5. E. T. Baker and D. Z. Piper, *Deep-Sea Res.* **23**, 181 (1976).
6. S. E. Calvert and N. B. Price, *Mar. Chem.* **5**, 43 (1977).
7. A *t*-test performed on the hypothesis that there is no difference between the calculated and observed means of the elemental percentages in the BNL resulted in acceptance at $P < .05$ for all samples except Al at stations B and C.
8. S. P. Hayes, *Proc. Offshore Tech. Conf. OTC-2774* (1977), p. 387.
9. A. F. Amos, O. A. Roels, A. Z. Paul, *Proc. Offshore Tech. Conf. OTC-2456* (1976), p. 341.
10 R. Young, *Mar. Geol.* **23**, M11 (1977).
11. P. Lonsdale and J. B. Southard, *ibid.* **17**, M51 (1974).
12. G. H. Keller, in *Civil Engineering in the Oceans* (American Society of Civil Engineers, Ann Arbor, Mich., 1968), p. 381.
13. E. Partheniades, *Proc. Am. Soc. Civ. Eng. J. Hydraul. Div.* **91**, 105 (1965).

14. We thank J. Nevins and G. Massoth for field and laboratory assistance. R. W. Sternberg, J. Cline, and J. Larrance critically read the manuscript. This study was supported by the NOAA Deep Ocean Mining Environmental Studies Program.

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Superconductivity of Americium

Abstract. *The metal americium becomes superconducting at temperatures as high as 0.79 K for the room temperature, double-hexagonal-close-packed phase. We also have evidence of a slightly higher transition temperature for the face-centered-cubic phase. This discovery of superconductivity in the midst of nonsuperconducting man-made elements is somewhat surprising.*

Americium, atomic number 95, is a member of the actinide series of elements in which all members above 92 are man-made. Our recent tests with single-phase, double-hexagonal-close-packed (dhcp) samples of Am all showed onsets of superconductivity between 0.79 K and 0.55 K. One sample with only the high-temperature face-centered-cubic (fcc) structure present showed an onset at 1.05 K. Samples containing mixtures of these two structures seemed to show the lowest transition temperatures, but experimental difficulties made the interpretation difficult.

Previous studies on americium metal (*1*) have shown that both a low-temperature (≲ 700°C) dhcp form and a high-temperature fcc form exist. The fcc form can be retained at room temperature by quenching the metal from high temperatures. In 1971, Hill (*2*) noted that Am might become superconducting in view of its similarities to La, although it seemed unlikely. In 1975, Johansson and Rosengren (*3*) predicted a superconducting transition temperature of 2 to 4 K on the basis of their parameterization of trends in properties among the 4*f* and 5*f* electron elements. At approximately the same time, the resistivity of Am from room temperature down to low temperatures was being measured (*4, 5*). As a result, possibly, of the prediction by Johannson and Rosengren, the studies were continued to about 2 K to look for superconductivity. None was seen.

Recently, the availability of multimilligram quantities of very pure ^{243}Am led to our tests for superconductivity to temperatures well below 2 K. The use of the 243 isotope, as opposed to the 241 species, reduced significantly the heat generated by the radioactivity (6.3 as compared to 115 mW/g), making the cooling problems less severe.

Our Am samples were prepared by reducing pure AmO_2 with Th metal, then distilling and condensing the more volatile Am metal on cooled quartz or tantalum receivers. We distilled most of the preparations a second time. The five different products were examined by spark-source mass spectrometry and, except for one of the products, the total impurities (excluding hydrogen, nitrogen, and oxygen) ranged from 50 to 240 ppm. Background corrections were not made, and thus these levels represent maximums.

The product exceeding these limits contained Yb at 2000 ppm as an additional impurity. The Yb was introduced through distillation equipment previously used for Yb even though the equipment had been acid-leached afterward. The presence of the Yb did not clearly affect the superconductivity of the Am.

We detected the superconductivity by measuring the a-c susceptibility of the samples in two different cryostats. The first was a ^{3}He system, capable of temperatures just below 0.4 K, in which we cooled the bare samples by submersion in liquid ^{3}He. Here we put the samples in one of two copper coils that were operated at their resonant frequencies (100 to 1000 Hz) while forming parts of two legs of an a-c bridge. We could move the samples, and their Bakelite basket, in and out of these coils during the measurements as a check against background effects.

The second cryostat was a ^{3}He-^{4}He dilution refrigerator capable of temperatures from above 4 K to below 11 mK when operated without radioactive samples. In this system we placed the samples, and a bit of vacuum grease, in copper and beryllium-copper holders since better cooling is observed by additionally making electrical contact between the samples and their colder surroundings than is seen by simple submersion in liquid helium. In the dilution refrigerator, loaded and empty dummy holders were placed in opposing secondary coils located within a large primary coil which applied an a-c magnetic field. We extracted the a-c susceptibility from these secondaries with a lock-in amplifier. In the dilution refrigerator we could not move the samples in and out of the coils without warming the system to room temperature. However, previous work with other superconducting samples of various sizes and shapes, as well as correlations with higher-temperature ^{3}He data give us confidence in the Am results. With radioactive samples, the need to confine contamination in the dilution refrigerator dictates that new holders must be used for each run. Occasionally magnetic behavior in the BeCu parts of the holders is seen and obscures the detection of superconductivity in the samples.

X-ray analysis of all samples before and after the low-temperature runs (*6*) showed that the sample structures were either single-phase dhcp, single-phase fcc, or mixed fcc and dhcp. The single-phase fcc structure (high-temperature form) was obtained because the thin depositions (5 to 10 μm thick) were collected on a cold receiver, which effected a quench.

It should be noted that radioactive superconductors often exhibit somewhat strange behaviors as a consequence of their self-heating coupled with the fact that materials have a drop in thermal conductivity associated with their superconducting transitions. The most obvious consequence of this is an increased temperature width of the superconducting transition. This arises because it is more and more difficult to cool the center of a sample as the interface with the superconducting outer region moves inward from the surface with decreasing temperatures. This increased width suggests, for superconducting radioactive materials, the assignment of T_c (transition temperature) to the intersection of the high-temperature base line with the extrapolation of the linear portion of the plot of susceptibility as a function of temperature. The conventional assignment of T_c as the temperature of the center of the transition would result in an unrealistically low T_c for Am. For some materials, full transitions can never even be seen.

A second, less obvious, phenomenon is oscillatory superconductivity. This was first reported by Olsen (*7*) but clearly occurs more generally than he discussed. In this situation, the center of the sample actually heats above its previous equilibrium temperature when the outer portion goes superconducting and thus causes the fraction of normal metal near the center to increase. This can in turn lower the temperature at the center. This mechanism can lead to observation of large-magnitude oscillations in the a-c susceptibility. We can minimize this effect by using thin samples and cooling by metallic contact. However, when it does occur, this effect is useful in demonstrating bulk superconductivity in the radioactive material.

All the Am samples with the dhcp structure showed onsets of superconductivity between 0.79 and 0.56 K, where this range of temperatures is likely due more to the various temperature gradients in differing sizes and shapes of samples caused by the self-heating as compared to such things as variations in sample purity. The sample with the 0.79 K onset showed superconducting oscillations in the ^{3}He cryostat but no oscillations in the dilution refrigerator. The center of its superconducting transition was at 0.41 K, and it was completed at 0.17 K. In contrast, the single sample of single phase fcc structure showed an onset at 1.045 K, a midpoint at 0.96 K, and leveling off about at 0.64 K. These thin flakes showed no evidence of oscillatory behavior. Samples taken from the products that were a mixture of both metal phases and consisted of extremely thin platelets (2 to 5 μm) showed either an onset of superconductivity near 0.5 K or none at all in the ^{3}He cryostat. Our attempt to run these extremely thin platelets in the dilution refrigerator failed the first time because of a magnetic piece of beryllium-copper and the second time because the Am metal had deteriorated into a black powder. This powder is presumably due to the extended exposure of the active metal to air and to vacuum grease. The depressed T_c's of the mixed phase materials might be due to the presence of Am atoms that possess a magnetic moment. The f^6 configuration is a somewhat fragile occurrence, and anything that disturbs the valence of a few atoms will give those atoms a magnetic moment.

Thus superconductivity was detected in many different samples from four of the five preparations. The fifth preparation showed uncertain results. Clearly dhcp Am becomes superconducting at about 0.79 K, and fcc likely becomes superconducting at a higher temperature. With regard to the occurrence of superconductivity in Am, which is surrounded in the periodic table by nonsuperconductors, it is obvious to draw a comparison to lanthanum which is also superconducting. The superconductivity is clearly somewhat similar in La and Am in spite of major differences in their *f* electron nature. Americium and La metal exhibit several similarities. Both metals are considered trivalent, have the same types of crystal structures, have similar metallic radii, and have no magnetic moments.

An important point of comparison for our purposes is the lack of a magnetic moment. In La this occurs because there are no localized *f* electrons. In Am, there are localized *f* electrons, but their unique f^6 configuration is nonmagnetic by either Hund's rules or *jj* coupling (*8*). Thus these elements both lack a magnetic moment but for different reasons. The experimental evidence for nonmagnetic behavior in Am has been reviewed by Nellis and Brodsky (*9*). The lack of magnetism and the possibility of superconductivity in Am was also shown by Hill *et al.* (*10*) who demonstrated that the T_c of La is not depressed when small amounts of Am are alloyed with it, in contrast to La alloys made with Np and Pu.

A final and very convincing argument for nonmagnetic and lanthanide-like behavior of Am is the entropy correlation work of Ward and Hill (*11*), who correlated electronic properties with metallic radii, magnetic transformations, and thermodynamics of vaporization. These correlations were developed from their observation that the magnetic entropy of a localized spin system must be included in calculations of entropies for solid, liquid, and gaseous systems. From these relations Ward and Hill were able to explain the trends in behavior of the physical properties among the rare earths and heavier actinides, and they have concluded that Am is trivalent and nonmagnetic.

The difficulty with dwelling on the similarities between La and Am is that it leads to generalizations to other elements. Schenkel (*4*) used the La T_c's of 4.9 K and 6.05 K for the dhcp and fcc structures to estimate Am T_c's of 0.6 K and 2 K by comparing the Debye temperatures, the density of states at the fermi level, and the electron-phonon interactions for the two elements. This prediction thus seems to work for Am but the very same analysis applied to the similarly trivalent and nonmagnetic elements Sc, Y, and Lu leads to the incorrect conclusion that they would be superconducting. It appears that Johansson and Rosengren (*3*) might be confronted by the same problem of predicting superconductivity in nonsuperconducting trivalent metals.

This sort of difficulty requires the usual conclusion that *f* electrons must play a beneficial role for the superconductivity. This viewpoint for La is reviewed by Gladstone *et al.* (*12*), and it should now be taken to include Am. In this context, the difference in the *f* electron nature of La and Am must not be forgotten. For La, the only *f*-like behavior is due to virtual states above the Fermi level. In contrast, for Am there must be contributions from the localized electrons whose energies must lie near to the Fermi level. This is not surprising since 5*f* electrons are far less buried inside their atoms than are 4*f* electrons. Thus, the superconductivity in La and Am is similar in that both probably require the *f* electron character to be present since other trivalent elements with no *f* electron character are not superconducting. Furthermore, the rather different electronic structure of La and Am still leads to very similar superconducting properties.

At first glance, the superconductivity of Am is a bit surprising. It is by far the most isolated superconductor in the periodic table. However, it must be emphasized that its superconductivity is allowed by its special nonmagnetic ground state. This result, taken with the seemingly different case of La, should provide insight into superconductivity in the 4*f* and 5*f* electron metals.

JAMES L. SMITH
Los Alamos Scientific Laboratory,
Los Alamos, New Mexico 87545
RICHARD G. HAIRE
Oak Ridge National Laboratory,
Oak Ridge, Tennessee 37830

References and Notes

1. P. Graf, B. B. Cunningham, C. H. Dauben, J. C. Wallmann, D. H. Templeton, H. Ruben, *J. Am. Chem. Soc.* **78**, 2340 (1956); D. B. McWhan, J. C. Wallmann, B. B. Cunningham, L. B. Asprey, F. H. Ellinger, W. H. Zachariasen, *J. Inorg. Nucl. Chem.* **15**, 185 (1960); J. C. Spirlet and W. Müller, *J. Less-Common Met.* **31**, 35 (1973).
2. H. H. Hill, *Physica* **55**, 186 (1971).
3. B. Johansson and A. Rosengren, *Phys. Rev. Sect. B* **11**, 2836 (1975).
4. R. Schenkel, thesis, Universität Saarbrücken (1976).
5. ———, R. O. A. Hall, H. E. Schmidt, J. C. Spirlet, *Proceedings of the Second International Conference on the Electronic Structure of the Actinides*, J. Mulak, W. Suski, R. Troć, Eds. (Ossolineium, Wroclaw, 1977), p. 269; R. Schenkel and W. Müller, *J. Phys. Chem. Solids* **38**, 1301 (1977); M. B. Brodsky and R. Schenkel, in preparation.
6. We thank R. B. Roof and D. T. Cromer for x-ray analyses after the thermal cycling of the samples.
7. C. E. Olsen, *Phys. Lett. A* **43**, 205 (1973).
8. It should be noted that the rare earth analog, Eu, chooses to change valence and adopt an f^7 configuration which makes it magnetic. Thus Am is the only element with the rather special nonmagnetic f^6 configuration.

9. W. J. Nellis and M. B. Brodsky, in *The Actinides: Electronic Structure and Related Properties*, A. J. Freeman and J. B. Darby, Eds. (Academic Press, New York, 1974), vol. 2, p. 265.
10. H. H. Hill, J. D. G. Lindsay, R. W. White, L. B. Asprey, V. O. Struebing, B. T. Matthias, *Physica* **55**, 615 (1971); H. H. Hill and F. H. Ellinger, *J. Less-Common Met.* **23**, 92 (1971).
11. J. W. Ward and H. H. Hill, in *Heavy Element Properties*, W. Müller and H. Blank, Eds. (North-Holland, Amsterdam, 1976), p. 65.
12. G. Gladstone, M. A. Jensen, J. R. Schrieffer, *Superconductivity*, R. D. Parks, Ed. (Dekker, New York, 1969), p. 665.
13. We thank B. T. Matthias, J. W. Ward, B. Johannson, M. B. Brodsky, and B. W. Veal for helpful discussions. Work was performed under the auspices of the Department of Energy.

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Fluorinated Molecule as a Tracer: Difluoroserotonin in Human Platelets Mapped by Electron Energy-Loss Spectroscopy

Abstract. *The intracellular distribution of fluorine has been delineated in human platelets incubated with 4,6-difluoroserotonin, utilizing a scanning-transmission electron microscope equipped with an energy-loss spectrometer. Discrete intracellular structures corresponding in location to dense bodies contained high concentrations of fluorine. Electron energy-loss spectroscopy, which apparently can detect less than 10^{-20} gram of fluorine in an area of 10 square nanometers, can thus localize fluorinated tracer molecules with biological activity.*

Fluorinated analogs of biologically significant organic molecules have proved to be extremely valuable biochemical and pharmacological agents. Substitution of fluorine for hydrogen introduces no serious steric alteration into the molecule, and the fluorinated analog frequently is recognized as its natural relative by enzymes, receptors, or transport systems (*1*). Continued synthetic activity in the area of organofluorine chemistry, which has provided a wide variety of fluorinated organic molecules, reflects the importance of these analogs (*2*).

In theory, fluorine associated with an organic molecule should provide an excellent tracer for determining at an ultrastructural level the distribution within the cell of a number of soluble compounds of importance in cellular function. Virtually no fluorine is present in cells under normal circumstances, and the substituent often allows an intracellular disposition mimicking that of the parent compound. This potential application of fluorinated compounds has been seriously hampered, however, by the lack of a suitable method for localizing fluorine inside cells. Conventional x-ray microanalysis systems, for example, are relatively insensitive to fluorine (*3*). We report that electron energy-loss spectroscopy, which we have utilized to localize a fluorinated analog of serotonin (5HT) sequestered intracellularly in human platelets, appears to provide a sensitive and specific method for the detection of fluorine in biological systems (*4*).

4,6-Difluoroserotonin (DF5HT) was synthesized by a method described elsewhere (*5*). The tritiated compound was prepared by acid-catalyzed decarboxylation of 4,6-difluoro-5-methoxytryptamine-2-carboxylic acid in tritiated water (5 Ci/ml), followed by demethylation. The intracellular disposition of tritiated DF5HT was compared with that of tritiated 5HT in human platelets by use of brief thrombin treatment and formaldehyde fixative to evaluate the amount of labeled material in the thrombin-releasable (vesicular) and non-thrombin-releasable (cytoplasmic) compartments of washed platelets (*6–8*) (Table 1). Although there are some differences in the behavior of the two compounds (*9*), comparable amounts of [^{3}H]DF5HT and [^{3}H]5HT enter platelet vesicles and cytoplasm at all time points and concentrations. Thus the intracellular sequestration of [^{3}H]DF5HT can provide a useful index for the compartmentation of [^{3}H]5HT.

Before electron microscopy, platelets were incubated for 60 minutes with an initial concentration of $10^{-5}M$[^{3}H]-DF5HT. When measured with thrombin and fixative as described above, cells contained on the average 1.9×10^{-17} mole per platelet of [^{3}H]DF5HT in a vesicular compartment and 0.2×10^{-17} mole per platelet in a cytoplasmic compartment. After incubation, platelets were air-dried by rapid blotting on copper grids coated with collodion and carbon, a procedure employed previously to analyze the content and distribution of platelet dense bodies (*6, 7, 10, 11*). Grids were examined at 100 kV in a JEOL JEM-100B electron microscope equipped with a scanning attachment, an electron spectrometer, and a Kevex multichannel analyzer (*12*). As imaged by utilizing all the transmitted electrons in the scanning-transmission electron microscopy (STEM) mode (spot size, 10 nm^2), most platelets contained dense bodies, which appeared dark because of their high calcium content and total scattering power (*6, 7, 10, 11*). Energy-loss spectra obtained from dense bodies probed with a 10-nm^2 stationary spot showed large fluorine ionization edges at

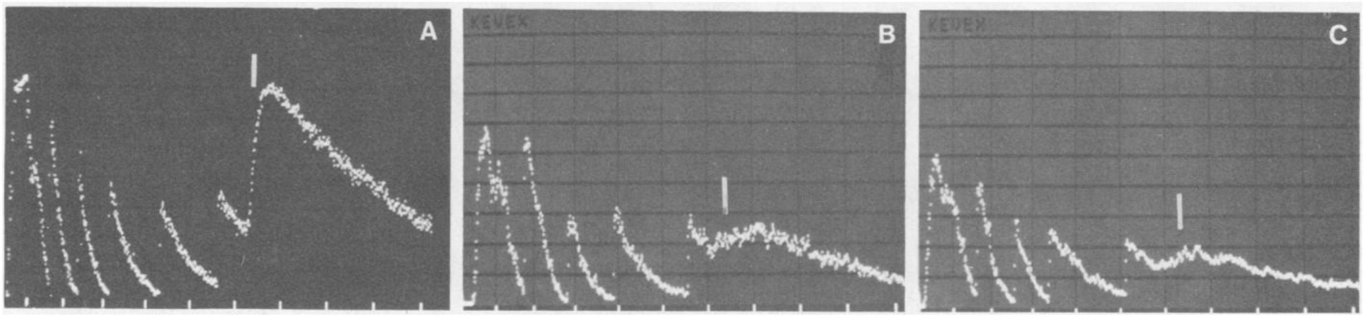

Fig. 1. Energy-loss spectra recorded from various portions of a platelet incubated with DF5HT. The region corresponding to an average loss of 680 eV (characteristic of fluorine *K*-shell ionization) is marked with a bar. The analysis system compensates for differences between the numbers of zero-loss and 680 eV-loss electrons by increasing the gain of the photomultiplier tube as the electron beam is scanned from zero loss to 680 eV loss. Thus, the breaks in the spectra at approximately 100-eV intervals represent points at which the gain of the photomultiplier tube was increased. Regardless of gain at 680 eV, the integral area of the peak rising above the descending curve of the background contribution is approximately proportional to the number of fluorine molecules interacting with the incident electron beam. (A) Spectrum recorded from a dense body. A prominent absorption edge for fluorine is present. (B) Spectrum from the cytoplasmic apron (organelle-free region) of a platelet. A small fluorine edge is present. (C) Spectrum from the supporting film immediately adjacent to the platelet. A very small fluorine edge is present.

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