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Study of the Superconductivity of the Intermetallic Compounds U_6Mn, U_6Fe, U_6Co, and U_6Ni and Alloys Formed between Them*

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Alloys were prepared between the superconducting compounds U_6X, where X=Mn, Fe, Co, and Ni, to provide a continuous variation in the average electron concentration per atom of the X component of the compounds. Alloys between the X elements themselves are ferromagnetic, and a correlation is found between the superconducting transition temperature T_c of the pseudobinary $U_6(X_i, X_j)$ and the ferromagnetic saturation magnetization per atom σ_M of the pure-element alloy (X_i, X_j). T_c for the compound U_6Ni is reported as (0.41 ± 0.02) °K.

I. INTRODUCTION

SUPERCONDUCTIVITY in compounds of uranium was first discovered by Chandrasekhar and Hulm in 1958.[1] They found UCo, U_6Mn, U_6Fe, and U_6Co to be superconducting with transition temperatures T_c of 1.7, 2.3, 3.9, and 2.3°K, respectively. Until now these were the only known superconducting compounds of uranium.[2,3] Our present work has added only one more compound to the list: U_6Ni, with $T_c=0.41$°K. Thus it of interest that all the known superconducting compounds of uranium contain a magnetic element.

For the isomorphous group of compounds U_6Mn, U_6Fe, and U_6Co, Chandrasekhar and Hulm plotted T_c versus average valence electron concentration N_V of the compounds[1] and noted that T_c did not vary with N_V according to the empirical rule obeyed by most transition metals and compounds containing transition metals.[4] It has subsequently been noted that this departure from the simple "valence-electron rule" seems to be characteristic of compounds containing magnetic elements.[5] It seemed to us of interest to investigate this anomalous behavior of the U_6X compounds in more detail and to determine just how the superconducting transition temperature is related to the magnetism of the X metals. Since these compounds are isostructural with almost identical lattice constants,[6] it seemed reasonable that pseudobinaries such as $U_6(Fe_{0.3}, Co_{0.7})$ could be formed with ease. We therefore proposed to study the variation of T_c as z, the average valence electron concentration per atom of the X component in U_6X, was varied continuously across the periodic table from $z=7$ at Mn to $z=9$ at Co and possibly to $z=10$ at Ni. The compound U_6Ni is also isomorphous with U_6Mn, U_6Fe, and U_6Co,[6] and was studied by Chandrasekhar and Hulm but found to be nonsuperconducting down to 1.1°K.[1] Their work indicated, however, that the superconducting transition of U_6Ni could probably be reached by using a liquid-He^3 cryostat.[1]

II. SAMPLES AND EXPERIMENTAL TECHNIQUE

Samples were prepared by arc melting together the appropriate amounts of uranium metal and the alloying constituent metals X in a Zr-gettered helium-argon atmosphere. The electrode of the arc furnace was of tungsten, and melting was performed on a water-cooled copper hearth. Total sample masses were usually ~10 g. Losses in the arc furnace were negligible for all alloys not containing manganese. The relatively high vapor pressure of manganese at its melting point[7] caused milligram losses of manganese during melting, but these losses were either corrected for in estimating actual resultant sample compositions or compensated for, previous to melting, by adding a slight excess of Mn. All buttons were melted, turned over, and remelted ten times to promote sample homogeneity. The Mn, Fe, Co, and Ni used were of commercial high-grade purity. Several batches of uranium were used, all depleted of the isotope U^{235} and all of relatively high purity. No significant variation in results occurred upon switching batches of uranium, although slight differences in T_c could be correlated with small variations in the silicon impurity content. The latter never exceeded 30 ppm for any batch, however.

Since the compounds U_6X all form peritectically,[8] one might expect arc melting, with its subsequent relatively rapid quench, to be a poor method of preparation.

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[1] B. S. Chandrasekhar and J. K. Hulm, J. Phys. Chem. Solids **7**, 259 (1958).

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[3] B. T. Matthias, T. H. Geballe, and V. B. Compton, Rev. Mod. Phys. **35**, 1 (1963).

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[8] Max Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Co., New York, 1958), 2nd ed.

Early in our study, however, we found that only arc-melted samples gave strictly reproducible results. Attempts to anneal samples for various lengths of time and at several different temperatures below the peritectic decomposition temperature yielded, in general, no appreciable improvement in the sharpness of the superconducting transition curves and gave small unpredictable shifts (usually increases) in the value of T_c. Since our goal was to make a *comparison* of T_c across the periodic table, we chose to work only with arc-melted samples. There was one outstanding exception to this practice, involving the sample $U_6(Co_{0.1}, Ni_{0.9})$. This sample in the arc-melted condition yielded a very broad transition curve which appeared to contain two distinct superconducting transitions. A second arc-melted sample was prepared, which yielded a single, but still broad transition curve. This sample was then annealed for several hours below its assumed peritectic decomposition temperature and then cooled slowly. The resulting curve was sharper but still relatively broad. Only this one sample composition exhibited such behavior in the series studied. Possibly, quenching from the annealing temperature would have again improved the transition curve.[9] This was not tried.

The superconducting transition curves for the samples were determined in a liquid-He^4 cryostat when possible and in a liquid-He^3 cryostat[10] whenever there was need to reach temperatures below 1.1°K. Also, several curves accessible in the He^4 region were remeasured in the He^3 cryostat to crosscheck the thermometry appropriate to each cryostat. In both cryostats, which were of conventional design, a germanium resistor calibrated against bath vapor pressure acted as a thermometer. In the He^4 cryostat, superconductivity was detected by the high-frequency (~100 kc/sec) Schawlow-Devlin technique.[11] In the He^3 cryostat the lower frequency (~200 cps) bridge technique of Lindsay *et al.*[12] was used. The cross-check measurements revealed that the high-frequency measurements yielded broader transition curves than the low-frequency method. For our purposes the difference was not important, but such behavior does indicate that the samples were not completely homogeneous in composition and/or possessed nonuniform internal stresses, as might be expected from the method of preparation. Several samples were broken up and remeasured in both apparatus to establish that the effect was not significantly dependent upon the part of the button studied and was of over-all minor importance. Also, samples with the compositions U_6Mn, $U_6(Mn_{0.5}, Fe_{0.5})$, U_6Fe, $U_6(Fe_{0.5}, Co_{0.5})$, U_6Co, and $U_6(Mn_{0.5}, Co_{0.5})$ were examined by metallographic and x-ray diffraction methods. Electron microprobe scans were also employed. These investigations revealed that the buttons not containing manganese were single phase and quite homogeneous, though sometimes strained. Those buttons which did contain manganese, however, possessed a less homogeneous U_6X matrix as well as small inclusions of α uranium. It would seem that the peculiar metallurgical nature of manganese[13–15] exhibits itself even in the U_6X series. It does not appear in the following, however, that this peculiarity detracts from the general, over-all behavior of the U_6X system.

Because of the relatively low vapor pressure of liquid He^3 below ~0.5°K and the consequent sensitivity to hydrostatic head and pumping effects of temperature calibrations based simply on bath vapor pressure, an attempt was made to better establish the temperature scale in this region by other means. Our primary concern was to accurately determine the superconducting transition temperature of the compound U_6Ni. A compacted cylinder of powdered cerium magnesium nitrate was placed inside the sample coil and its effective paramagnetic susceptibility at 200 cps measured down to the lowest attainable temperature. This yielded a calibration for the germanium resistance thermometer at low temperatures which agreed quite well with a straight-line extrapolation to low pressures of a plot of the logarithm of the resistance of the thermometer versus the logarithm of the bath pressure determined at higher pressures. Using this calibration T_c (midpoint) for U_6Ni was established as 0.392°K (+0.010, −0.000°K). As a further check, the superconducting transition temperature of an arc-melted bead of ruthenium was determined to be 0.443°K, which is slightly below typical accepted values.[16] This same bead was kindly remeasured for us by Geballe and Hull of Bell Telephone Laboratories, who found $T_c = 0.480°K$, a more reasonable value. It would seem that perfect thermal equilibrium was not obtained in the He^3 cryostat, although the possible reason for this or other sources of error is not apparent. The uncertainty in our result may be expressed as $T_c(U_6Ni) = (0.41 \pm 0.02)$ °K.

III. EXPERIMENTAL RESULTS

The principal results of our investigation are displayed in Fig. 1, which shows the dependence of T_c upon alloy composition as the X component of the superconducting alloys U_6X is varied continuously from $X = Mn$ to $X = Ni$. The transition curve widths are indicated in the figure by denoting the spread of the transition from the temperature corresponding to 10%

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[9] G. Katz and A. J. Jacobs, Trans. Met. Soc. AIME **221**, 1273 (1961).

[10] The liquid-He^3 measurements were performed in conjunction with J. D. G. Lindsay and R. W. White of Los Alamos in a cryostat of their design and construction. We are grateful to these gentlemen for the privilege of working in their laboratory and for their help in making the measurements.

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[12] J. D. G. Lindsay, R. W. White, and R. D. Fowler, Cryogenics **6**, 213 (1966).

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[16] B. W. Roberts, Ref. 2, p. 159; T. H. Geballe and B. T. Matthias, IBM J. Res. Develop. **6**, 256 (1962); D. K. Finnemore and D. E. Mapother, Phys. Rev. Letters **9**, 288 (1962).

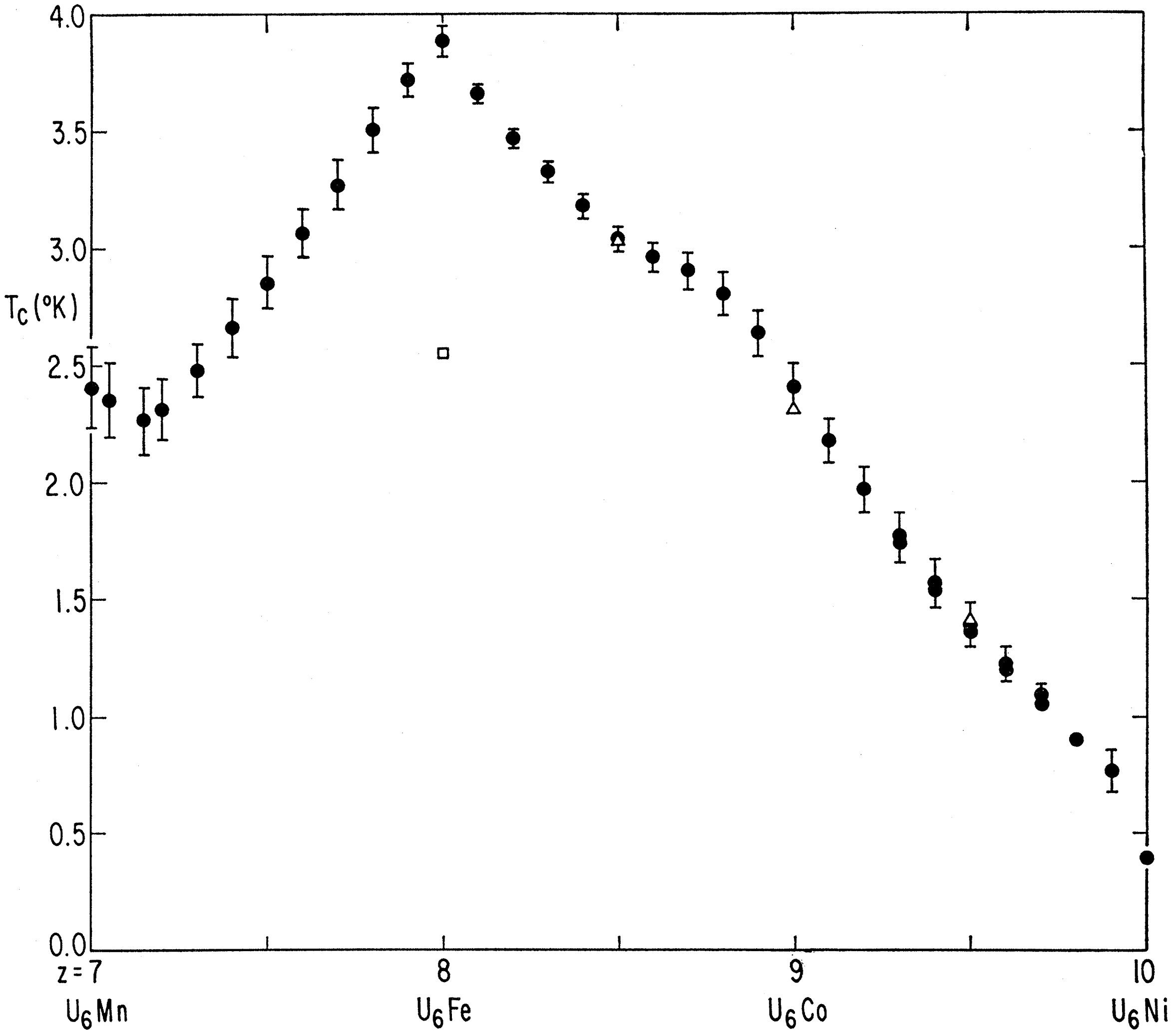

FIG. 1. Superconducting transition temperatures of alloys formed between the U_6X compounds, where X=Mn, Fe, Co, Ni, as a function of z, the average number of valence electrons ($3d+4s$ electrons) per atom of the X component. Midpoints of transition curves are plotted, with vertical bars denoting the widths of the curves, as described in the text. The square point represents a U_6(Mn, Co) alloy, and the three triangular points represent U_6(Fe, Ni) alloys. All other points denote alloys formed between X "nearest neighbors." Curve widths are not shown for the three U_6(Fe, Ni) points. These widths were approximately twice those of the corresponding "nearest-neighbor" points. The vertical bars for the U_6(Mn, Co) alloy, for U_6Ni, and for $U_6(Co_{0.2}, Ni_{0.8})$ are of small extent and lie within their respective data points. The double points between U_6Co and U_6Ni are the results of measurements made in separate cryostats. The lower points of each set were determined in a liquid-helium-three cryostat. Their corresponding curve widths are not indicated.

of the total superconducting signal to that corresponding to 90% of the total signal. In those cases where runs were made in both the He^4 and He^3 cryostats, only the midpoint for the curve determined in the He^3 cryostat is indicated. As mentioned above, the He^3-determined curves (low-frequency curves) had narrower widths than the He^4-determined curves. Also, the midpoints of the differently determined curves did not coincide. This was more a result of the differing shape and width of the frequency-dependent transitions than of discrepancies in comparative thermometry. In spite of these differences, the crossover from the He^4 measurements to the He^3 measurements is quite smooth. The abnormal width of the transition for the $U_6(Co_{0.1}, Ni_{0.9})$ sample is evident in the figure.

Almost all of Fig. 1 is made up from X elements which are neighbors in the periodic table (exceptions will be noted below). Thus, because of our failure to produce single-phase, homogeneous samples whenever manganese was a sample constituent, that portion of Fig. 1 to the left of U_6Fe is necessarily subject to some question. In particular, the minimum in the curve at the composition $U_6(Mn_{0.85}, Fe_{0.15})$ might be thought to arise as a result of some fault in the sample preparation. This does not seem likely, however; certain characteristics of the minimum suggest that it is real. There is an almost monotonic decrease in curve width as one passes from U_6Mn to U_6Fe, thus indicating no sharp break in sample characteristics at any point in between. Also, our transition temperature for U_6Mn agrees reas-

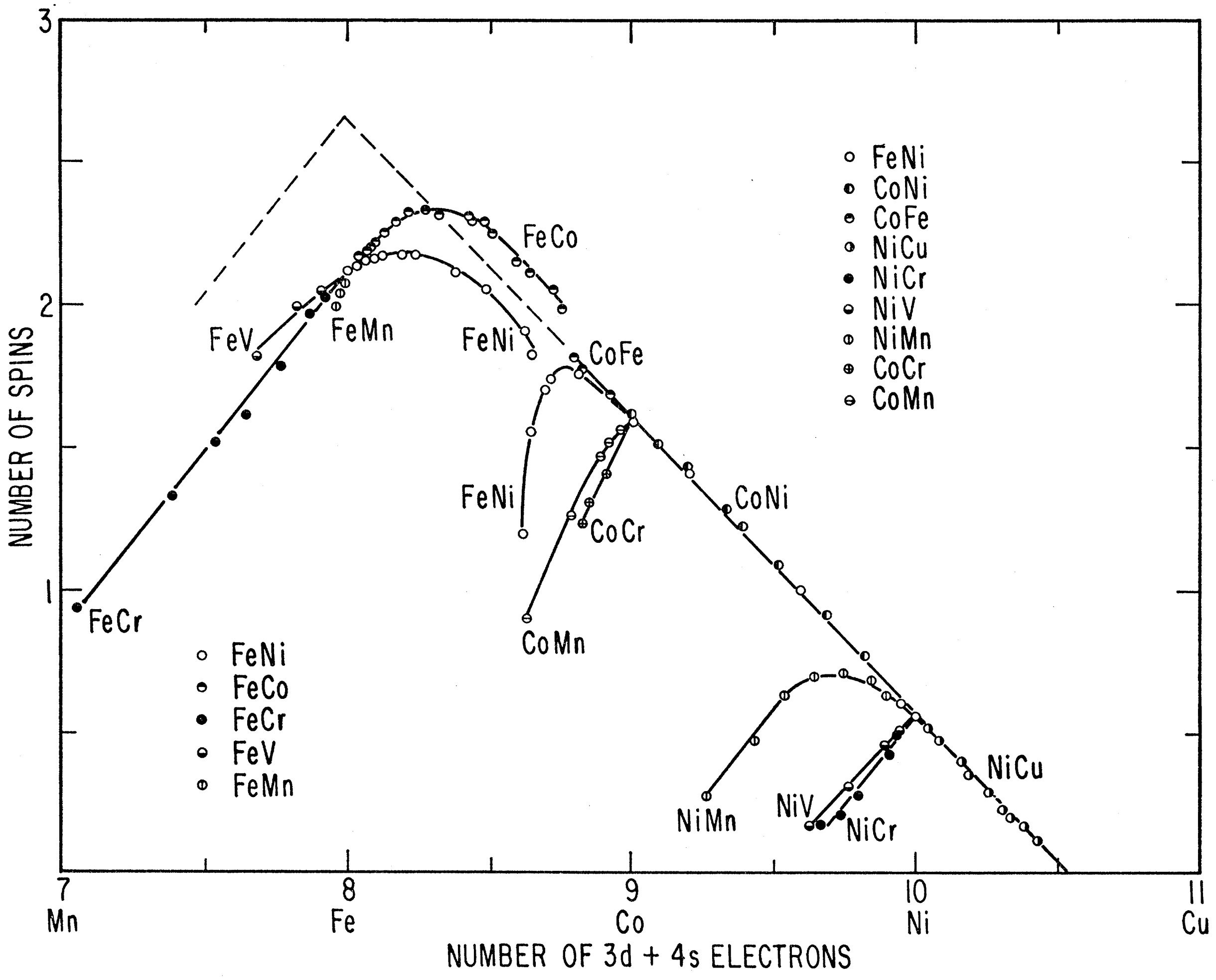

FIG. 2. The "Slater-Pauling" curve of saturation magnetization versus electron concentration among the ferromagnetic iron-group alloys, compiled here from the data of Crangle and Hallam (see Ref. 19). The average number of unbalanced electron spins per atom n_S is plotted against z, the average number of $(3d+4s)$ electrons per atom in the alloy. The breaks in the smooth Fe–Co and Fe–Ni curves are due to phase changes in these systems. On the iron-rich side of the breaks, the alloys have the bcc structure of iron. On the Co- and Ni-rich sides, they have the fcc structure of Ni and cubic Co. The dashed line is an "idealization" of the curve described in the text.

onably well with that of Chandrasekhar and Hulm,[1] implying that our preparation problems could not have been too serious, and our T_c for U_6Fe also agrees with that of Chandrasekhar and Hulm.[1] Neither near U_6Mn nor U_6Fe in Fig. 1, however, do the intermediate points suggest that there should necessarily be a monotonic increase in T_c as one moves from U_6Mn to U_6Fe. Because of the uncertain metallurgy on the Mn end of Fig. 1, however, it seems wise to consider this portion of the curve as depicting only the general behavior of the system in this region.

Study of the behavior of T_c on the Co and Ni side of U_6Fe should be more rewarding. Here the samples were all single phase, permitting an unambiguous study of the dependence of T_c upon the average valence-electron concentration z of the X component in the compound (valence electrons$\equiv 3d+4s$ electrons). That the three compounds U_6Fe, U_6Co, and U_6Ni are truly isomorphous and that T_c in this composition range depends only on z is demonstrated by the fact that three samples made from the non-neighbors Fe and Ni had superconducting transition temperatures almost identical to those of samples made from the neighbors Fe–Co and Co–Ni which had identical average $(3d+4s)$ electron numbers. Thus the transition temperatures of $U_6(Fe_{0.75}, Ni_{0.25})$, $U_6(Fe_{0.50}, Ni_{0.50})$, and $U_6(Fe_{0.25}, Ni_{0.75})$ were very nearly equal to those of $U_6(Fe_{0.50}, Co_{0.50})$, U_6Co, and $U_6(Co_{0.50}, Ni_{0.50})$, respectively. These three "next-nearest-neighbor" sample results are indicated by triangles in Fig. 1.

Both our results and those of Chandrasekhar and Hulm[1] indicate that U_6Mn and U_6Co have almost identical superconducting transition temperatures. Our value of $T_c=2.4$°K (midpoint of transition curve) differs slightly from that reported by these authors, who found $T_c=2.3$°K. This difference is very likely due to the difference in sample preparation. Our samples were arc melted, while those of Chandrasekhar and Hulm were furnace melted and cooled slowly. There is no disagreement in the case of U_6Fe.

IV. DISCUSSION OF RESULTS

One notices the similarity between Fig. 1 and the "Slater-Pauling" curve[17,18] of Fig. 2 where, in essence, the saturation magnetization per atom σ_M of the ferromagnetic alloys among the iron-group elements is plotted against the average number of $(3d+4s)$ electrons z. There is a definite correlation between T_c and σ_M, and the pattern of superconductivity in the U_6X series would seem to warrant discussion in terms of the correlation.

A. Slater-Pauling Curve

Our Fig. 2 is derived from recent plots of saturation magnetization due to Crangle and Hallam,[19] who have converted σ_M to n_S, the number of unbalanced electron spins per atom. The number n_S differs slightly from σ_M because of the apparent incomplete quenching of the atomic orbital angular momentum in Fe, Co, and Ni and their alloys.[20] The relation between n_S and σ_M is $n_S=(2/g)\sigma_M$, where g is the spectroscopic splitting factor, and σ_M is expressed in Bohr magnetons. It can be shown that $g=2(1+M_0/M_s)$, where M_0 and M_s are the magnetizations associated with orbital and spin angular momentum, respectively. For Fe, Co, and Ni, the g values are 2.09, 2.17, and 2.19, respectively.[20] Thus the magnetization of these elements (and their alloys) is primarily of spin origin. The values of g are determined by magnetic resonance experiments and, in the alloys, vary continuously between the values appropriate to the individual elements.[21]

Much work has gone into the development of theories of the electronic properties of transition metals and their alloys. The "Slater-Pauling" curve depicts one of the essential properties to be explained, namely the variation with electron concentration of the saturation moment of ferromagnetic alloys formed between members of the first row of the transition metals. Slater[17] and Pauling[18] were two of the first to address themselves to this problem, and we discuss their approaches briefly and in a simplified manner below to provide a basis for considering how superconductivity in the U_6X system might be related to the ferromagnetism of the X alloys. Comprehensive discussions of the status of the theory of magnetism in the transition elements may be found in Refs. 22–25 The general approach of the band theory of magnetism is given in Refs. 26–28, among other sources.

B. Band Theory

In the theory of Slater,[17] the d electrons of the transition metals are considered to be itinerant electrons which can move throughout the lattice and which occupy states whose energies lie within a continuous, unfilled d band. Ferromagnetism results in the $3d$ elements when there is a net spin alignment among the $3d$ electrons. This occurs as a result of an intra-atomic exchange interaction between two d electrons when they are simultaneously near the same atomic site. One may regard the band as being divided into spin-up and spin-down half-bands and the exchange interaction as an effective internal magnetic field.[29] This field raises the energies of the spin-up states relative to those of the spin-down states by an amount equal to the exchange energy, causing a net transfer of electrons from spin-up to spin-down states.[29]

The exchange forces are usually sufficiently strong so as to completely fill all the empty states in the spin-down (positive-moment) half-band, and the resulting moment per atom is equal to the number of holes per atom in the spin-up band multiplied by μ_B, the Bohr magneton. Thus Slater suggests that Ni and Co have ~0.6 and ~1.6 holes per atom, respectively (see Fig. 2). The average moment of alloys formed between Ni and Co may be understood by assuming that these elements share common bands and that, as one moves from pure Co to pure Ni, say, the substitution of Ni atoms for Co atoms reduces the net moment of the alloy by one Bohr magneton per Ni atom added, as a consequence of Ni's contributing one more $3d$ electron per atom than Co to the partially filled $3d$ spin-up half-band of the alloy. The number of $4s$ electrons per atom (~0.6) is assumed to remain approximately constant. Similarly, the addition of Cu (full d band) to Ni drives the saturation moment of Ni to zero at ~60% Cu (Fig. 2).

This simple picture becomes more complicated as one moves from Co to Fe because the moment does not increase continuously from ~1.6 μ_B to ~2.6 μ_B per atom, as might be anticipated, but rather peaks out at ~(70%Fe, 30%Co) with a value of ~2.4 μ_B/atom and then falls to ~2.2 μ_B/atom at Fe (Fig. 2). It is thought that the exchange interaction in Fe is not strong enough to attain "saturation," that is, completely fill the spin-down half-band.[30] Accordingly, there might be ~0.2 holes per atom in the spin-down half-band and only ~2.4 holes per atom in the spin-up half-band

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[28] D. H. Martin, *Magnetism in Solids* (Iliffe Books Ltd., London, 1967), p. 227.

[29] W. Schockley, Bell System Tech. J. **18**, 645 (1939), p. 704.

[30] W. Hume-Rothery, Ref. 13, p. 252; Edmund C. Stoner, Ref. 22, p. 90.

of Fe, if the number of *s* electrons per atom were again ~0.6.[31]

C. Pauling Theory

Pauling[18] has offered an alternative explanation of the magnetism in Fig. 2, which is expressed in terms of atomic orbitals.[32,33] Some of the *d*-electron orbitals combine with the *s*-electron orbitals to form hybridized bonding orbitals and thus provide metallic cohesion. Electrons in these *bonding* orbitals are paired with similar electrons on adjacent atoms and are nonmagnetic. The remaining *d*-electron orbitals are localized, unhybridized *atomic* orbitals, and electrons occupying these orbitals are assumed to distribute themselves in such a manner as to create the maximum spin imbalance possible, consistent with the Pauli exclusion principle (Hund's rule). Thus the *atomic* orbitals are the source of ferromagnetism.

In Ni, all the *atomic* orbitals of each atom are assumed to be occupied by an electron of positive moment, but ~0.6 *atomic* orbitals per atom have negative-moment vacancies. In Co there are ~1.6 negative-moment vacancies per atom, and one might expect ~2.6 such vacancies per atom in Fe if there were at least that number of *atomic* orbitals available. However, because the saturation magnetization curve bends over before Fe is reached and Fe's moment is only ~2.2 μ_B per atom, Pauling concludes that there are in fact only 2.4 *atomic* orbitals available and that in Fe there are 0.2 positive-moment vacancies as well as 2.4 negative-moment vacancies, the moment arising solely from the 2.2 positive-moment electrons.

D. "Idealized" Iron

Both the Slater[17] and the Pauling[18] proposals derive most of their quantitative aspects from the behavior of the Co, Ni, and Cu alloys in Fig. 2, and, as indicated above, the simple pattern in each scheme of raising the moment by one Bohr magneton per electron removed in passing from (60% Cu, 40% Ni) to Ni to Co would ascribe a moment of ~2.6 μ_B per atom to Fe. To account for the observed value of ~2.2 μ_B per atom for Fe, the band theory suggests that the moment in Fe is not saturated, and Pauling limits the number of available magnetic orbitals to less than 2.6. Let us assume that iron can, in principle, maintain the "extrapolated" moment of ~2.6 μ_B per atom on its unfilled *d* shell and does not do so in its crystalline form only for reasons peculiar to, say, the details of its band structure and the strength of the exchange forces. Accordingly we have sketched a dotted line onto Fig. 2 representing an idealized behavior for Fe alloys at high Fe concentrations and pure Fe itself. There is then an almost one-to-one correlation between T_c in Fig. 1 and n_S in Fig. 2. The ratio of the transition temperatures for U_6Fe and U_6Co ($3.9/2.4=1.6$) is the same as the ratio of the saturation spin moments for (idealized) Fe and Co ($2.6/1.6=1.6$). The agreement is less satisfactory when U_6Ni is similarly used for comparison, but this is due in part to the sudden dip in T_c just before U_6Ni in Fig. 1, which is not characteristic of the rest of the curve.

In both curves it is possible to essentially duplicate Fe–Co and Co–Ni results by adjusting Fe–Ni combinations to yield the equivalent number of $(3d+4s)$ electrons, as mentioned above for the superconducting case and as indicated in Fig. 2 for the ferromagnetic case.

If our present assumption is correct, that $T_c(U_6X)$ is roughly proportional to $n_S(X)$ and thus probably not simply a function of N_V, the average number of valence electrons per atom in the compound, or of z, the average number of $(3d+4s)$ electrons in the X component, as was suggested before, then a compound with the composition $U_6(Mn_{0.5}, Co_{0.5})$ should have a transition temperature approximately the same as that of U_6Mn or U_6Co rather than that of U_6Fe, which has the same numbers N_V and z. This follows because in Fig. 1 U_6Mn and U_6Co have almost identical transition temperatures, and correspondingly, in our idealized Fig. 2, Mn and Co have approximately the same moments. [Pure Mn, of course, is not actually ferromagnetic,[34] and the effective moment that would be ascribed to it here is that of a $(Cr_{0.5}, Fe_{0.5})$ alloy, as indicated in Fig. 2].

The transition temperature of $U_6(Mn_{0.5}, Co_{0.5})$ was measured and found to be little different from that of U_6Mn and U_6Co, as indicated by the one lone square point in Fig. 1 at $z=8$. In spite of the previously mentioned metallurgical difficulties with samples containing manganese, the transition curve for this composition was quite sharp. It would thus seem that this measurement provides evidence that the transition temperatures of the U_6X series are not a function of average valence electron numbers *per se*, but rather a function of the saturation spin moment of the X alloys.

It would have been interesting to continue our U_6X studies beyond U_6Mn on the left and U_6Ni on the right by diluting the Mn with Cr and the Ni with Cu. One sample was made with 10% Cr, 90% Mn. The transition temperature was almost identical to that of U_6Mn, probably indicating a good alloy was not formed. This is consistent with the fact that the compound U_6Cr does not exist.[8,35] No attempt was made to add Cu to Ni in U_6Ni. The transition temperature of U_6Ni proved to be lower than expected and near the low-temperature limit of our cryostat, and we were not particularly en-

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[31] B. R. Coles, Ref. 23, p. 177, suggests that this number is actually ~0.9.

[32] Further discussion of the Pauling theory may be found in the following: R. E. Rundle, *Intermetallic Compounds*, edited by J. H. Westbrook (John Wiley & Sons, Inc., New York, 1967), p. 17, see p. 28; F. Seitz, Ref. 26, p. 429; W. Hume-Rothery and G. V. Raynor, *The Structure of Metals and Alloys* (The Institute of Metals, London, 1962), p. 81; see also Ref. 13.

[33] Developments of the original Pauling hypothesis may be found in the following papers: L. Pauling, Proc. Roy. Soc. (London) **A196**, 343 (1949); Proc. Natl. Acad. Sci. U.S. **39**, 551 (1953); see also Ref. 15, p. 393.

[34] See for example, Ref. 27, p. 438; Ref. 28, p. 264.

[35] P. Gordon, thesis, MIT, 1952, published as USAEC Report AECU-1833, 1952.

couraged by the insolubility of Cu in U,[8] but such a study might prove of interest.

In reference to our idealized Slater-Pauling curve, which attributes a moment of ~2.6 μ_B per atom to Fe rather than the observed ~2.2 μ_B, there are indications that iron does, on occasion, exhibit moments larger than ~2.2 μ_B per atom. Shull and Yamada[36] suggest on the basis of neutron diffraction measurements that the *s* electrons in pure (bcc) iron are polarized and contribute -0.2 μ_B per atom to the net moment. Thus the *d*-shell moment would be ~2.4 μ_B per atom. Other neutron diffraction studies by Collins and Forsyth[37] on Fe–Ni alloys show that the moment on the iron lattice sites increases to ~2.5–2.7 μ_B as Ni is added to Fe to bring the magnetization up to the Fe–Ni peak in Fig. 2. Similarly in Fe–Co alloys, the Fe moment rises to a value of ~3.0–3.2 μ_B per atom.[37] The moment on the iron site in the fcc nickel-rich Fe–Ni alloys is ~2.6–2.8 μ_B per atom[37] as would be expected from Fig. 2.

Weiss[38] has suggested that the latter moment (~2.7 μ_B per atom) is actually characteristic of a ferromagnetic electronic state in the high-temperature fcc phase of iron. This state is normally not the ground state for the iron atoms, but becomes so in the ferromagnetic fcc alloys of iron with Pt and Pd,[38,39] which are not themselves ferromagnetic. Mott[25] shows why the suspected different shape of the density-of-states curve for fcc—as opposed to bcc—transition metals would attribute to fcc iron the indicated saturated moment.

Cadeville and Daniel[40] have recently measured the saturation magnetization of several transition-metal borides and alloys formed between them. The moments found for the monoborides and semiborides of Fe and Co can be explained by assuming boron adds ~1.7 electrons per atom to the *d* band of Fe or Co, as the authors suggest,[40] and that these *d* bands contain ~2.7 and ~1.7 holes per atom, respectively, prior to the addition of the boron.

E. Occurrence of Superconductivity

In addition to the "point-by-point" correlation between the magnetism of the *X* elements and the superconductivity of the U_6X compounds and alloys suggested by the similarities of Fig. 1 and Fig. 2, other evidence indicates that the *occurrence* of superconductivity in compounds of uranium seems dependent upon the presence of a magnetic element,[41] as has already been mentioned. In this context, manganese is regarded as magnetic by virtue of its antiferromagnetism.[34] Besides the U_6X compounds, only UCo is superconducting.[2,3] UMn and UFe do not exist,[6,8] and there is doubt concerning the existence of UNi.[6,8] A sample with the composition UNi was found to be normal to 1.04°K.[1]

The dependence upon the presence of a magnetic element was noted by Chandrasekhar and Hulm.[1] The compounds UC and UN had been studied and found to be nonsuperconducting down to 1.2°K,[42] although NbN, which is isomorphous with them,[1] has a transition temperature of 15.6°K.[2] Chandrasekhar and Hulm measured U_2Ti, U_3Si, and UAl_2.[1] These were all also normal to 1.1°K, although the first two compounds have average valence electron numbers favorable for the occurrence of superconductivity (~5 and ~7, respectively[4]), and the last compound has the cubic Laves-phase structure (*C*15),[43] which is often favorable for superconductivity.[3] On the other hand, the superconducting U_6X compounds do not have particularly favorable average numbers of valence electrons[1] or structure,[3] and the superconducting compound UCo has a generally unfavorable average number of valence electrons (7.5)[44] and possesses a distorted CsCl structure,[6] which would seem to be definitely unfavorable for superconductivity.[44]

The compounds UOs_2 and UIr_2 have the cubic Laves-phase structure,[3] and UOs_2 has the same average number of valence electrons as $ThIr_2$, which also has this structure and is superconducting at 6.5°K.[3] Neither uranium compound is superconducting to ~0.35°K.[3] (In this category, however, $ThRu_2$ is superconducting but $ThOs_2$ is not,[3] although they should be essentially equivalent.)

Both Mo and W, which occupy the same column in the periodic table as uranium, form several superconducting compounds each with Re,[2] but URe_2 is nonsuperconducting to 1°K,[3] although it has a distorted hexagonal Laves-phase structure (*C*14),[45] and the *C*14 structure is considered a favorable one.[3]

The compound USi_2 has a favorable average number of valence electrons[4] (4.8) and is of the same structure as $ThSi_2$, which is superconducting at 3.2°K,[3] but USi_2 is nonsuperconducting to 0.35°K.[3] The structure of UCu_5 is closely related to the *C*15 Laves-phase structure,[6] but UCu_5 is not superconducting above 1.0°K.[3] UIn_3, UGa_3, UGe_3, UIr_3, URh_3, and URu_3 are not superconducting down to 1°K[2] (UGe_3 has been checked to 0.35°K[3]). All have the cubic Cu_3Au structure,[2] which is not particularly favorable for superconductivity, except that La_3In has a T_c of 10.4°K.[44] UIn_3 and UGa_3 have a favorable average valence electron number (5). Superconducting compounds with Rh and Ru are formed by each of Mo, W, and Th.[2] Chromium, which occupies

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[36] C. G. Shull and Y. Yamada, J. Phys. Soc. Japan **17**, Suppl. B-III, 1 (1962); C. G. Shull, Ref. 14, p. 69.

[37] M. F. Collins and J. B. Forsyth, Phil. Mag. **8**, 401 (1963).

[38] R. J. Weiss, Proc. Phys. Soc. (London) **82**, 281 (1963); Phil. Mag. **9**, 361 (1964).

[39] J. Crangle, Phil. Mag. **5**, 335 (1960); J. Crangle and W. R. Scott, J. Appl. Phys. **36**, 921 (1965).

[40] M. C. Cadeville and E. Daniel, J. Phys. (Paris) **27**, 449 (1966).

[41] The limited range of occurrence of the structure U_6X in the periodic system is also indicative of a particular relationship between uranium and these elements.

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

[43] W. Hume-Rothery and G. V. Raynor, Ref. 32, p. 228.

[44] B. W. Roberts, *Intermetallic Compounds*, edited by J. H. Westbrook (John Wiley & Sons, Inc., New York, 1967), p. 581.

[45] Rodney P. Elliot, *Constitution of Binary Alloys, First Supplement* (McGraw-Hill Book Co., New York, 1965).

the same column in the periodic table as uranium but is itself magnetic and not superconducting, forms its only superconducting compounds with Ir and Ru.[2]

The small number of superconducting compounds formed by chromium and uranium distinguish these elements from the other two in the same column, Mo and W, which form many. The similarity between Cr and U may extend to the low-temperature behavior of uranium.[46] Uranium (α-U)[47] becomes superconducting (above 0.1°K, anyway) only if it is prevented from going through an apparent electronic phase change at $\sim$43°K.[48] This phase transition temperature may be lowered, evidently, by the application of pressure,[46] just as in the case of the Néel temperature of chromium,[46,49] and under 10 kbar of pressure uranium is superconducting at 2°K.[50]

The compound U_6Mn is still the only known superconducting compound containing manganese.[2] Only one superconducting compound containing iron exists other than U_6Fe.[2] Thus, while superconductivity in uranium compounds depends upon the presence of a magnetic element such as Mn or Fe, the converse has a tendency to be true, also. This is probably related to the $5f$-$6d$ character of uranium,[51] which is thought to be responsible[50,52] for the low-temperature behavior just described. The exact nature of the interplay between the magnetic $3d$ elements and the uranium which so favors superconductivity is not immediately obvious, however, and will be considered further below.

Another interesting series of superconducting compounds containing X=Fe, Co, and Ni is the Th_7X_3 group.[53] Here the transition temperatures are all roughly the same (1.86, 1.83, and 1.98°K for X=Fe, Co, and Ni, respectively[5]), indicating that the correlation we have found between the saturation magnetization of the X alloys and the transition temperature of the U_6X series of alloys is peculiar to that system. There is, of course, no $5f$ character in Th,[51,54] and this is surely of significance, as indicated above, but a study of the crystal structures of the U_6X[6] and the Th_7X_3[53] series reveals that the dominant factor in the difference in behavior of T_c is probably the lack of interaction between the $3d$ shells of the transition-metal atoms in the Th_7X_3 series. In the U_6X structure (tetragonal, 28 atoms per unit cell[6]) the X atoms are tied together in linear chains along the c_0 axis and thus interact with each other within the chains, each X atom having two X-atom nearest neighbors,[6] while in the Th_7X_3 structure (hexagonal, 20 atoms per unit cell[53]) the X atoms have only Th nearest neighbors[53] and do not interact with each other. This makes understandable the major role played by the X elements in the superconductivity of the U_6X alloys (as evidenced by the similarity of T_c in Fig. 1 to n_S in the Slater-Pauling curve), as opposed to the situation in the Th_7X_3 series, where the transition temperatures are almost independent of the magnetic X element used[5] and are little removed from that of pure Th[2] or those of Th_7X_3 compounds with nonmagnetic X elements[2,3] (X=Rh, Ir, Os).

Other examples illustrate the relationship between the superconductivity of the U_6X compounds and the magnetic nature of the X elements and possibly uranium itself. The compounds UFe_2 and UMn_2, which are dominated by their respective transition-metal constituents, are ferromagnetic and antiferromagnetic, respectively, at low temperatures.[55] Likewise the compound Np_6Fe,[56] wherein Np probably possesses strong $5f$ character,[51,57] is not superconducting down to 0.5°K.[56] Thus in between that region where the $3d$ and/or $5f$ magnetic character is too weak (Th_7Fe_3) and the region where it is too strong (UFe_2, Np_6Fe), there is apparently a region wherein its presence enhances the occurrence of superconductivity (U_6Fe).

F. Theoretical Discussions of Superconductivity

To find a theoretical basis for the pattern of superconductivity in the U_6X system, we shall examine the BCS theory in its usual form and also some treatments which might focus more upon the apparent magnetic character of the compounds.

In the BCS theory of superconductivity,[58] the superconducting transition temperature is given by the relation

$$kT_c \cong 1.14\hbar\omega_{\text{av}} \exp[-1/N(0)V]. \quad (1)$$

Here ω_{av} is an average lattice phonon frequency (proportional to the Debye frequency[59] and hence to Θ_D), $N(0)$ is the electronic density of states at the Fermi surface, and V is a parameter measuring the strength of the attractive interaction between the members of pairs of conduction electrons which is responsible for condensation into the superconducting state. This inter-

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[46] W. E. Gardner and T. F. Smith, Phys Rev. **154,** 309 (1967).

[47] The high-temperature β and γ phases of uranium may be stabilized at room temperature only by alloying and quenching. They then become superconducting at $\sim$0.8°K and $\sim$2°K, respectively [see, B. T. Matthias *et al.*, Science **151,** 985 (1966); and Ref. 1].

[48] E. S. Fisher and H. J. McSkimin, Phys. Rev. **124,** 67 (1961); C. S. Barrett, M. H. Mueller, and R. L. Hitterman, *ibid.* **129,** 625 (1963).

[49] Tadayasu Mitsui and C. T. Tomizuka, Phys. Rev. **137,** A564 (1965).

[50] James C. Ho, Norman E. Phillips, and T. F. Smith, Phys. Rev. Letters **17,** 694 (1966).

[51] B. T. Matthias, W. H. Zachariasen, G. W. Webb, and J. J. Engelhardt, Phys. Rev. Letters **18,** 781 (1967).

[52] T. H. Geballe, B. T. Matthias, K. Andres, E. S. Fisher, T. F. Smith, and W. H. Zachariasen, Science **152,** 755 (1966).

[53] John V. Florio, N. C. Baenziger, and R. E. Rundle, Acta Cryst. **9,** 367 (1956).

[54] J. E. Gordon, H. Montgomery, R. J. Noer, G. R. Pickett, and R. Tobón, Phys. Rev. **152,** 432 (1966).

[55] J. S. Kouvel, Ref. 44, p. 529.

[56] The existence of this compound has not been reported in the literature, to our knowledge. However, Pu_6Fe is isomorphous with U_6Fe and completely miscible with it (F. H. Elliger, Ref. 57, p. 281). The existence of Np_6Fe thus seems highly likely. An arc-melted sample with the composition Np_6Fe was found to remain normal down to 0.5°K (present investigation).

[57] W. H. Zachariasen, *The Metal Plutonium*, edited by A. S. Coffinberry and W. N. Miner (University of Chicago Press, Chicago, 1961), p. 99.

[58] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108,** 1175 (1957).

[59] David Pines, Phys. Rev. **109,** 280 (1958).

action is an indirect one which occurs when one conduction electron, in moving through the crystal, deforms the lattice and creates a phonon which is absorbed by a second electron.[60] The electrons have equal and opposite momenta and spins, and the phonon is a virtual phonon, being created and absorbed within the brief time $\Delta t \sim \hbar/\Delta E$, where ΔE is the net energy change in the interaction.[60]

The parameter $N(0)$ is most easily discussed in terms of the band model, of course. We have seen above how the band theory accounts for the magnetism of the X metals and alloys as portrayed in the Slater-Pauling curve. A common $3d$ band is assumed for Fe, Co, Ni, and Cu, and the saturation magnetization is reduced as one moves from Fe to Ni and on to Cu by the filling of holes in the negative-moment sub-band.[61] Since the added electrons fill states at the Fermi level, it is apparent from the linearity of the Slater-Pauling curve[61] that the magnetic behavior can be described quite well by the assumption that $N(0)$ is constant in the range of interest for these alloys. It is, of course, not possible to determine from this just how the density of states at the Fermi surface of the U_6X alloys would vary with X composition, but it would not be unreasonable to assume that $N(0)$ remained fairly constant in moving from U_6Fe to U_6Co to U_6Ni in the same manner as for Fe, Co, and Ni themselves.[61] The departures from linearity in Fig. 1 might well reflect the nonconstancy of $N(0)$, but the general features of Fig. 1 are probably not explained by the dependence in Eq. (1) of T_c upon $N(0)$.

If one assumes a Pauli-type band paramagnetism for the U_6X alloys, the values of their magnetic susceptibilities support the assumption that $N(0)$ is roughly constant, for the susceptibilities (χ) of U_6(Fe, Co, and Ni) are all the same (at room temperature) to within $\sim 4\%$ of each other, [35,62] and one would expect χ to be proportional to $N(0)$.[29] The values of χ are $(1.97, 1.95, \text{and } 2.03)\times 10^{-6}$ emu per g, respectively.[35,62] The value for U_6Mn is 2.11×10^{-6} emu per g.[63] For comparison, we may consider the susceptibility of the β phase of uranium, which is tetragonal with 30 atoms per unit cell[64] and thus structurally more similar to the U_6X compounds than the α or γ phases, which are orthorhombic and cubic, respectively.[64] For β-U, χ is temperature-independent and equal to $\sim 2.0\times 10^{-6}$ emu per g.[35,64] Since, by weight, the U_6X compounds are $\sim 96\%$ uranium, their gram susceptibilities would seem to indicate that their electronic densities of states at the Fermi surface are not significantly dependent upon the presence of the X component.The product $N(0)V$ in Eq. (1) would have to change by a factor of ~ 2 to bring about the observed factor of 10 change in T_c between U_6Fe and U_6Ni.

The paramagnetic susceptibilities of the U_6X compounds are fairly large (about twice that of niobium,[23] e.g., on a per atom basis) and thus characteristic of a transition metal with a high density of states $N(0)$ at the Fermi surface. These high densities probably arise from a narrow band, principally of $5f$-$6d$ character,[65] which overlaps a $7s$-conduction band of low state density. Pines[59] has discussed the behavior of the electron-phonon parameter V in transition metals in some detail. He concludes that one can expect V to be "decoupled" from $N(0)$ and not appreciably sensitive to changes in $N(0)$ as one moves across the periodic table in the different transition series.[59] The variations in $N(0)$ are considerable in these cases,[59] as opposed to the cases with the U_6X series, wherein $N(0)$ seems to be determined primarily by the uranium matrix and apparently varies only slightly in passing from U_6Mn to U_6Ni. Thus one would expect V to remain almost constant across the U_6X series.

Debye temperatures for the U_6X compounds have been determined only for U_6Fe,[66] to our knowledge, but the strict isomorphism and almost identical lattice constants in the series[6] suggest that the various values of Θ_D would be very similar. Since the term $\hbar\omega_{\text{av}}$ in Eq. (1) is proportional to $k\Theta_D$,[59] this term would not be expected to vary much in the U_6X series.

This analysis of the terms in Eq. (1) would suggest that the behavior of T_c in Fig. 1 is not explained by its dependence on the parameters in Eq. (1). We shall see below, however, that the electron-phonon interaction of the BCS theory does indeed play a significant role in the superconductivity of these compounds, as evidenced by measurements on the isotope effect.

Several models for superconductivity and also ferromagnetism have concerned themselves specifically with the interactions between conduction electrons and the unfilled d shells of the transition metals or, similarly, the f-electron orbitals of lanthanum and uranium.

Hamilton and Jensen[67] proposed that the superconductivity of uranium and lanthanum arises from an exchange coupling between neighboring lattice ions which, because of the proximity of these elements to Np

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[60] J. Bardeen and J. R. Schrieffer, *Progress in Low Temperature Physics*, edited by J. C. Gorter (North-Holland Publishing Co., Amsterdam, 1961), Vol. III, p. 170.

[61] We neglect here the region of curvature in Fig. 2 between Fe and Co. This curvature has been discussed above and does not affect, for our present consideration, the general band picture.

[62] *Landolt-Börnstein Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, und Technik*, edited by K.-H. Hellwege and A. M. Hellwege (Springer-Verlag, Berlin, 1962), Vol. 2, Pt. 9, pp. 1-91, 3-240. (The figure captions for Figs. 13 and 14, p. 1-91, are reversed in this reference.)

[63] χ increases slightly with temperature for all species (see Refs. 35 and 62).

[64] C. W. Tucker, Jr., Acta Cryst. **4**, 425 (1951); L. F. Bates and D. Hughes, Proc. Phys. Soc. (London) **67B**, 28 (1954).

[65] J. Friedel, J. Phys. Chem. Solids **1**, 175 (1956).

[66] J. P. Maita of Bell Telephone Laboratories has measured the specific heat of U_6Fe from $T=2.7$ to $T=10$°K and has kindly made his unpublished results available to us. From the data we find $\Theta_D \sim 125$°K, $\gamma \sim 156$ mJ/mole deg^2, and $C_{es}(T_c)/\gamma T_c \sim 2.5$, where γ is the normal-state electronic specific heat coefficient and C_{es} is the electronic specific heat in the superconducting state.

[67] D. C. Hamilton and M. Anthony Jensen, Phys. Rev. Letters **11**, 205 (1963).

and Ce, respectively, in the periodic table, is antiferromagnetic in sign. A conduction electron, in scattering off of a lattice ion, polarizes the ion by exciting an f state. It then becomes energetically favorable for a second conduction electron with opposite spin to pair with the first by scattering off of and exciting a neighboring ion. The significance of the f character of uranium in interpreting its superconducting behavior has most recently been cited in connection with the measurement of the isotope effect in α uranium.[68]

Engelhardt *et al.*[69] have proposed that in those transition metals with high superconducting transition temperatures the pairing of the conduction electrons for superconductivity is enhanced by the scattering of conduction electrons into particular d orbitals important for bonding. A conduction electron may be scattered into an unfilled d shell configuration on a lattice site, creating a new d configuration which is particularly stable, as indicated by the strength of its bonds (in other environments) with similar neighboring d shells. By virtue of this incipient bonding interaction, it becomes energetically advantageous for a second conduction electron to pair with the first by similarly scattering into a neighboring unfilled d shell. Interactions between d electrons and their relationship to superconductivity were discussed in band theory terms by Pines.[59] Kondo[70] has considered the effects of s-d and s-f interband interactions. The influence of the d electrons on superconductivity is evidenced by the difference in the pattern of superconductivity in the periodic system shown by the transition versus the nontransition metals[4] and by the departures from the normal isotope effect found in the transition metals.[69,71]

Zener has advanced a theory of ferromagnetism in which the exchange interaction between localized d-shell spins which is responsible for their spontaneous parallel alignment is an indirect interaction transmitted by the itinerant s electrons.[72] A conduction electron scattering off an unfilled d shell tends to align the d spin parallel to its own via an s-d exchange interaction, in accordance with a generalized Hund's rule.[72] This influence is felt by each subsequent d shell in the path of the conduction electron, and the collective effect of all the conduction electrons, which are themselves partially polarized, is a net d-spin alignment throughout the lattice. The vital role of the conduction electrons in producing ferromagnetism in the theory[73] is consistent with the relative scarcity of ferromagnetic insulators.[74]

There are similarities in these models for superconductivity and ferromagnetism, as might be anticipated from the similarity of the behavior of T_c in the U_6X series and the saturation magnetization of the X alloys. Other correlations between superconductivity and ferromagnetism have been noted previously.[75] It seems that the two phenomena can even coexist in the same sample.[76] One of the indications that the interaction between conduction electrons and lattice ions responsible for superconductivity may be intimately related to that responsible for ferromagnetism is the fact that, e.g., the pseudobinary (Gd, Y)Os_2 is either superconducting or ferromagnetic depending on the relative amounts of Gd and Y in the sample, and there is a crossover composition (7% Gd) at which the superconducting transition temperature is equal to the ferromagnetic transition temperature.[77] Also, the compound $ZrZn_2$, formed between two superconductors, is itself ferromagnetic.[78]

The question of the occurrence or enhancement of superconductivity in magnetic or magneticlike environments and the related problem of superconducting pairs with parallel spins (triplet pairing) have both been considered theoretically by several authors.[79–83] Balian and Werthamer[80] conclude that the latter phenomenon, which requires p-state pairing,[80] is feasible in superconductors and would distinguish itself by showing less reduction of T_c due to magnetic impurities than to nonmagnetic impurities. Bardasis and Schrieffer[81] show that the low-energy excitations of a superconductor with an attractive p-wave potential at the Fermi surface are spin-density waves among the conduction electrons. Akhiezer and Akhiezer[82] have considered the coexistence of ferromagnetism and superconductivity and find that, if triplet pairing occurs, an additional attraction between conduction electrons may arise from the virtual exchange of spin-wave excitations among localized lattice spins. There need be no spatial separation of superconducting and ferromagnetic re-

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[68] R. D. Fowler, J. D. G. Lindsay, R. W. White, H. H. Hill, and B. T. Matthias, Phys. Rev. Letters **19**, 892 (1967).

[69] J. J. Engelhardt, George W. Webb, and Bernd T. Matthias, Science **155**, 191 (1967).

[70] J. Kondo, Progr. Theoret. Phys. (Kyoto) **29**, 1 (1963).

[71] G. Rickayzen, *Theory of Superconductivity* (Interscience Publishers, Inc., New York, 1965), p. 197; E. Bucher, J. Müller, J. L. Olsen, and C. Palmy, Phys. Letters **15**, 303 (1965).

[72] C. Zener, Phys. Rev. **81**, 440 (1951); **83**, 299 (1951); C. Zener and R. R. Heikes, Rev. Mod. Phys. **25**, 191 (1953).

[73] C. Zener, Phys. Rev. **82**, 403 (1951).

[74] Charles Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1966), 3rd ed, p. 463.

[75] B. T. Matthias, IBM J. Res. Develop. **6**, 250 (1962); Science **144**, 378 (1964); B. T. Matthias, E. Corenzwit, and W. H. Zachariasen, Phys. Rev. **112**, 89 (1958); B. T. Matthias, H. Suhl, and E. Corenzwit, Phys. Rev. Letters **1**, 92 (1958).

[76] B. T. Matthias, H. Suhl, and E. Corenzwit, Phys. Rev. Letters **1**, 449 (1958); R. A. Hein, R. L. Falge, B. T. Matthias, and E. Corenzwit, *ibid.* **2**, 500 (1959); R. M. Bozorth, D. D. Davis, and A. J. Williams, Phys. Rev. **119**, 1570 (1960); Norman E. Phillips and B. T. Matthias, *ibid.* **121**, 105 (1961).

[77] Bernd Matthias, J. Appl. Phys. Suppl. **31**, 23S (1960).

[78] B. T. Matthias and R. M. Bozorth, Phys. Rev. **109**, 604 (1958); R. L. Falge, Jr., and R. A. Hein, *ibid.* **148**, 940 (1966).

[79] P. W. Anderson and H. Suhl, Phys. Rev. **116**, 898 (1958); P. W. Anderson and P. Morel, *ibid.* **123**, 1911 (1961); David J. Thouless, Ann. Phys. **10**, 553 (1960); V. L. Ginzburg, Zh. Eksperim. i Teor. Fiz. **31**, 202 (1956) [English transl.: Soviet Phys.—JETP **4**, 153 (1957)].

[80] R. Balian and N. R. Werthamer, Phys. Rev. **131**, 1553 (1963).

[81] A. Bardasis and J. R. Schrieffer, Phys. Rev. **121**, 1050 (1961).

[82] A. I. Akhiezer and I. A. Akhiezer, Zh. Eksperim. i Teor. Fiz. **43**, 2208 (1962) [English transl.: Soviet Phys.—JETP **16**, 1560 (1963)].

[83] I. A. Privorotskii, Zh. Eksperim. i Teor. Fiz. **43**, 2255 (1962) [English transl.: Soviet Phys.—JETP **16**, 1593 (1963)].

gions in the same sample, and ferromagnetic impurities added to an otherwise nonmagnetic superconductor may raise its T_c.[82]

Privorotskii[83] shows that superconductivity may occur in an *anti*ferromagnet if the pairing is in the triplet state and with zero spin projection along the axis of lattice magnetization. A net attraction occurs via an exchange of lattice spin waves, each conduction electron reversing its spin direction upon emission or absorption of a spin wave. The lattice phonon frequency ω_{av} in Eq. (1) becomes replaced by a characteristic spin-wave frequency, which is proportional to the exchange coupling between and the spin moment upon the lattice sites[84] (assumed to be unfilled d shells[83]). The term equivalent to V in Eq. (1) measures the strength of the spin-wave exchange interaction.

The relationship we have found between the superconductivity of the U_6X compounds and the magnetism of the X elements would seem likely to find expression in these approaches to superconductivity just mentioned, which concern themselves with the magnetic nature of the superconducting environment. The connection is not self-evident, however. Privorotskii's treatment[83] shows how T_c in an antiferromagnet might be proportional to the moment on the lattice sites, but there is no concrete evidence for such moments in the U_6X system, even though a consideration of the temperature dependence of the magnetic susceptibilities[63] of the compounds led Gordon to suggest that they might be antiferromagnetically ordered.[35] Our discussion of the significance of the interactions between the d shells in the U_6X structure would suggest that any such ordering is probably among these shells, and, of course, if localized moments should be present on these sites, the susceptibility results[35,63] show that they must almost certainly be antiferromagnetically ordered. The possible role of the f character of the uranium remains unspecified.

A significant factor in these considerations is the recently reported measurement[85] of the superconducting isotope effect in U_6Fe, determined by changing the isotopic mass of the uranium in the compound. The result found was $T_c \propto M^{\alpha}$, $\alpha = -0.5$, which is the dependence of T_c upon M to be expected if the source of superconductivity in the compound were exclusively the electron-phonon interaction of the BCS theory.[58,60] In addition, no unusual behavior is found for the pressure dependence of T_c.[46]

V. SUMMARY

A correlation exists between the superconductivity of the U_6X compounds and the magnetic nature of the X elements which may be illustrated by the correspondence between $T_c(U_6X)$ and $n_S(X)$ in the Slater-Pauling curve, by the occurrence of superconductivity among uranium and X-element compounds, and by the apparent importance of interactions between the $3d$ shells of the X atoms in the U_6X structure. Notably the transition temperature of U_6Fe is almost twice that of uranium under the most favorable of conditions. This correlation would not seem to be explained by valence-electron rules or by the customary theoretical approach to superconductivity. Theoretical discussions of superconductivity in magnetic environments do provide a basis for understanding this behavior. There is, however, no evidence of magnetic ordering in the compounds, nor do measurements of the uranium isotope effect or pressure dependence of T_c in U_6Fe indicate anomalous behavior. Possibly neutron diffraction measurements, such as have been done on UFe_2,[86] or a determination of the iron isotope effect in U_6Fe would prove enlightening.

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[84] Ref. 74, p. 485.

[85] Referred to in Ref. 68.

[86] Y. Hamaguchi, S. Komura, N. Kunitomi, and M. Sakamoto, J. Phys. Soc. Japan **17**, Suppl. B-III, 46 (1962).