

Electronic density of states in amorphous Zr-Pd and Zr-Ni alloys

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(Received 18 April 1983; revised manuscript received 27 September 1983)

We have produced amorphous Zr-Pd and Zr-Ni films by means of rf diode cosputtering techniques. Measurements were made of the superconducting transition temperature T_c , the normal resistivity ρ , and the upper critical field H_{c2} . From ρ and $(dH_{c2}/dT)_{T_c}$ we determined the dressed density of states at the Fermi level $N^* = N(1 + \lambda)$, where λ is the electron-phonon coupling constant and N is the bare density of states. In contrast to amorphous Zr-Cu and Zr-Rh alloys, a direct proportionality between T_c and N^* was not observed for these alloys. Thus the composition dependence of N^* and T_c is not consistent with the suggestion that N^* is the most important factor in determining T_c .

In a recent work,¹ we reported the fabrication of amorphous Zr-Rh, Zr-Ru, and Zr-Re films as well as the determination of the dressed density of states at the Fermi level N^* for these materials. For our Zr-Rh films, we estimated $N = N^*/(1 + \lambda)$, where λ is the electron-phonon coupling constant, and compared the results with values of N for amorphous Zr-Cu alloys.² For alloys with high Zr concentrations, the magnitude and composition dependence of N was found to be approximately the same for the two alloy series. These results were then compared with a simple model wherein the density of states has two peaks, one near E_F determined by Zr but not by Rh or Cu. For this split-band model, the dilution of Zr atoms determines the concentration dependence of N , for high Zr concentrations. As the percentage of Zr atoms decreases, the behavior of N must be calculated using the recursion method³ or some other calculational scheme. In any case, the experimental results were in good agreement with the simple model and were consistent with recent ultraviolet photoelectron spectroscopy (UPS) measurements on similar alloys.⁴⁻⁶ This encouraging result suggested that UPS measurements might indicate other alloy systems for which the composition dependence of N might be readily understandable in terms of this simple model. In this respect, both Zr-Pd and Zr-Ni alloys seemed to be good candidates for our studies, since UPS measurements seemed to suggest that these alloys might present split-band behavior.⁴⁻⁶ For amorphous alloys of both Zr-Pd⁷ and Zr-Ni,⁸ low-temperature specific-heat measurements are available to furnish values of the Debye temperature Θ_D , thus facilitating the problem of estimating λ . In addition, these alloys have been studied by other techniques.⁹⁻¹³ Our results were somewhat different than initially expected from UPS data. However, they provide some interesting insights into the relationship between the density of states, N , and T_c for amorphous transition-metal superconductors.

The alloys studied in this work were prepared by rf diode cosputtering techniques as described in Ref. 1. X-ray diffraction scans, obtained with Cu $K\alpha$ radiation, showed no crystalline peaks, thereby indicating the amorphous nature of our materials. The composition of each individual sample was determined by energy-dispersive x-ray spectroscopy (EDS), while wavelength-dispersive x-ray spectroscopy (WDS) was used to check the samples for included Ar gas. Sample compositions, given in Table I, should have an absolute accuracy of 5 at.%, but a relative accuracy of 1-2

at.%. For the Zr-Pd alloys, the Ar level was ~ 0.5 at.% and was not included in the compositions of Table I. Auger-electron spectroscopy (AES) indicated the absence of light-element contamination in the Zr-Pd alloys. For the Zr-Ni alloys, WDS measurements established an upper limit of 0.1-0.2 at.% for included Ar. Some light-element contamination (carbon and oxygen) was, however, observed in these alloys, but the total was always less than 6 at.%.

Also included in Table I are values of the superconducting transition temperature T_c , determined resistively as in Ref. 1. These data are shown in Fig. 1, along with T_c values for similar materials from Refs. 7 and 9. We observe a sharp decrease in T_c as the Pd fraction increases. The slight T_c differences observed in the figure can be easily understood in terms of the uncertainties in the composition, mentioned earlier, or in terms of the different methods used to fabricate the various samples.¹⁴ In Table I, values for the critical-field slope $(dH_{c2}/dT)_{T_c}$ and the normal resistivity at 25 K, ρ_{25} , are also given. Our resistivity values are in good agreement with a value for Zr₇₀Pd₃₀ of Ref. 15. Also in Table I are values of N^* , calculated from $(dH_{c2}/dT)_{T_c}$ and ρ_{25} , using Eq. (1) of Ref. 1. We note that, for the highest Zr concentrations, the calculated values of N^* are in good agreement with those found for Zr-Rh alloys¹ of similar composition, as is to be expected. For the amorphous Zr₇₀Pd₃₀ of Ref. 15, we calculated $N^* = 1.03$ states/eV atom spin. From the coefficient of the linear specific-heat term ($T > T_c$), obtained in Ref. 7 for amorphous Zr₇₀Pd₃₀, we find $N^* = 0.96$ states/eV atom spin, in good agreement with our results.

In Fig. 2 we show our values of N^* as a function of x for the Zr_{1-x}Pd_x alloys. Except for a slight decrease in N^* for $x \sim 0.29$, the density of states N^* is seen to be approximately independent of x . In light of our previous discussion, this is an unexpected result. For amorphous Zr₇₀Pd₃₀, the UPS spectrum consists of a peak near E_F and another at a binding energy of ~ 3.6 eV. The calculations of Ref. 16 suggest that, for Zr₇₅Pd₂₅, the Pd states make a negligible contribution to N at the Fermi energy. This being the case, it was expected that a simple dilution model such as that of Ref. 1 might describe the composition dependence of N . In this case we would expect to see a monotonic decrease in N with increasing x . The fact that we see at most a slight dip in the curve N^* vs x of Fig. 2 indicates either that a split-band model is not appropriate for the Zr-Pd system or that the dilution model is inadequate for describing the compo-

TABLE I. Superconducting properties of alloys studied.

Composition	T_c (K)	$-(dH_{c2}/dT)_{T=T_c}$ (kG/K)	ρ_{25} ($\mu\Omega$ cm)	N^* (states/eV atom spin)
Zr ₆₅ Pd ₃₅	1.98 ± 0.01	30.7 ± 1	165	1.07
Zr ₆₆ Pd ₃₄	2.10 ± 0.02	27.5	151	1.06
Zr ₆₈ Pd ₃₂	2.24 ± 0.04	28.0	137	1.19
Zr ₆₉ Pd ₃₁	2.34 ± 0.03	28.2	179	0.92
Zr ₇₁ Pd ₂₉	2.49 ± 0.02	26.3	180	0.86
Zr ₇₃ Pd ₂₇	2.60 ± 0.01	28.6	172	0.99
Zr ₇₇ Pd ₂₃	2.84 ± 0.02	30.1	168	1.08
Zr ₇₈ Pd ₂₂	2.88 ± 0.03	30.1	170	1.08
Zr ₈₀ Pd ₂₀	2.91 ± 0.02	29.8	168	1.09
Zr ₆₉ Ni ₃₁	2.44 ± 0.01	41.2	118	1.91
Zr ₇₀ Ni ₃₀	2.58 ± 0.02	38.2	140	1.50
Zr ₇₁ Ni ₂₉	2.64 ± $\begin{smallmatrix} 0.04 \\ 0.08 \end{smallmatrix}$	41.3	163	1.41
Zr ₇₆ Ni ₂₄	2.94 ± 0.02	38.4	193	1.14
Zr ₇₉ Ni ₂₁	3.06 ± 0.02	36.6	180	1.19
Zr ₈₀ Ni ₂₀	3.17 ± 0.03	33.3	175	1.12
Zr ₈₂ Ni ₁₈	2.98 ± 0.02	30.4	166	1.09
Zr ₈₃ Ni ₁₇	3.00 ± 0.02	29.7	168	1.06
Zr ₈₄ Ni ₁₆	3.06 ± 0.01	28.1	154	1.10

sition dependence of N . These conclusions are supported by the soft-x-ray spectroscopy (SXS) measurements by Hague *et al.*¹⁷ on amorphous Zr₇₀Pd₃₀. The SXS measurement, which furnish the individual contributions (Zr or Pd) to the total density of states near the Fermi level, indicate that the Pd band contributes little to the density of states at E_F , as was previously supposed. However, the Zr $4d$ states cover the whole width of the total density of states and make substantial contributions at high binding energies. Thus the two peaks in the UPS spectrum cannot be individually as-

signed to a single component of the alloy and, therefore, a split-band model will not furnish a good description of the density of states in this case. We cannot expect a dilution model to describe the composition dependence of N , since the hybridization of Zr and Pd d states is very strong in these alloys.¹⁷

The above discussion is valid whether we discuss N or N^* , since both are approximately independent of x . To calculate $N = N^*/(1 + \lambda)$ from the measured N^* values, it is necessary to estimate λ . We estimated λ by inverting the McMillan equation, using the measured value of T_c and assuming⁷ $\Theta_D = 180$ K and $\mu^* = 0.1$ for all alloy compositions.

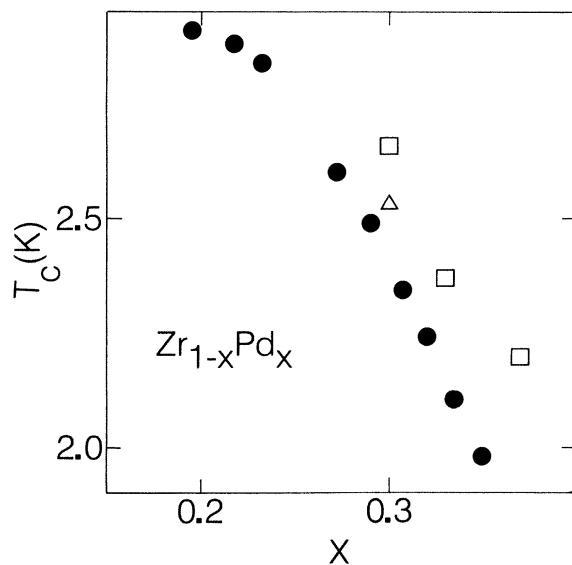


FIG. 1. Superconducting transition temperature T_c vs x for amorphous Zr_{1-x}Pd_x alloys: ●, sputtered films, this work; Δ, splat quenched sample, Ref. 7; □ splat quenched samples, Ref. 9.

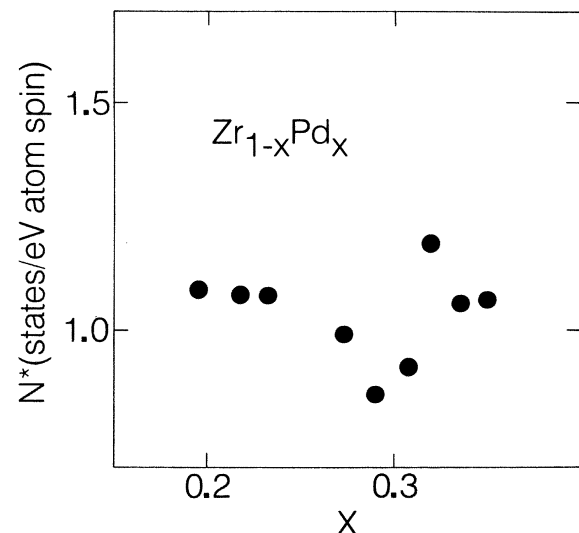


FIG. 2. Dressed density of states N^* vs x for amorphous Zr_{1-x}Pd_x alloys.

As expected, λ decreased with decreasing T_c , going from $\lambda = 0.58$ for $x = 0.20$ to $\lambda = 0.52$ for $x = 0.35$. The T_c variation was not a reflection of a change in N , which remained roughly constant between the extremes of composition. The present results touch upon a central theme of Ref. 1: the relationship between N^* and T_c . The importance of the density of states in determining T_c in amorphous transition-metal alloys has been repeatedly stressed.¹⁸⁻²⁰ Previously we pointed out exceptions to expected behavior²¹ and the present results are a further indication that the T_c systematics of all amorphous superconductors cannot be understood in terms of a single parameter.

In Table I we also provide the T_c values for the Zr-Ni alloys studied here. Again we note a reasonably good agreement with other values from the literature^{8,10-13} and we mention especially the results of Ravex, Lasjaunias, and Béthoux for as-sputtered $Zr_{76}Ni_{24}$ ($T_c = 3.15$ K) and annealed $Zr_{76}Ni_{24}$ ($T_c = 3.00$ K), which should be directly comparable with our results. The normal resistivity ρ_{25} and the critical-field slope $-(dH_c/dT)_{T_c}$ are also given in Table I, as well as the calculated values of N^* , obtained using Eq. (1) of Ref. 1. We note that the N^* values for the highest Zr concentrations are in good agreement with those obtained for Zr-Rh (Ref. 1) and Zr-Pd alloys, as one would expect. For the Zr-Ni alloys, the literature values of N^* are quite variable: for melt-spun $Zr_{70}Ni_{30}$, Karkut and Hake¹⁵ obtained $N^* = 1.04$ states/eV atom spin, while Tenhover and Johnson²² found $N^* = 1.0$ states/eV atom spin for liquid-quenched material of the same composition. Very recent results by Altounian and Strom-Olsen²³ for melt-spun material agree (to within our experimental uncertainty $\sim 10\%$) with our values of N^* for high Zr concentrations, but are in disagreement with our three highest Ni concentrations. For the sputtered films, Ravex *et al.*⁸ obtained $N^* = 1.64$ and 1.27 states/eV atom spin, for the as-quenched and annealed materials, respectively. We emphasize again that, for melt-spun and sputtered amorphous Zr-Rh alloys of the same composition, we found the T_c values are higher, while the N^* values are generally lower, for melt-spun alloys than for the corresponding sputtered material.¹⁴ The apparent discrepancies between our results (and Ref. 8) and those of Ref. 23 for the highest Ni concentrations may be another manifestation of this phenomenon.

For our Zr-Ni alloys the increase in N^* with increasing x is quite pronounced for higher Ni concentrations. This behavior seems to differ from that observed by Altounian and Strom-Olsen.²³ It may be the case that these differences are due to the different methods used to prepare the samples. However, we wish to make a number of observations. First, it is far from obvious, in retrospect, that a split-band model should give a good description of N in Zr-Ni. The density-of-states peak is at a binding energy ~ 3.6 eV in $Zr_{75}Cu_{25}$, while it occurs around ~ 2.1 eV in $Zr_{75}Ni_{25}$. Thus we expect a much greater contribution of the Ni $3d$ orbitals to $N(E_F)$ than was the case for Cu (Ref. 1) and we certainly should observe an overlap of the Ni and Zr bands. In fact, band-structure calculations by Moruzzi *et al.*¹⁶ for close-packed crystalline $Zr_{75}Ni_{25}$ show that the contribution of the Ni $3d$ orbitals to $N(E_F)$ is small but finite and indi-

cate a very strong Zr contribution at the position of the Ni peak. Thus it is not possible to make a separate identification of UPS peaks with Ni and Zr.

Secondly, UPS spectra were obtained by Oelhafen, Hauser, Güntherodt²⁴ for $Zr_{76}Ni_{24}$ and $Zr_{63}Ni_{37}$ which showed a peak at a binding energy ~ 1.7 eV. For the case of $Zr_{63}Ni_{37}$, the peak had shifted to lower binding energy and had greatly increased in size. The increase in size may be understood by the observation that the photoemission cross section for the Ni $3d$ states is larger than that of the Zr $4d$ states. However, the decrease in binding energy of the UPS peak suggests that the Ni states make an increasingly important contribution to $N(E_F)$. As in the case of Zr-Pd, we do not expect a simple dilution model to describe N for Zr-Ni and, therefore, do not expect a monotonic decrease in N^* with x .

Finally, we note that the results of Ravex *et al.*,⁸ for sputtered films, indicate that these materials are very sensitive to the thermal history of the sample. Recently, Gibbs, Evetts, and Leake,²⁵ considering relaxation processes in glasses, postulated the existence of a nonequilibrium contribution to the density of states for these processes, which might be either positive or negative depending upon the thermal history of the glass. Perhaps part of the difference between our values for N^* and those of Ref. 23 for Ni-rich compositions may be due to effects of this kind.

Now if we consider the dependence of T_c upon N^* for our Zr-Ni films, we find that there is an inverse correlation between these two quantities, similar to that which we observed²¹ previously for $(Mo_{0.6}Ru_{0.4})_{1-x}Si_x$ and $(Mo_{1-y}T_y)_{1-x}Si_x$. Whether or not the present results are representative of pure Zr-Ni films may be open to discussion. However, this inverse correlation between T_c and N^* for these amorphous alloys is inconsistent with a Varma-Dynes²⁶ type of analysis for which the states near E_F result from a single type of orbital. The authors of Ref. 26 do not suggest how their results would be changed if their treatment were to be generalized to the case of two orbitals at E_F . They do, however, mention experimental results for Nb_3Sn , Nb_3Al , and Nb_3Sb . For these materials the dominant orbitals are different and the corresponding values of λ/N are quite different. Thus for these Nb compounds we do not expect a direct proportionality between T_c and N^* .

In conclusion, we have determined the dressed density of states N^* for a series of amorphous Zr-Pd and Zr-Ni alloys. For our very pure Zr-Pd materials, our values of N^* are approximately independent of composition, while, for the Zr-Ni alloys, N^* seems to increase with decreasing Zr fraction. The composition dependence of T_c and N^* in these alloys is not consistent with the suggestion that N^* is the most important factor in determining T_c .

ACKNOWLEDGMENTS

We wish to thank Sonia Frota-Pessôa for many useful discussions. This research benefited from the overall support of energy conversion at Energy Conversion Devices, Inc., by the Atlantic Richfield Company.

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