

produce the Bordoni peaks in fcc metals. Furthermore, we feel that the different response of the bcc metals to annealing can be attributed to the action of efficient dislocation pinning points (gaseous interstitials and/or carbon) known to exist in bcc metals.

We wish to thank P. H. Miller, Jr., for encouragement and support and E. Moxley for her technical assistance.

\*This work was supported by the U. S. Atomic Energy Commission.

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### ABSENCE OF AN ISOTOPE EFFECT IN SUPERCONDUCTING RUTHENIUM

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(Received February 17, 1961)

Within the accuracy of our measurements, ( $0.001^\circ$ ), naturally occurring ruthenium and its isotopes of mass 99 and 104 have identical superconducting transition temperatures,  $T_{SC}$ . Our results are presented in Fig. 1. This lack of dependence of  $T_{SC}$  on atomic mass is quite different from the results obtained for the isotopes of other superconducting elements.<sup>1</sup> All elements which have been previously measured, Sn, Hg, Tl, and Pb, show an isotope shift of  $T_{SC}$  which is essentially proportional to  $M^{-1/2}$ . However, they are all nontransition elements, having  $s$  and  $p$  electrons only. Ruthenium is the first of the transition elements to be checked with respect to an isotope shift. The reason for this lack of data may have been—in part, at least—experimental difficulties. The superconducting properties of ruthenium and osmium have been discovered and reported by Goodman<sup>2</sup> and Hulm and Goodman.<sup>3</sup> With the exception of these two metals, transition element superconductors have critical temperatures which change strongly with small amounts of dissolved nitrogen or oxygen. These variations exceed the shift that may be expected from an isotope effect. There is no good way at present to get rid of these gases in a quantitative way with the small amounts of material available.

Ruthenium isotopes were obtained in powder form from Oak Ridge National Laboratory through the courtesy of P. V. Arow. The isotope analysis furnished is given in Table I. After our initial results, a second analysis was made at the Oak Ridge Laboratory which was in good agreement with the first. Spectrographic analysis at Oak

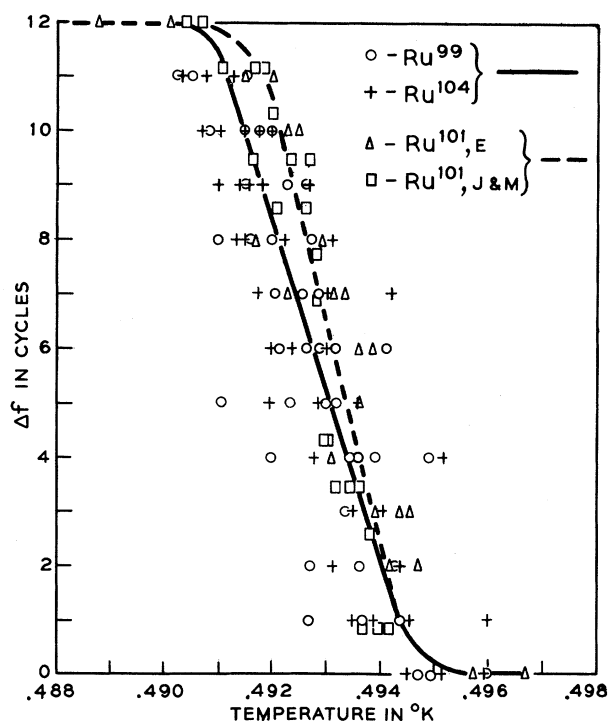


FIG. 1. Change in frequency of oscillator circuit as a function of temperature for arc-melted pellets of ruthenium. Samples  $Ru^{99}$  and  $Ru^{104}$  were made from enriched powders of  $Ru^{99}$  and  $Ru^{104}$ ; sample J&M was made from Johnson-Matthey powder and sample E from Englehard Industries' natural powder.

Ridge indicated an absence of all transition metal impurities which might falsify the results, with the possible exception of iron. However, a further analysis indicates less than 10 parts per

Table I. Isotopic analysis of Oak Ridge ruthenium.

Ruthenium	Isotope	Atomic percent	Ruthenium	Isotope	Atomic percent
99	96	<0.02	104	96	<0.03
Series IL	98	0.38	Series IL	98	<0.03
Sample 1017a	99	89.82	Sample 1021a	99	0.09
	100	6.71		100	0.11
	101	1.49		101	0.28
	102	1.23		102	3.18
	104	0.34		104	96.35

million of iron.<sup>4</sup> Such a concentration can only reduce  $T_{SC}$  by about two-tenths of a millidegree.

The powders were measured as received and showed broad ( $\sim 0.08^\circ$ ) transitions commencing near  $0.48^\circ$ . Somewhat sharper transitions near  $0.48^\circ$  were obtained with natural powders. Electron diffraction pictures of natural ruthenium showed a size distribution of the powder particles ranging down to 500 Å.<sup>5</sup> This result indicates that the broad transitions were due to the small particle size, since 500 Å is in the order of the penetration depth. Therefore, the powder was melted into a pellet in an arc furnace. The preliminary results with natural ruthenium immediately gave sharp transitions with widths of the order of a few millidegrees. Different methods of melting were tried and possible contamination was checked for by comparison of the measured  $T_{SC}$ , but no significant differences were noted. The following procedure was finally adopted. About 0.35 gram of powder was pressed, out-gassed, and then melted in an argon arc furnace using a ruthenium cathode instead of the customary wolfram tip. The sample, resting on a water-cooled copper hearth, was melted in just one pass, lasting only seconds. The samples lost varying amounts of weight upon melting, ranging between 0.5 and 10%.

The transitions were measured by immersing the samples in a bath of helium-3. The large temperature gradients which exist in helium-3 made it necessary to mount a thermometer in good thermal contact with the sample. A non-encapsulated four-terminal germanium thermometer was used. It was calibrated against the vapor pressure of helium-3 under conditions where thermal gradients were avoided by stirring; thermomolecular pressure corrections

were made using the data of Roberts and Sydoriak.<sup>6</sup>

The superconductivity was detected using the oscillator circuit of Schawlow and Devlin,<sup>7</sup> in which the sample is in the center of the tank circuit coil. The natural frequency of the oscillator circuit, 30 kc/sec, increased about 12 cps when the sample became superconducting. This inductance change of the coil is due to the superconducting penetration depth being smaller than the skin depth which is about  $10^5$  Å. This causes the small frequency change when the sample changes from normal to superconducting. There was, of course, a much larger change in the case of the powders. The oscillator current produced a magnetic field of about 0.02 gauss; the earth's field was reduced by a mu-metal shield to about 0.003 gauss.

The change in oscillator frequency as a function of temperature for pellets prepared from four samples of ruthenium powder is plotted in Fig. 1. Several warming and cooling curves were taken for each sample and the points are included. The frequency was read to the nearest cycle. The Johnson-Matthey powder is of spectroscopic grade in which detectable impurities are in the parts per million range or less. It is believed that chemical impurities are present in such small concentrations in all four samples that they have no measurable effect on  $T_{SC}$ . A second pellet of Ru<sup>99</sup> (not shown in Fig. 1) was less pure. This sample had roughly twice the skin depth in the normal state and gave a broader transition curve about  $0.004^\circ$  below the others. Repeated arc-melting (three times) apparently boiled out the impurity somewhat and brought the transition temperature within  $0.0015^\circ$  of the others.

A shift for the Ru<sup>104</sup> curve of 0.012° below the Ru<sup>99</sup> curve, which would be expected if  $T_{SC}$  were proportional to the inverse square root of atomic mass, is clearly nonexistent. In fact, the Oak Ridge samples are within 0.001° of each other. From the agreement of these isotopes within themselves and with the natural ruthenium, we conclude that less than 10% of the normal isotope shift is present. This is considered as an indication that mechanisms other than electron-phonon interaction may also lead to superconductivity. Mechanisms such as *s-d* interactions, for instance, have been already recognized in the past for their importance to the superconductivity of the transition elements.<sup>8</sup>

We wish to thank P. P. Cioffi for measuring the residual earth's field. We are grateful to J. P. Remeika for help in providing answers to questions of sample purity. We are particularly happy to acknowledge the work of L. D. Longinotti in the design and construction of the helium-3 cryostat, the details of which will be published

elsewhere. We are indebted to R. L. Garwin for sharing his knowledge of helium-3 with us and to P. W. Anderson, H. Fröhlich, C. Herring, H. W. Lewis, A. L. Schawlow, and P. A. Wolff for many discussions over the last six years of isotope effects in transition elements.

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<sup>4</sup>We are indebted to Dr. Bell of Lucius Pitkin, Inc., for carrying out the analysis.

<sup>5</sup>We are indebted to Miss Koonce of our Laboratories for taking the electron microscope pictures.

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## EXCHANGE POLARIZATION AND THE MAGNETIC INTERACTIONS OF RARE EARTH IONS\*

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(Received February 13, 1961)

We are reporting results of a study of the contribution of spin or exchange polarization<sup>1</sup> to the magnetic interaction of a rare earth ion with its neighbors and with its own conduction electrons. This investigation was carried out by means of conventional analytic Hartree-Fock (H-F) calculations<sup>2</sup> for the Gd<sup>+3</sup> and Gd<sup>+</sup> ions and a spin-polarized H-F calculation<sup>2</sup> for the Gd<sup>+3</sup> ion. While the conventional H-F results are of interest in themselves, since they represent the first time such information has been available for the rare earths, we shall only discuss a result of the spin-polarized calculation which may have important consequences for the magnetic behavior of these elements. Our results suggest that the rare earth ions carry a "paired" electron spin density which is negative in their outer reaches. Since the unfilled 4*f* shell electrons are imbedded in the interior regions of the ions, this outer

spin distribution can play an important (and perhaps even dominant) role in the magnetic interactions of rare earth ions. In fact, as will be shown, these ions may even appear to their neighbors as having negative spins (i. e., antiparallel to the 4*f* spin direction) and some experimental results are discussed on this basis.

The contribution of "paired" electrons to the magnetic properties of solids has been the object of recent studies<sup>2,3</sup> which have utilized the spin-polarized Hartree-Fock method. Two effects have been studied. The first of these is the contribution of the core *s* electrons, via the Fermi contact term, to the effective magnetic field at a nucleus in a ferromagnet.<sup>3</sup> This contribution appears to be the dominant source of the recently observed negative effective<sup>4</sup> fields in ferromagnets. Secondly, computations<sup>2,5</sup> for the contribution of the "paired" electron spin density<sup>6</sup> to an