T. H. Geballe*
B. T. Matthias*

Isotope Effects in Low Temperature Superconductors†

Abstract: The critical temperatures of different isotopes of osmium and of zinc have been measured. The results are that Os has no isotope effect, while with Zn the critical temperature is proportional to $M^{-1/2}$. These findings, together with our previous work on ruthenium, are consistent with the statement that there is no isotope effect for the transition elements, whereas the full $M^{-1/2}$ effect exists for nontransition elements.

The isotope effect has been very important in the development of superconductivity theory. The variation of T_c with $M^{-1/2}$ was predicted by the Fröhlich-Bardeen theory and was found in the nontransition elements Sn, Pb, Hg, and Tl. Since transition element superconductors seem to exhibit a different kind of a superconductivity, we were interested in seeing if they also had an isotope effect. Netzel and Dillinger[1] have looked at Ti, but they observed irregularities (possibly because of dissolved gases) that made it difficult to investigate the isotope effect. We looked at Ru and found the transition temperature to be independent of atomic mass, i.e., no isotope effect at all; the results have been published recently.[2]

In our measurements, the sample is immersed in liquid He^3 and surrounded by a coil. The change in state of the sample is reflected as a change in the resonant frequency of the coil. This setup also affords a convenient way of testing the purity of the sample, since we can measure the skin depth of the material in the normal state. In this way we measure the residual resistivity of the samples, as well as the transition into the superconducting state.

Figure 1 shows the data on Ru. The difference in T_c is much smaller than predicted by the $M^{-1/2}$ law. In fact the exponent is smaller than 10% of $-\frac{1}{2}$. The scatter in the data is probably due to thermal gradients in the He^3 which we recently have been able to reduce. (See Fig. 5.)

These results raise the question of whether Ru is representative of transition-metal superconductors as a whole, or of whether the isotope effect disappears for all materials with a low transition temperature (an order of magnitude lower than Sn and Pb). To try to answer this question we obtained some isotopes of Zn and Os, and measured their T_c values.

The zinc powders, Zn^{64} and Zn^{68}, which we obtained from Oak Ridge gave rather broad transition curves. The normal techniques of preparing high-purity single crystals did not work for the small amount of material available here. By distilling the zinc in an oven with a temperature gradient and a quartz tube, we were able to condense little globules of the zinc on the cold end of the quartz tube. It was these little globules that we examined, and the results are shown in Fig. 2. The expected difference in T_c between Zn^{64} and Zn^{68} would be about 27 millidegrees if the $M^{-1/2}$ relation held, and that is about what we

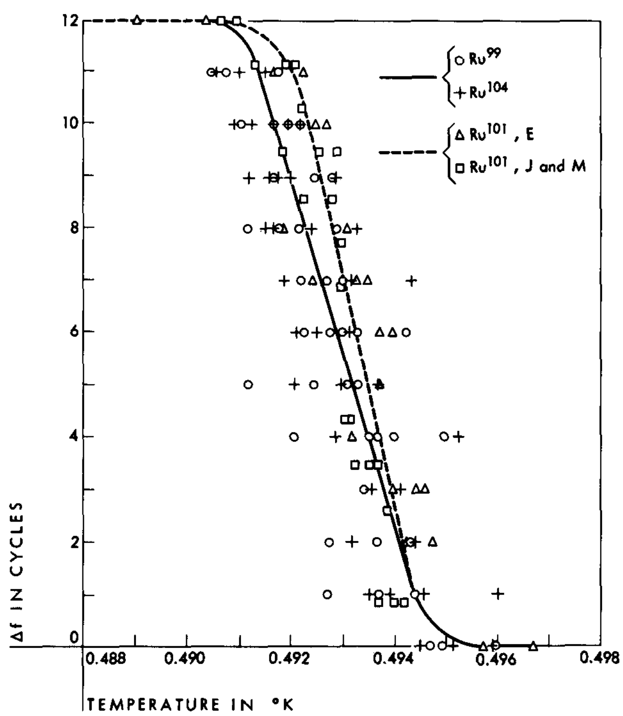

Figure 1 **The superconducting transitions for samples prepared from different enriched isotopes of ruthenium.** *Ru^{99} and Ru^{104} were obtained from Oak Ridge, and the natural samples were prepared from Johnson-Mathey and Englehard ruthenium.*

* Bell Telephone Laboratories, Murray Hill, New Jersey.
† Presented at IBM Conference on Fundamental Research in Superconductivity, Yorktown Heights, N.Y., June 1961.
The editors are indebted to Dr. Geballe for permission to publish the transcript of his talk, which he subsequently edited.

observed. We are plotting inverse frequency, so that the curve drops at the transition into the superconducting state. The sharp curve for the $Zn^{65.38}$ was from a very pure natural zinc single crystal with a resistance ratio of 30,000. We were unable to get the isotopic globules any sharper by redistillation, annealing, and so forth. However we do not feel that we are making a very large error in picking either the 50% point or the 25% point for the transition.

Figure 3 is a plot of $1 + \log T_c$ against the log of the mass. The straight line is drawn with a slope of $-\frac{1}{2}$. The points are our three measured samples, with the 50% point taken for the transition. A line through the transitions taken from the 25% points has a slope that is a little less than $\frac{1}{2}$, perhaps about 0.45. To this accuracy, the normal isotope effect thus occurs in zinc.

Os was a little harder to handle than Ru. As a matter of fact, the Os^{186} was not even superconducting in the form in which we received it from Oak Ridge. However, on repeated arc-melting by E. Corenzwit the samples gave off a lot of gas, and we were able to bring them all to within 10 millidegrees of each other,[3] although they varied from one melting to the next by about 5 millidegrees. Since the total expected effect was 8 millidegrees, at first we were not able to say whether we had an isotope effect or not. However, vacuum annealing at around 1900° (through the courtesy of E. Buehler) improved the situation a great deal. Now our residual resistance ratios are as good as for our Ru and the reproducibility of the transition temperature is likewise as good. Figure 4 shows a log-log plot of T_c against mass. Between the 186 enriched (187.4 mean mass), the 188 and the natural (190.2 mass) there is no effect at all. The 192 mass sample, which we are still remelting and annealing, shows a slight effect. The line is drawn with a slope of -0.1. We feel reasonably confident that there is no isotope effect in Os. Our results, therefore, are consistent with the statement that there is no isotope effect for transition elements, whereas the full $M^{-1/2}$ effect exists for nontransition elements.

References and footnotes

1. R. G. Netzel and J. R. Dillinger, *Proceedings of the Seventh International Conference on Low Temperature Physics*, edited by G. M. Graham and A. C. Hollis Hallett, University of Toronto Press, Toronto, 1960; p. 191.
2. T. H. Geballe, B. T. Matthias, G. W. Hull, Jr., and E. Corenzwit, *Phys. Rev. Letters*, **6**, 275 (1961).
3. The Os transition temperature is 0.655°K. This is a little lower than the 0.71°K that J. K. Hulm and B. B. Goodman reported, *Phys. Rev.* **106**, 659 (1957), and it is higher than J. A. Carruthers and A. Connolly "Proceedings of the Fifth International Conference on Low Temperature Physics and Chemistry" edited by J. R. Dillinger, University of Wisconsin Press, Madison, 1958.

Note added in proof: Figure 5, taken from an *x-y* recording, shows more recent data with reduced thermal gradients.

Received October 9, 1961

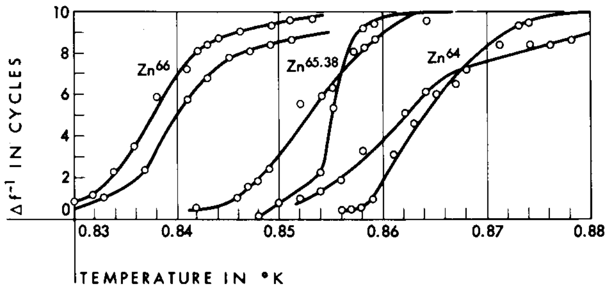

Figure 2 **The superconducting transition for different isotopes of zinc.**

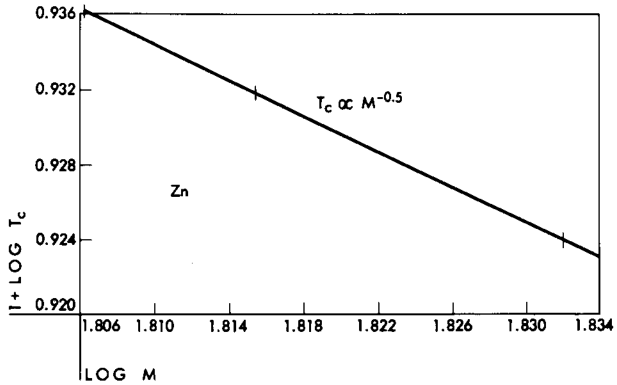

Figure 3 **Variation of $1 + \log T_c$ with $\log M$ for zinc isotopes.**
The slope of the line gives the exponent of the mass for the isotope effect.

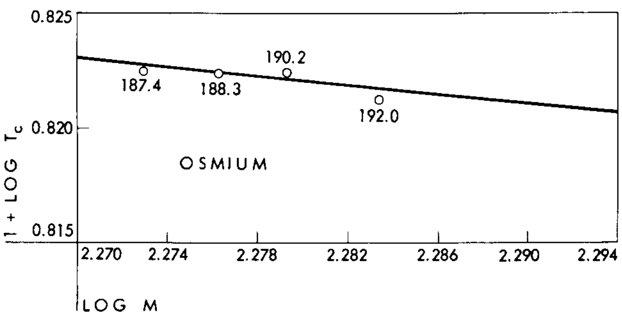

Figure 4 **Variation of $1 + \log T_c$ with $\log M$ for osmium isotopes.**
The small slope of the line indicates little or no isotope effect.

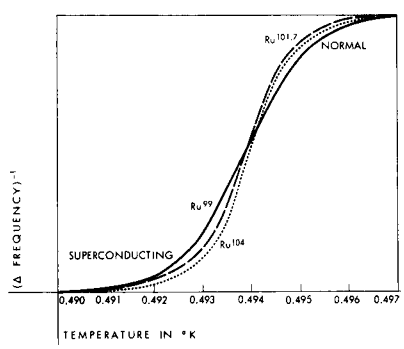

Figure 5