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SUPERCONDUCTIVITY IN "AMORPHOUS" TRANSITION METAL ALLOY FILMS

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The superconducting transition temperature of "amorphous" transition metal alloys has been measured. The variation of T_c as a function of the electron to atom ratio is consistent with the presence of an atomic-like parameter characterizing the systematics of T_c . The data does not support a recent explanation based entirely on a simple averaging or smearing of the crystalline electronic density of states.

In this letter we report measurements of the superconducting transition temperature, T_c , for disordered 4d and 5d transition metal alloy films.¹ We have observed that the T_c in amorphous (or highly disordered) transition metals differs strongly from that of crystalline transition metals (see Figs. 1 and 2). This behavior is believed to be a manifestation of "the dominance of atoms and their local environment in determining superconducting parameters . . ." ² and thus indicates the existence of an atomic-like local parameter that characterizes the systematics of superconductivity in the transition metal series. This view differs from a recent explanation of the T_c in disordered transition metals based entirely upon a simple smearing or averaging of the electronic density of states.^{3,4}

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The superconducting transition temperature of the amorphous films of the 4d and 5d transition metal alloys are shown in Fig. 1(a) and Fig. 2. The primary feature of the data is that T_c increases as a function of the number of electrons per atom (e/a) in a smooth, nearly linear fashion to a definite triangular peak near the middle of the d-series. The peak occurs for the 4d series at $e/a = 6.4$ in contrast to the crystalline peak at 6.7. T_c then decreases at nearly the same slope, followed by a more rapid decrease at $e/a \sim 7$. An extrapolation of the linear decrease in T_c just to the right of the peak results in a zero intercept near Pd (not shown), the last transition metal in the series. In the 5d series, the amorphous T_c peak occurs near $e/a = 6.8$; the crystalline peak is not well established in the 5d series.

This variation in T_c for the amorphous transition metal alloys is in marked contrast to the familiar Matthias type curve⁵ for solid solution alloys, indicated in Figs. 1 and 2 by the dashed curves. Most noticeable in the amorphous data are the absence of the peak in T_c between Zr and Nb and the valley between Nb and Mo in the 4d series. A similar effect is evident in the 5d series. The smooth behavior in T_c across two phase regions of the binary alloys Y-Zr, Zr-Nb, Zr-Mo and Mo-Ru in the 4d case (the 5d case is similar), demonstrates that e/a determines T_c in the "amorphous" state, independent of the normal crystal structure.

A combination of a 4 and 5d metal, Mo and Re respectively, was also studied in place of Mo-Tc and for comparison with Mo-Ru because of the greater amount of crystalline data available and the fact that technetium could not be used due to its radioactivity. The amorphous T_c curve for Mo-Re, shown in Fig. 1(b), is nearly identical to the amorphous Mo-Ru at the same e/a ratio, while the corresponding crystalline T_c for these alloys are markedly different.

This supports the dependence of T_c on e/a for the "amorphous" case. In detail the T_c peak for Mo-Re alloys is not as sharp as those for Mo-Ru alloys (this may be a result of the larger uncertainty in composition in Mo-Re) and occurs at a lower e/a of ~ 6.3 .

The above data can be explained by recent theoretical developments.^{2,6-8} The electron-phonon interaction parameter, λ , is given by McMillan's strong coupling theory,⁶

$$\lambda = \frac{N(0)\langle I^2 \rangle}{M\langle \omega^2 \rangle},$$

where M is the atomic mass; $\langle \omega^2 \rangle$ is the mean squared renormalized phonon frequency; $N(0)$ is the electronic density of states; and $\langle I^2 \rangle$ is the square of the electron-phonon matrix element averaged over the Fermi surface. McMillan notes that $N(0)\langle I^2 \rangle$ is approximately constant for the bcc transition metals and thus the large variation in $1/\langle \omega^2 \rangle$ dominates the behavior of λ and T_c in the crystalline state. Since the crystalline $N(0)$ exhibits a still unexplained strong correlation with θ_D ^{2,6,9} (and therefore $\langle \omega^2 \rangle$) it cannot be excluded as a factor controlling λ and T_c .

Hopfield² explained the approximately constant value of $N(0)\langle I^2 \rangle$ by noting that it is a local atomic parameter, η , which is independent of $N(0)$ and varies smoothly across the transition metal series. This has been confirmed by recent calculations.^{7,8} We are thus led to believe that η will be independent of crystal structure.

An analysis using the McMillan equation yields a weakly varying $\langle \omega^2 \rangle$ as a function of e/a for the amorphous T_c data.¹⁰ Thus if the electronic density of states is still correlated with $1/\langle \omega^2 \rangle$ (i.e. in the amorphous state), then it too is roughly constant. This conjecture is consistent with

the smearing or averaging out of the density of states in disordered transition metals as has been proposed^{3,4} and will be discussed below. We believe that the smearing of $N(0)$ makes it possible to observe the variation of an atomic-like local parameter across the transition metal series.

We believe our data is the first experimental evidence that show features characteristic of an atomic-like local parameter and its variation across the series. An unexpected feature is the indication that η has a triangular peak in the middle of the d-band instead of a smooth peak at a larger e/a .⁷ We will present in a longer article¹⁰ other evidence based on theoretical considerations and using published data that indicate that the triangular shaped variation of an atomic parameter as found from the data presented here is also a feature in the crystalline state.

The amorphous T_c data cannot be explained solely on the basis of a smearing of the density of states by the disorder, as has been proposed to explain these and similar results.^{3,4} This argument states that due to a short mean free path in the disordered alloys the electron energy states are broadened, and the sharp structure in the density of states characteristic of the transition metal series is averaged over energy. This results in those alloys with a high T_c in the crystalline states having a lower T_c in the disordered state, and vice versa for those alloys with a low T_c . Our arguments that the data are not due simply to a density of states smoothing, though the smoothing is required to observe the effects of η , are as follows:

1. At the Mo rich end of the Mo-Ru alloys the crystalline T_c are rather high (5-7°K) and correspond to a peak in the density of states in the bcc phase. The T_c for the amorphous case are even higher, contrary to what would be expected on the basis of the simple averaging argument. A similar result

is found in the data shown in Fig. 2 on the 5d series, where the amorphous T_c are higher than the crystalline T_c , even though the crystalline T_c occurs at peaks in the density of states. It is not possible to explain these observations using the simple argument of a smearing in the density of states.

2. The position of the amorphous peaks does not have any relationship to the density of states peaks or crystalline T_c peaks, but instead appears to be related to the position of a half-filled d-shell, as judged from an examination of the bulk cohesive energy¹¹ and by the position of half-filled d-shell in the respective atoms,¹² i.e., ground state configurations.

3. A dominant feature of the amorphous T_c in the 4-d alloys, in the 4d-5d alloys (Mo-Re), and in the 5-d alloys, is the sharp triangular peak in the amorphous T_c . It does not seem possible to explain this feature on the basis of a smoothed density of states alone. Instead we believe that this feature must be explained by an atomic-like or local parameter.

Past studies of amorphous transition metals,^{3,13,14} motivated by the possibility of higher T_c 's via lattice disorder, have not been as extensive as that presented here. This study was stimulated by our previous data,¹⁴ which suggested that there may be a regular variation of T_c across the amorphous transition metal series. A similar suggestion by Gamble and Geballe appeared at about the same time.¹³

The metal films were prepared by electron beam evaporation onto a sapphire substrate at 4.2°K in a vacuum of 8×10^{-8} to 1×10^{-7} torr, and at rates of 50-300 Å/sec. Gas impurities (O_2) up to 3×10^{-6} torr produced no significant change in T_c .¹⁵ T_c was measured resistively in situ and the films were then warmed to 300°K, cooled back down to 4.2°K and T_c was remeasured. Film composition was determined by electron microprobe analysis resulting in an

accuracy of ± 3 at.% for 4d alloys, ± 5 at.% for Mo-Re and ± 4 at.% for the 5d alloys. Experimental aspects will be discussed in detail later.¹⁵

Figure 3 shows the values of T_c for the 4d series and Mo-Re measured following the warming to 300°K and then re-cooling. Except for a few cases the T_c 's have changed toward the bulk crystalline value. Those exceptions, indicated by the arrows, also did not exhibit any significant change in resistivity during the temperature cycling from 4 to 300°K and back. In fact, the annealing behavior, subsequent T_c and electron diffraction data form a coherent picture as follows: Those alloys for which there was an annealing step (a relatively sharp change in resistivity) also showed a change in T_c towards the bulk crystalline T_c , and the electron diffraction and electron micrographs indicated the normal crystal structure with grain sizes ranging from 50 to 1000 Å. (The broadened transition widths of many of these films may be the result of varying grain sizes or incomplete annealing.) On the other hand for those films for which the T_c and resistivity did not change, electron diffraction pictures revealed diffuse three or four-ring patterns, characteristic of liquid or amorphous materials. In addition, electron micrographs revealed no grain structure to the limit of resolution of the microscope (≈ 20 -25 Å). Similar results were found for the 5d series (not shown). On the basis of this data we infer that all our specimens (this is not as obvious in the case of the hcp elements Zr and Ru), were prepared in an "amorphous" state and those with compositions corresponding to equilibrium two phase regions remain in this state up to room temperature. The annealing and electron microscopy results are discussed more fully elsewhere.^{15,16}

In conclusion the T_c data presented here cannot be explained simply by a smearing of the electronic density of states; it is however consistent with the

presence of an atomic parameter characterizing the systematics of T_c in transition metals.

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FIGURE CAPTIONS

Figure 1. The superconducting transition temperature of vapor quenched (a) 4d transition metal alloys and (b) a 4d-5d alloy is shown as a function of the number of electrons per atom (e/a). This data is consistent with the presence of an atomic-like parameter controlling T_c in the amorphous or disordered transition metals. The corresponding crystalline T_c data is indicated by the dashed curve with the exception of Mo-Ru alloys which is shown by the dotted curve. In (a) the amorphous data are for Y-Zr, Nb-Zr, Mo-Zr, Nb-Mo, and Mo-Ru alloys. At $e/a = 6$ to 7 the crystalline data (dashed curve) represents Mo-Tc and Mo-Re alloys. The amorphous data in (a) for $e/a = 6$ to 7 is to be compared with the lower dotted curve. The Mo-Re crystalline data is again reproduced in (b) for comparison with the amorphous Mo-Re films. The transition widths indicated were determined by the 10 to 90% of normal resistance interval.

Figure 2. The superconducting transition temperature of vapor quenched 5d transition metal alloys is shown as a function of the number of electrons per atom. The corresponding crystalline T_c data is indicated by the dashed curve. The amorphous T_c data are for the 5d elements and Ta-W, Ta-Re(Δ), W-Re and Re-Ir alloys.

Figure 3. The superconducting transition temperature of (a) 4d transition metal alloys and (b) Mo-Re alloys after warming to 300°K. The T_c 's generally returned to or toward their corresponding crystalline values (dashed and dotted curves) and had exhibited large irreversible decreases in resistivity during the warming cycle. The exceptions, indicated by arrows, were found to be "amorphous-like" when examined by electron diffraction (see text).

XBL 7111-4832

Fig. 1

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Fig. 2

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Fig. 3

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