PHYSICAL REVIEW VOLUME 97, NUMBER 1 JANUARY 1, 1955

Empirical Relation between Superconductivity and the Number of Valence Electrons per Atom

B. T. MATTHIAS
Bell Telephone Laboratories, Inc., Murray Hill, New Jersey

(Received September 28, 1954)

The relation between the transition temperature of a superconductor and its number of valence electrons/atom has been investigated. Optimum conditions for the occurrence of superconductivity seem to exist for 5 and 7 valence electrons/atom.

IN a previous paper[1] an attempt was made to find for superconductors the empirical relation between their transition temperatures and the electronic configurations of their atoms. It was found that for an average valence electron/atom ratio (R) slightly below 5 the transition temperatures tend toward a maximum. Anomalous results, however, were obtained for the transition elements and their compounds, which had much larger R values.

The purpose of this paper is to resolve this anomaly and to include in the discussion all the recently discovered compounds and alloys, as well as technetium.[2]

When Daunt and Cobble discovered the superconducting transition temperature of technetium near 11°K, it became obvious that the maximum of transition temperatures for compounds and elements with an R near 5 could not be the only one because Tc has seven valence electrons/atom.[3] As a matter of fact, superconducting transition temperatures in the horizontal rows of the periodic system seemed to be more or less symmetrical with respect to the sixth column (see Table I).

The study of alloys of Mo with elements of the eighth column further strengthened the validity of this assumption,[4] so that today it seems very probable that a second maximum for superconducting transition temperatures occurs for elements and compounds with an R near 7.

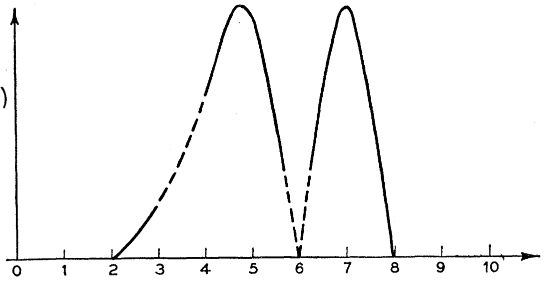

FIG. 1. Variation of superconducting transition temperature with number of valence electrons per atom.

Our data now suggest tentatively that the qualitative dependence of the transition temperature on R is as indicated in Fig. 1.

In this plot the effects of mass and volume, which are now well recognized, are neglected.[1,5,6]

In the next four paragraphs, we would like to give four examples of how this curve was traced experimentally.

(a) SOLUTIONS OF RHODIUM IN ZIRCONIUM

We have found that up to approximately 15 percent Rh can be dissolved in Zr without appreciably[7] changing the size of the lattice constant. Above 15 percent Rh, additional lines in the x-ray powder photograph indicate that either a superlattice or a new crystal structure closely related to that of Zr exists. (Further investigation of the crystallography of this system will be carried out by S. Geller.) Whereas results obtained for Zr-Rh alloys with more than 15 percent Rh have therefore to be considered with caution, it becomes obvious for smaller Rh amounts how strongly the superconducting transition temperature is affected by the electron concentration, i.e., the R value (see Fig. 2).

These data on the Zr-Rh system should be considered only of preliminary nature outside the range of 1 percent to 30 percent Rh. For Rh percentages below 1 percent the purity of our Zr (99 percent) was not good enough, and above 33 percent Rh we seem to have

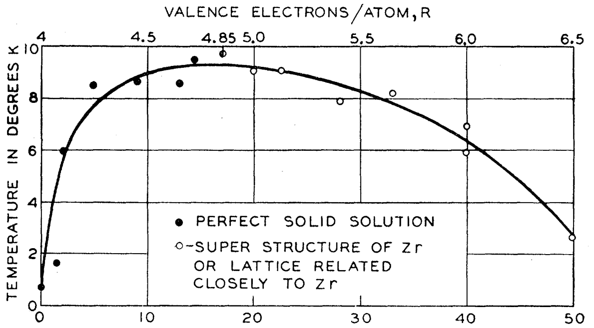

FIG. 2. Superconductivity of Zr-Rh alloys.

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[1] B. T. Matthias, Phys. Rev. 92, 874 (1953).

[2] L. G. Daunt and L. W. Cobble, Phys. Rev. 92, 507 (1953).

[3] Valence electrons are here considered to be all electrons outside of closed shells.

[4] B. T. Matthias and E. Corenzwit, Phys. Rev. 94, 1069 (1954).

[5] P. Marcus, Phys. Rev. 94, 837 (1954).

[6] D. Shoenberg, Nuovo cimento 10, Suppl. No. 4 (1953).

[7] By "appreciably" we mean to an extent which would affect the transition temperature if we assume $T_c \sim (\text{Volume})^{10}$.

TABLE I. Superconducting transition temperatures for elements of the fourth to the eighth column.

IV	V	VI	VII	VIII
Zr 0.7°	Nb 8.6°	Mo[a]	Tc 11°	Ru 0.47°
Hf 0.35°	Ta 4.4°	W[a]	Re 1.7°	Os 0.71°

[a] Not superconducting above 0.05°K.

a two-phase system.[8] All we wish to show now is how the maximum transition temperature occurs here for an R value slightly below 5 as observed so often before.[1]

(b) SUPERCONDUCTING COMPOUNDS WITH THE BETA-*W* STRUCTURE

Because in this type structure it was not possible to vary the R value continuously, we were limited to a number of discrete points corresponding to the available compounds. In order not to confuse the issue too much by variation of mass and volume, we restricted ourselves to compounds of two elements, niobium and molybdenum, which are next to one another in the periodic system. Figure 3 shows the variation of the superconducting transition temperature with R. It shows the existence of maxima near 5 and 7 and a minimum near 6. Mo_3Si and Mo_3Ge and their superconducting transition temperatures have been described recently by Hardy and Hulm.[9] The niobium compounds were discovered in the course of this work and will be described in detail.[10]

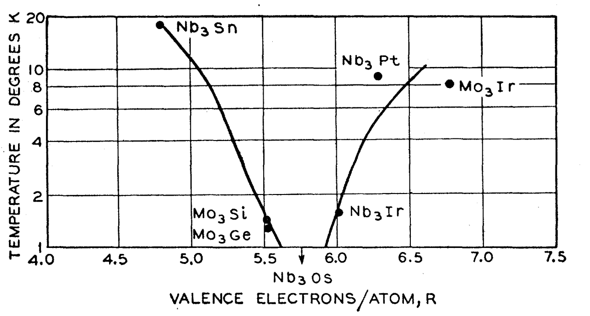

FIG. 3. Superconductivity of compounds with the β-*W* structure.

(c) THE RHODIUM-SELENIUM AND RHODIUM-TELLURIUM SYSTEMS

Rhodium-selenide crystallizes in the pyrite structure over a wide homogeneity range from about $RhSe_{1.5}$ to $RhSe_{2.5}$.[10] As reported before[11] superconductivity occurs only inside this range. The cell size decreases with increasing Se content, but considering that the transition temperature appears proportional to not more than the tenth power of the volume this change is negligible. The maximum transition temperature at 6°K was observed for $RhSe_{1.75}$ corresponding to an R value of 7.1. The structure of $RhTe_2$, at which composition the transition temperature reaches the maximum at 1.51°K is unknown[10] but may be related to that of $RhSe_2$. Its R value is 7.

TABLE II. Transition temperatures of Mo and W alloys.

Alloy	Crystal structure	Average number of valence electrons/atom	Transition temperature °K
Mo_3Os	β-*W*	6.5	7.2
Mo_3Ir	β-*W*	6.75	8.8
1 Mo:1 Ru	hcp[a]	7	9.5 −10.5
1 Mo:1 Rh	hcp[a]	7.5	1.97
1 Mo:1 Ir	hcp[a]	7.5	below 1
1 Mo:4 Ru	hcp[a]	7.6	1.66
W_3Os	?	6.5	3.02−2.21
W_3Ir	?	6.75	3.82−2.1
1 W:1 Ru	hcp[a]	7	7.5
1 W:1 Rh	hcp[a]	7.5	3.37−2.64; 1.9

[a] Hexagonal close packed.

(d) THE MOLYBDENUM AND TUNGSTEN ALLOYS

These again serve to illustrate the maximum transition temperature near R values of 7.[4] However, as W is nearly twice as heavy as Mo the comparison is not quite so clear cut. Table II and Fig. 4 compare the observed values of transition temperature with the corresponding R values.

Raub had discovered[12] that these alloys of the body-centered cubic Mo and W with the face-centered cubic Rh, Ir, and Pt form a hexagonal close-packed phase.

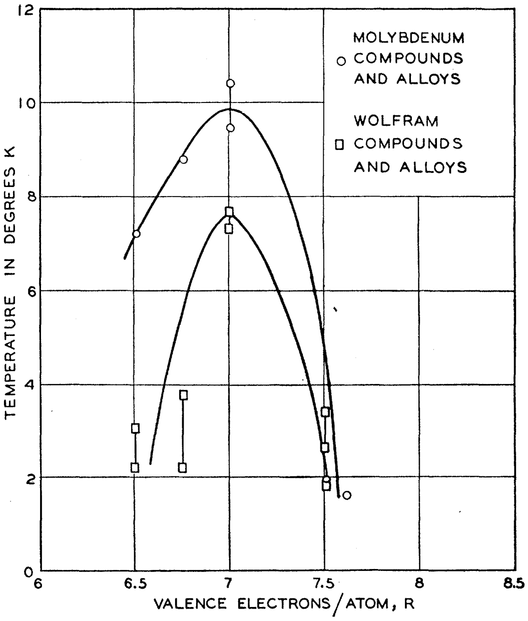

FIG. 4. Superconductivity of Zr-Rh alloys.

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[8] We were not able to find any literature on the Zr-Rh system.

[9] G. F. Hardy and J. K. Hulm, Phys. Rev. **93**, 1004 (1954).

[10] S. Geller (to be published).

[11] Matthias, Corenzwit, and Miller, Phys. Rev. **93**, 1415 (1954).

[12] E. Raub and P. Walter, Festschrift Heraeus 100 Jahre; Seite 124 E. Raub, Z. Metallkunde **45**, 23 (1954).

This seems to be an averaging which produces behavior like that in the elements which are intermediate in the periodic table. The large solubility of Mo in Ru enables us to simulate technetium quite closely both in crystal structure and superconducting transition temperature, thus strengthening our faith in the validity of this point of view.

An additional remark may be justified concerning these alloys: previously superconductivity had only been observed, apart from the elements, in either well defined compounds with very small homogeneity ranges or in solid solutions. We believe this is the first time that disordered alloys of nonsuperconducting elements have become superconducting and it may indicate that superconductivity is a long-range order effect rather than a short-range one.

CONCLUSION

There seems to be a rule linking the superconducting transition temperatures to the number of electrons outside filled shells, the valence electrons. At present we do not understand the theoretical implications of this. It seems, however, reasonable to suggest that a large number of valence electrons is quite favorable for the occurrence of superconductivity. Then why is there a dip for a value near six valence electrons? The answer to this may be roughly that this dip corresponds to the dip in paramagnetic susceptibility and in electronic specific heat for the same elements, which is commonly supposed to be due to a low effective number of free electrons.

My thanks to P. W. Anderson and J. K. Galt for their enlightening discussions.

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Paramagnetic Resonance Absorption in Praseodymium Trichloride*

JOHN H. ANDERSON† AND CLYDE A. HUTCHISON, JR.
Institute for Nuclear Studies and Department of Chemistry, University of Chicago, Chicago, Illinois

(Received August 5, 1954)

Paramagnetic resonance absorption in crystalline solutions of $PrCl_3$ in $LaCl_3$ has been investigated at a frequency of 2.32×10^{10} sec^{-1} and at the boiling point of He. The apparent g's, when H is parallel and perpendicular to the c axis have been found to be 1.79 and 3.98 respectively. The results have been discussed in terms of the known crystalline structure and Stark splittings.

INTRODUCTION

THE static magnetic and optical spectroscopic properties of crystalline praseodymium compounds have been successfully interpreted, at least in general outline, by Van Vleck,[1] Penney and Schlapp,[2] Kynch,[3] Spedding,[4] Hellwege and Hellwege,[5] and others. The ground state of the trivalent magnetic ion is the Hund state, $^3H_4$, for two $4f$ electrons[1] and Russell-Saunders coupling is obeyed approximately. The perturbations by the crystalline electric field play an important role in determining the temperature variation of the magnetic susceptibility and the details of the optical absorptions. The magnitudes of these perturbations are found generally to be considerably smaller than the spin-orbit coupling energies as is to be anticipated on the basis of the theoretical expectation that $4f$ orbitals lie deep inside the magnetic ion.

Recently Davis, Kip, and Malvano,[6] Altshuler, Kurenev, and Salikhov,[7] and Bleaney and Scovil[8] have observed magnetic resonances in compounds of praseodymium. The general theory of the paramagnetic resonance absorption in rare-earth salts has been given in great detail by Elliott and Stevens[9–12] although they have given only brief consideration to the specific case of Pr^{+3}.

In this paper experimental results of an investigation of paramagnetic resonance in a solution of $PrCl_3$ in $LaCl_3$ are presented and their interpretation discussed.

EXPERIMENTAL

Preparation of Crystals

The crystals employed for the measurements were right circular cylinders with their crystallographic c axes perpendicular to their cylinder axes. These were cut

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* This work received financial support from the U. S. Office of Naval Research and from the U. S. Atomic Energy Commission.

† U. S. Atomic Energy Commission Predoctoral Fellow, 1951–1953.

[1] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (The Oxford University Press, London, 1932).

[2] W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932).

[3] G. J. Kynch, Trans. Faraday Soc. **33**, 1402 (1937).

[4] F. H. Spedding, Phys. Rev. **58**, 255 (1940).

[5] A. M. Hellwege and K. H. Hellwege, Z. Physik **127**, 334 (1950).

[6] Davis, Kip, and Malvano, Alti. accad. mayl, Lincei **11**, 77

[7] Altshuler, Kurenev, and Salikhov, Doklady Akad. Nauk S.S.S.R. **70**, 201 (1950).

[8] B. Bleaney and H. E. D. Scovil, Phil. Mag. **43**, 999 (1952).

[9] K. W. H. Stevens, Proc. Phys. Soc. (London) **A65**, 209 (1952).

[10] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A215**, 437 (1952).

[11] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A218**, 553 (1953).

[12] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 387 (1953).