thus quite similar in appearance and markedly different from that of Th. We wish to suggest therefore that the mechanism responsible for superconductivity in Pa and U is different from that in Th.

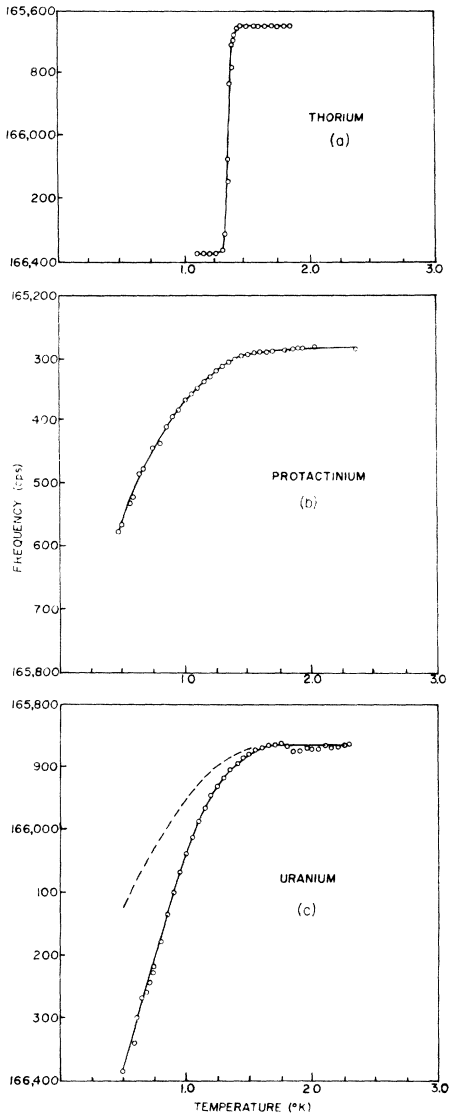

FIG. 1. Superconducting transitions of (a) thorium, (b) protactinium, and (c) uranium.

As has been shown previously, superconductivity in lanthanum and uranium is very probably due to the incipient $4f$ and $5f$ natures, respectively, of these metals.[3-5] While uranium does not contain localized $5f$ electrons in the metallic state, atomic uranium has three $5f$ electrons, and undoubtedly there is some $5f$ character present in the conduction electrons of the metal.[5] Since Pa(IV) seems to have a $5f$ electron,[6] it is likely that the mechanism responsible for superconductivity in uranium is also responsible for the very similar superconducting behavior of protactinium.

Thus thorium, and not protactinium, would be the last of the actinide elements subject to valence electrons and structure considerations,[3] since the superconductivity of Pa and U (and La) seems to be much less sensitive to these factors. Of course it is possible that the expected increase in transition temperature for the valency of 5 between Th and U could have been exactly compensated for by the change in crystal structure, but this seems unlikely.

The sample was prepared by reduction of PaF_4 with lithium vapor at 1300°C.

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ENERGY-GAP ANISOTROPY IN In-DOPED Sn

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One of the fundamental problems yet to be solved in the physics of type-I superconductivity is that of determining the relation between the anisotropy of the superconducting energy gap, the band structure, and the phonon density of states of a real metal (cf. Douglass and Falicov[1]). The most detailed energy gap measurements on a given material are those on Sn made by the ultrasonic absorption[2-4] and electron tunneling[5] techniques. It is the purpose of this Letter to report the following: (1) the direct observation by improved ultrasonic[6] techniques of the variation with impurity concentration of the anisotropy of the superconducting energy gap in a series of In-doped Sn single crystals (<1 ppm to 0.1 at.% In); and (2) the comparison of two models for the temperature dependence of the compressional-wave attenuation in the superconducting state.

The Bardeen-Cooper-Schreiffer (BCS)[7] theory predicts that for an isotropic superconductor the ratio of the compressional-wave attenuation in the superconducting state to that in the normal state is given by

$$\alpha_s/\alpha_n = 2f(\Delta) = 2\{\exp[\Delta(T)/kT]+1\}^{-1}, \qquad (1)$$

where $\Delta(T)$ is the temperature-dependent superconducting energy gap. This result has been shown to be independent of sound frequency and electron mean free path for impurity-limited scattering.[8] Morse, Olsen, and Gavenda[2] and Leibowitz[3] have assumed that the form of Eq. (1) is correct for anisotropic superconductors, but that for a given crystal direction the value of the limiting energy gap $\Delta(0)$ can assume a value different from the BCS value of $1.76kT_c$, where T_c is the transition temperature. The $\Delta(0)$ for a given crystallographic direction is obtained by measuring the slope of a plot of $\ln(\alpha_s/\alpha_n)$ vs T_c/T over the low-temperature range, for which $f(\Delta)\sim e^{-\Delta/kT}$ and $\Delta(T)\sim\Delta(0)$. The measurements[2] on pure Sn indicate an anisotropy of ~20% for compressional-wave propagation along the [001] and [110] directions. Tunneling data[5] indicate that in addition to a possible anisotropy associated with one piece of Fermi surface there are several gaps observed for some crystalline directions in Sn which can be related to the multiple energy surfaces found in the higher Brillouin zones. That there are multiple energy gaps in a real metal such as Sn is not surprising and in fact had been predicted previously by an extension of the BCS theory to a multiband model.[9] At present there is no detailed theory for the effect of multiple gaps on the ultrasonic attenuation. It is not at all clear what the effect of interband pairing and scattering will be on the quasiparticle phonon scattering matrix. The simplest assumption is that of a complete neglect of interband effects, i.e.,

$$\frac{\alpha_s}{\alpha_n} = \sum_i \frac{A_i}{\exp[\Delta_i(T)/kT]}, \qquad (2)$$

where the summation is over all bands, and the constants A_i are subject to the condition $\sum_i A_i = 2$. This form has been used for a two-energy-gap fit for Sn with some success.[10] There is only one model for anisotropic superconductors which has been used to predict the ultrasonic attenuation.[11] The result does not give quantitative agreement with the data for Sn.

It is well established that small amounts of impurity added to a pure superconductor tend to reduce the transition temperature.[12] The reduction is linear in l_e^{-1}, where l_e is the electron mean free path, and according to the current theories[13,14] of dirty superconductivity, the decrease in transition temperature is simultaneous with a smearing out of the energy-gap anisotropy. The energy gap should be approximately isotropic when $\Delta(0) < \hbar\tau^{-1}$, where τ is the impurity-limited relaxation time. For