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# Superconductivity and Spin Fluctuations in the *Ir*-Ni, *Ir*-Co, and *Ir*-Fe Alloy Systems*

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The superconducting transition temperatures of *Ir*-Ni, *Ir*-Co, and *Ir*-Fe alloys have been measured in the temperature interval 0.10–0.040 °K. It is shown that the rates of change of $\ln T_c$ with impurity concentration for these systems provide quantitative evidence that localized spin fluctuations are responsible for the suppression of superconductivity when these rates are compared with the rates of increase of the specific-heat coefficient $\gamma$ and the susceptibility $\chi$.

## I. INTRODUCTION

Spin fluctuations are believed to be responsible for suppressing superconductivity in numerous alloy systems on the right end of the 4*d* and 5*d* transition-metal series.[1,2] However, solid evidence that this is the case is difficult to come by. We have found that very small concentrations of Ni, Co, and Fe in Ir rapidly destroy the latter's superconductivity. Because the suppression of superconductivity is strictly an impurity effect, certain theoretical simplifications can arise which permit a quantitative comparison between theory and experiment.

## II. EXPERIMENTAL

Temperatures as low as 0.035 °K were obtained by adiabatic demagnetization, using a cryostat similar in construction to several reported elsewhere.[1] Superconductivity was detected by the low-frequency mutual inductance method. The temperature was measured with a 100-Ω $\frac{1}{2}$-W Speer carbon resistor which was calibrated to within a few millidegrees Kelvin with the aid of the known transition temperatures of certain high-purity superconductors and also with cerium magnesium nitrate (CMN).

One of the principal experimental difficulties was sample preparation. Samples were about 200 mg and were prepared by arc-melting 99.999%-pure starting material in an argon arc furnace. The melting point of iridium is close to the boiling points of iron, cobalt, and nickel. Consequently, the weight loss of the volatile impurity during arc melting can be considerable. This makes it difficult to determine the sample composition for such small samples and small impurity concentrations. The *Ir*-Fe samples were prepared after first preparing a master alloy containing 2.1-at.% Fe. The master was then broken up and further diluted with iridium to obtain the final samples. Fortunately, the master can be prepared with less than a few percent iron weight loss by careful arc melting. It is reasonable to assume that there is negligible iron weight loss upon further dilution and that the composition can be determined from the weights of the starting materials. However, there was a 30% cobalt weight loss in the preparation of a 3.9% cobalt master. The starting material for the *Ir*-Co alloys prepared from this master was weighed on a Mettler balance with a limiting accuracy of 0.01 mg before and after arc melting, and the composition determined by attributing any further weight loss to the volatile cobalt impurity. For these alloys, a 10% error in composition is still possible. For the *Ir*-Ni alloys as well, the composition was determined by assigning any weight loss to the nickel impurity. The problem of determining the composition is less severe because the nickel concentration in alloys of interest is higher.

## III. RESULTS

The experimental results are given in Table I and Figs. 1 and 2. The iridium used was obtained from the United Mineral Corp. It was quoted to be 99.999% pure with calcium (1 ppm), silicon (5 ppm), and sodium (2 ppm) as the principal impurities. Its transition temperature $T_c$ was 0.105 °K and the transition width $\Delta T_c$ for 90% of the transition was 0.004 °K. Surprisingly, adding iron to iridium reduces the transition width, so that the width of the 0.033%-Fe alloy was only about half a millidegree. The error in the compo-

TABLE I. Transition temperatures $T_c$ and transition widths $\Delta T_c$ for 90% of the transition of various *Ir*-Fe, *Ir*-Co, and *Ir*-Ni alloys.

| Alloy | $T_c$ (°K) | $\Delta T_c$ (°K) |
|---|---|---|
| Ir [99.999%] | 0.105 | 0.004 |
| Ir [0.017% Fe][a] | 0.070 | 0.001 |
| Ir [0.033% Fe] | 0.051 | 0.0005 |
| Ir [(0.23 ± 0.02)% Co] | 0.057 | 0.004 |
| Ir [(0.38 ± 0.04)% Co] | 0.046 | 0.004 |
| Ir [(1.2 ± 0.1)% Ni] | 0.057 | 0.008 |
| Ir [1.65% Ni] | 0.052 | 0.006 |

[a]All percentages refer to at. %.

sition of the Ir (1.2% Ni) sample is quoted to be ± 0.1% Ni because of the use of a less sensitive balance to weigh the starting materials for this alloy.

In Fig. 1, $T_c$ is plotted on a logarithmic scale vs impurity concentration for these three alloy systems. As has been found for the *Ru*-Fe, *Ru*-Co, and *Ru*-Ni systems,[2] iron suppresses $T_c$ the most rapidly, followed by cobalt and nickel, in that order. For superconducting spin-fluctuation systems, it is found experimentally that $\ln T_c$ decreases initially nearly linearly with impurity concentration.[3] This behavior is followed for the *Ir*-Fe system, as can be seen from Fig. 2. The dashed line represents the curve the points would fall on if the decrease in $T_c$ were linear with concentration. If a pair-breaking mechanism, such as a magnetic moment on the iron impurity sites, were responsible for suppressing superconductivity, then the points would fall slightly below this dashed

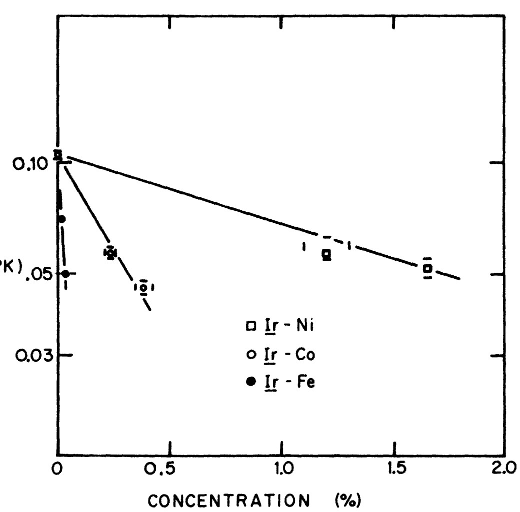


FIG. 1. Superconducting transition temperature $T_c$ plotted on a logarithmic scale vs impurity concentration in at. % for the *Ir*-Fe, *Ir*-Co, and *Ir*-Ni alloy systems.

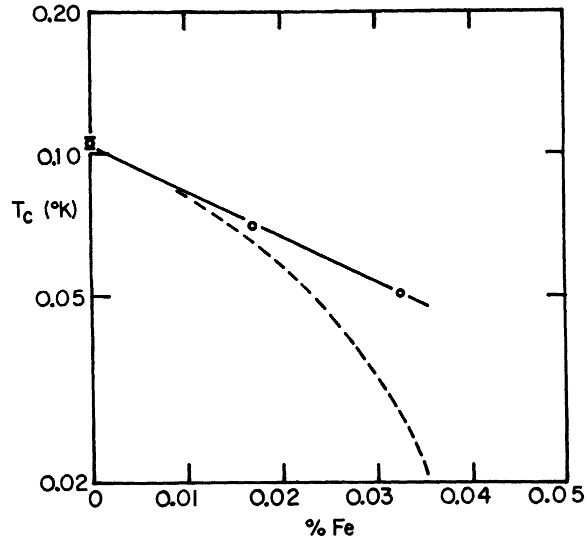


FIG. 2. Transition temperature $T_c$ plotted on a logarithmic scale vs iron impurity concentration in at. % for *Ir*-Fe alloys. The points would fall on the dashed curve if $T_c$ decreased linearly with concentration.

curve according to the theory of Abrikosov and Gor'kov.[4] Such was not expected to be the case, since low-temperature susceptibility measurements show that the iron impurities in *Ir*-Fe alloys with 1% or less iron do not possess a moment.[5] Nor is it likely that this is a Kondo system, since no resistivity minimum is observed.[6]

## IV. DISCUSSION

McMillan has derived the following equation for the transition temperature $T_c$ in terms of the Debye temperature $\Theta_D$, the electron-phonon coupling constant $\lambda_{ph}$, and the Coulomb pseudopotential $\mu^*$[7]:

$$T_c = \frac{\Theta_D}{1.45} \exp\left[\frac{-1.04(1+\lambda_{ph})}{\lambda_{ph} - \mu^*(1+0.62\lambda_{ph})}\right]. \tag{1}$$

$\mu^*$ is given in terms of the Coulomb repulsion $\mu$ by

$$\mu^* = \frac{\mu}{[1 + \mu \ln(E_F/k\Theta_D)]}, \tag{2}$$

where $E_F$ is the Fermi energy. One would not expect the screened Coulomb interaction to be responsible for the destruction of superconductivity in these alloy systems. Physically, it is easy for the electrons of a superconducting pair to correlate their motion so as to be instantaneously far enough apart to avoid the nearly instantaneous short-range Coulomb repulsion while still taking advantage of the strongly retarded phonon attraction. Mathematically, the Coulomb interaction must be cut off at energies of the order $E_F \gg k\Theta_D$, resulting in $\mu$ being replaced by the reduced value $\mu^*$ of Eq. (2) when considering the effect of this interaction on superconductivity.

However, as the energy difference $\Delta E$ between a nonmagnetic and magnetic local-moment impurity state becomes smaller, local spin fluctuations can exist for longer and longer times $\tau$, where $\tau$ is determined by the energy uncertainty relation $\Delta E\tau \sim h$. Spin fluctuations will give rise to an additional contribution to the Coulomb interaction.[8,9] This additional term should be cut off at energies of the order of $h\nu_{spin}$, where $\nu_{spin}=1/\tau$. If $h\nu_{spin} \ll E_F$, and, in particular, if $h\nu_{spin} \sim k\Theta_D$, then this term can have the major effect on suppressing superconductivity.

The additional electron-electron interaction term can be pictured to arise from the emission by one electron of a virtual paramagnon which a second electron then absorbs. Let $\lambda_{spin}$ be the coupling constant for the spacially averaged electron-paramagnon interaction. This interaction will enhance the specific-heat coefficient $\gamma$ just as the electron-phonon interaction does. The equation for $\gamma$ in terms of $\lambda_{ph}$ and $\lambda_{spin}$ becomes

$$\gamma = \tfrac{2}{3}\pi^2 k_B^2 N(0)(1+\lambda_{ph}+\lambda_{spin}) = \gamma_0(1+\lambda_{ph}+\lambda_{spin}), \qquad (3)$$

where $N(0)$ is the band-structure density of states. Provided that typical paramagnon or spin-fluctuation frequencies are of the same size as typical phonon frequencies, then one would expect to be able to replace Eq. (1) by

$$T_c = \frac{\Theta_D}{1.45}\exp\left[\frac{-1.04(1+\lambda_{ph}+\lambda_{spin})}{\lambda_{ph}-\lambda_{spin}-\mu^*(1+0.62\lambda_{ph})}\right], \qquad (4)$$

when considering the effect of spin fluctuations on superconductivity. There is a $+\lambda_{spin}$ in the numerator of the exponential because of the density-of-states renormalization effect represented by Eq. (3). There is a $-\lambda_{spin}$ in the denominator because of the repulsive character of the interaction. As a result of the very rapid decrease of $T_c$ with impurity concentration for the *Ir*-Fe system in particular, it is reasonable to assume that $\lambda_{ph}$, $\mu^*$, and $N(0)$ are changing slowly relative to $\lambda_{spin}$. If $\lambda_{ph}$, $\mu^*$, and $N(0)$ can be taken to be constant, Eqs. (3) and (4) provide two equations in one unknown $\lambda_{spin}$ and a quantitative comparison between theory and experiment is possible.

There is experimental evidence that $h\nu_{spin} \sim k\Theta_D$ for the *Ir*-Fe system. Rivier and Zuckermann have argued that for temperatures greater than a spin-fluctuation temperature $T_{spin}=h\nu_{spin}/k_B$ thermal fluctuations will become faster than spin fluctuations, so that the properties of the system, including, in particular, the temperature dependence of the magnetic susceptibility, will begin to behave as if a local moment were present.[10] The temperature dependence of the susceptibility of *Ir*-Fe alloys suggests that $T_{spin}$ is of the order of 100 °K, which is less than the Debye temperature of 425 °K.[5]

In the dilute limit, $\lambda_{spin}$ will increase linearly with impurity concentration $n_I$, so that $\alpha = d\lambda_{spin}/dn_I$ will be a constant. It follows from Eq. (4) that

$$\ln\left[\frac{T_c(n_I)}{T_c(0)}\right] = \left\{\ln\left[\frac{1.45T_c(0)}{\Theta_D}\right]-1\right\}\left\{\frac{\alpha n_I}{\lambda_{ph}-\mu^*(1+0.62\lambda_{ph})} + \frac{\alpha^2 n_I^2}{[\lambda_{ph}-\mu^*(1+0.62\lambda_{ph})]^2}+\cdots\right\}. \qquad (5)$$

Equation (5) explains the linear decrease of $\ln T_c$ vs $n_I$ at low concentrations. Maple, Huber, Coles, and Lawson have recently investigated the superconductivity, electrical resistivity, thermoelectric power, and magnetic susceptibility of *Th*-U alloys and have found this system to be a spin-fluctuation system with $T_{spin}=100$ °K.[11] For thorium, $\Theta_D$ is equal to 170 °K. Because their measurements of $T_c$ extend over the large temperature range 1.37 – 0.050 °K, their data allow one to observe clearly deviations from the simple linear decrease of $\ln T_c$ vs concentration which arise from higher-order terms of Eq. (5). In fact, the concentration dependence of $T_c$ is given remarkably well by Eq. (4) using only the as-

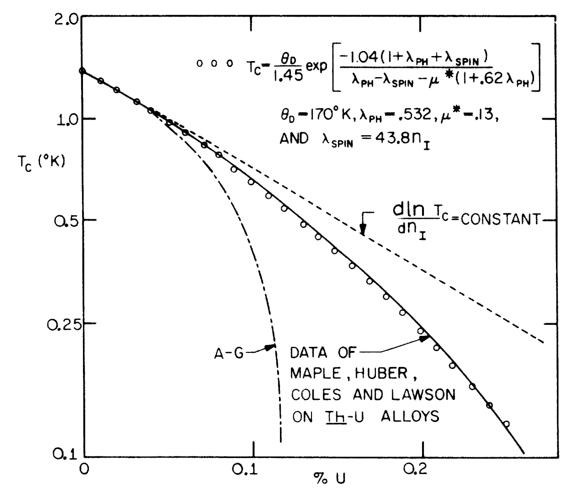


FIG. 3. $T_c$ for *Th*-U alloys plotted on a logarithmic scale vs uranium impurity concentration from the data of Maple, Huber, Coles, and Lawson. The dotted curve follows from Eq. (4) and the assumption that $\lambda_{spin}$ increases linearly with impurity concentration. The solid curve would be coincident with the dashed curve if $T_c$ decreased such that $d\ln T_c/dn_I=$ const. The curve labeled A-G would apply if uranium possessed a magnetic moment in thorium according to the theory of Abrikosov and Gor'kov (Ref. 4).

TABLE II. Values of $d\lambda_{spin}/dn_I$ and $(1/\gamma_0)\,d\gamma/dn_I$ derived from transition-temperature and specific-heat data, respectively, as well as the percentages of the latter which can be attributed to the spin-fluctuation enhancement effect. Also given are values of $-d\log T_c/dn_I$ and $d\chi/dn_I$ for these alloy systems.

| Alloy system | $-\frac{d\log T_c}{dn_I}$ | $\frac{d\chi}{dn_I}$ ($10^{-6}$ emu/%) | $\frac{d\lambda_{spin}}{dn_I}$ | $\frac{1}{\gamma_0}\frac{d\gamma}{dn_I}$ | % spin |
|---|---|---|---|---|---|
| *Ir*-Fe | 1000 | 120 [a] | 45 | 66 [b] | 70 |
| *Ir*-Co | 100 | 12 [c] | 4.5 | ? | ? |
| *Ir*-Ni | 20 | 3 [c] | 0.85 | 1.6 [d] | 50 |

[a] Reference 5.

[b] T. H. Geballe, B. T. Matthias, A. M. Clogston, H. J. Williams, R. C. Sherwood, and J. P. Maita, J. Appl. Phys. 37, 1181 (1966).

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sumption that $n_I$ increases linearly with concentration (see Fig. 3).

The experimental values of $\alpha = d\lambda_{spin}/dn_I$ determined from our data using Eq. (5) and McMillan's values of $\mu^* = 0.13$ and $\lambda_{ph} = 0.34$ for iridium[7] are given in Table II. Assuming $N(0)$ and $\lambda_{ph}$ to be essentially independent of $n_I$, one has from (3) that

$$\frac{1}{\gamma_0}\frac{d\gamma}{dn_I} = \frac{d\lambda_{spin}}{dn_I}$$

as well. The values of $d\lambda_{spin}/dn_I$ based on specific-heat data are given in Table II for the *Ir*-Fe and *Ir*-Ni systems for which such data are available. The values of $d\lambda_{spin}/dn_I$ derived from data on superconductivity are 70 and 50%, respectively, of those values derived from specific-heat data (entry labeled % spin). The discrepancies might be attributed to an increase in the density of states $N(0)$ with concentration, which has been assumed to be zero. The formation of resonant states on the Fe impurity sites would give a contribution to $N(0)$ linear in concentration for low concentrations.[12] In the case of the *Ir*-Ni system, it might be attributed to a high cutoff energy $h\nu_{spin}$, which could mean that the quantity called $\lambda_{spin}$ in Eq. (4) underestimates the actual $\lambda_{spin}$ just as $\mu^*$ is smaller than $\mu$.

Also tabulated in Table II are $-d\log T_c/dn_I$ and $d\chi/dn_I$, where $\chi$ is the room-temperature susceptibility. The values of $d\chi/dn_I$ for the *Ir*-Co and *Ir*-Ni systems are based on measurements of $\chi$ for Ir (3.9% Co) and Ir (2.9% Ni) samples by Chaikin. It is evident that the ratio of these two quantities is nearly the same for all three alloy systems, although the individual values vary by a factor of 50. This fact can be understood in terms of the detailed model of local spin fluctuations that has been proposed by Lederer and coworkers.[13] According to this model $d\chi/dn_I$ and the spin-fluctuation contribution to $d\gamma/dn_I$ ($=\gamma_0 d\lambda_{spin}/dn_I$) are proportional to the inverse of the spin-fluctuation temperature $T_f$ where the constants of proportionality should not depend on whether the impurity is Fe, Co, or Ni.

## V. CONCLUSIONS

A very rapid suppression of the superconductivity of iridium by nickel, cobalt, and particularly iron impurities has been observed. The linear decrease of $\ln T_c$ with impurity concentration is consistent with spin fluctuations being the explanation. For *Ir*-Fe alloys in particular, the rapid decrease of $T_c$ with impurity concentration and the low frequencies, of the order of the Debye frequency, of the local spin-fluctuation modes allows one to write an equation for $\ln(T_c)$ in terms of the impurity concentration, known constants, and $d\lambda_{spin}/dn_I$. The values of $d\lambda_{spin}/dn_I$ derived from transition-temperature data using this equation suggest that 70% of the increase in $\gamma$ with concentration is due to the spin-fluctuation enhancement effect. This is the first quantitative evidence that spin fluctuations are responsible for the disappearance of superconductivity in this region of the Periodic Table.

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# Unusual Strain Dependence of $T_c$ and Related Effects for High-Temperature (*A*-15-Structure) Superconductors: Sound Velocity at the Superconducting Phase Transition

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The sound velocities (elastic moduli) of $V_3Ge$ and $V_3Si$ are found to have very large discontinuities in their temperature derivatives at the superconducting transition. A thermodynamic treatment of these data (with the specific-heat behavior) for a second-order phase transition is shown to yield a general dependence of $T_c$ on strain. It is found that all strains greater than roughly $10^{-3}$ will lower $T_c$ for cubic $V_3Si$ and raise $T_c$ for $V_3Ge$. The results show that these strain dependences are very large, mainly quadratic, and directly responsible for some of the anomalous behavior of the superconductors. They predict, quantitatively for $V_3Si$: (a) the reduction in $T_c$ which results from the structural transformation, (b) the arrest of the structural phase transformation at $T_c$, (c) the strain dependence of the specific-heat discontinuity at $T_c$, (d) the strain dependence of the structural-transformation temperature, and (e) the anisotropic stress dependence of $T_c$. The predicted dependence of $T_c$ upon the lattice parameter is a major factor in accounting for the different $T_c$'s among the *A*-15-structure compounds. The microscopic source of this large strain dependence is discussed in terms of the Labbe-Friedel (density-of-states peak) model. It is a surprising result that this model does *not* predict the large strain dependence of $T_c$ for $V_3Si$.. Finally, the "approximate" nature of the sound velocity data at a phase transition is discussed and the general thermodynamic form for the corrections to the nonideal case is given.

## I. INTRODUCTION

The *A*-15- ($\beta$-tungsten)-structure superconductors have yielded a plethora of "anomalies", [1-12] singularly outstanding in magnitudes and perplexing in their physical origins because they occur in those materials which, today, have the highest known temperatures for superconductivity. It is known, for example, that the high-$T_c$ superconductors exhibit elastic softening, while those with low $T_c$ do not. [13] Some samples of $V_3Si$ and $Nb_3Sn$ undergo a cubic-to-tetragonal transformation at temperatures $T_m$ somewhat above (but never below) $T_c$. For $V_3Si$, where extensive studies have been made, it was found that for nontransforming crystals, the very large elastic softening on cooling is arrested with the onset of supercondivity. [14] In transforming crystals, which exhibit of continuous increase in the degree of tetragonality when cooled below $T_m$, the transformation itself is arrested at $T_c$. [9,14]

In this paper we attempt to reduce the number of seemingly independent anomalies. This we do by analyzing the behavior of the sound velocity near the superconducting transition, and, by thermodynamic arguments, extending these results to "predictions" of some "anomalies" outstanding. Some new and unexpected correlations also occur, and these are presented here and in the following paper (which also lists much of the data relevant to our findings).

It is known that for a second-order phase transition (superconductivity) one may expect some discontinuities in the behavior of the sound velocities (elastic moduli). These discontinuities are analytically related to the strain dependence of the thermodynamic critical field. [15] In Sec. II we show a simple extension of this usual result to yield the general strain dependence of the transition temperature if the specific heat is known. For longitudinal strains the linear and quadratic strain dependences of $T_c$ are related to the discontinuities in magnitudes and temperature derivatives, respectively, of the elastic moduli. For shear strains, only the quadratic dependence of $T_c$ is allowed and only the "slope" discontinuities may occur.