Superconductivity and spin fluctuations in M-Zr metallic glasses
($M =$ Cu, Ni, Co, and Fe)

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The superconducting transition temperature, upper critical field, and magnetic suscepti-bility have been measured in four binary metallic glass systems: Cu-Zr, Ni-Zr, Co-Zr, and Fe-Zr. For each alloy system, a full and continuous range of Zr-rich compositions accessi-ble by melt spinning has been examined. For Cu-Zr, the range is $0.75 > x > 0.30$; for Ni-Zr, $0.80 > x > 0.30$; for Co-Zr, $0.80 > x > 0.48$, and for Fe-Zr, $0.80 > x > 0.55$ (x being the con-centration of Zr in at. %). The results show clearly the influence of spin fluctuations in reducing the superconducting transition temperature. The data have been successfully analyzed using a modified form of the McMillan equation together with expressions for the Stoner enhanced magnetic susceptibility and the Ginsburg-Landau-Abrikosov-Gor'kov ex-pression for the upper critical field.

I. INTRODUCTION

Metallic-glass superconductors formed by quenching from the melt fall into two broad categories. Most studied have been transition metal alloys (such as Mo or Ru) containing a metalloid, like B or P, as a glass former. To maintain the sta-bility of the glassy phase the composition must be held close to the eutectic of about 20 at. % metal-loid, and changes in the superconducting properties can only be obtained by going to a ternary alloy with two transition metals, whose relative proportions may be varied. The second category consists of sim-ple binary alloys such as La-Au or Cu-Zr. In many such alloys the eutectic is effectively very broad so that the glass may be prepared over a wide range of composition, thus avoiding the need for a ternary al-loy. Superconducting properties of both kinds of al-loy have been quite extensively studied: Good recent reviews are given by Johnson[1] and Poon.[2]

Developments have also been made in crystalline superconductivity,[3] the principal feature of which relevant to the present work has been the realization that in order to have a quantitatively accurate calcu-lation of T_c, it is frequently necessary to include the influence of spin fluctuations, even in those systems which are not generally thought of as strongly enhanced magnetically. For example, Rietschel and Winter[4] showed that in Nb and V, T_c came out to be about a factor 2 too large if spin fluctuations were ignored and more recently Orlando and Beasley,[5] analyzing various properties of some well-known $A15$ compounds, arrived at similar conclusions. It has even been suggested that spin fluctuations may prove to be an ultimate barrier against high T_c.[3]

since the high density of states necessary for super-conductivity is also favorable to the formation of spin fluctuations.

So far as we can determine, no similar effort has been made to incorporate spin fluctuations into an understanding of superconductivity in metallic glasses, though their potential importance has been recognized.[6] Perhaps this is not surprising in view of the relative newness of the field; furthermore, sys-tems on which systematic surveys have been made are those with low (but, as we shall show, not negli-gible) spin-fluctuation effects. For example, a recent study on Cu-Zr (Ref. 7) described the entire data us-ing the simple McMillan equation, and even the simple BCS equation gave a good description of cer-tain aspects of the data.[8] Though these approaches are adequate as a first approximation, they lead, as we shall see, to incorrect values for some physical parameters. Even in crystalline systems, little effort has been made to examine the effects of systemati-cally varying the spin fluctuations. One problem is that some of the most obvious candidates for such a study, for example Ni-Nb or Pd-Zr, do not exist as solid solutions across the compositional range and so present difficulties associated with mixed phases and changing crystal structure. Each crystal structure offers in general a different phonon spectrum and electronic density of states—quite dramatically so in some cases[8]—so that it is difficult to segregate out convincingly the effects of spin fluctuations. It is at this point that a great advantage of working with the glassy state appears. The very systems which do not mix in the crystalline phase form eutectic mix-tures, and so are frequently ideal for glass forma-tion. Glasses offer a more or less homogeneous

structure with relatively smooth, often monotonic, change of physical parameters with composition, as is well illustrated by Cu-Zr.[8,9] We therefore believe that metallic glasses should serve as an excellent matrix for examining systematic changes in spin fluctuations and their influence on superconductivity, and this has been the motivation for the present study. We have chosen to look at four binary systems: Zr containing, respectively, Cu, Ni, Co, or Fe. These systems have the advantage that they are relatively simple to make, have been extensively studied, and, consequently, are quite well characterized. They also offer a wide range of both superconducting and magnetic properties, allowing the transition from one regime to another to be followed closely.

II. EXPERIMENTAL METHODS

The amorphous ribbons were prepared by melt-spinning buttons of approximately 1.5 g of crystalline material. The buttons were prepared by arc melting appropriate amounts of Zr (99.99% pure) with Cu, Ni, Co, or Fe (all 99.999% pure) under titanium-gettered argon. Each button was melted several times to ensure homogeneity. The melt spinning was carried out under helium at 50 kPa pressure on to the rim of a copper wheel whose tangential velocity was about 50 ms.$^{-1}$ Debye-Scherrer x-ray photographs of the resulting ribbons using Ni-filtered Cu$K\alpha$ or Zr-filtered Mo$K\alpha$ radiation showed no sharp lines after 24 h exposure. The ribbons were typically 20-μm thick and 1.5-mm wide and after manufacture were stored in liquid nitrogen. Most of the ribbons were examined by electron beam microprobe; they were found to be homogeneous of the nominal concentration to within the resolution of the instrument (± 0.15 at. %). Each alloy system was subjected to an exhaustive analysis of crystallization characteristics using differential scanning calorimetry (DSC), x-ray photography, electrical resistance, and magnetic susceptibility. The results, which have been published elsewhere,[9] or are in preparation,[10] gave us great confidence in the quality of our samples and in the reproducibility of our methods of preparation. As will appear below, this is of particular importance in the case of Fe-Zr.

Superconductivity was studied through changes in the electrical resistance. The resistance was measured by a sensitive four-terminal method.[11] The temperature range available for resistance measurement was 60 mK to 1000 K, using different facilities for various ranges. The temperature dependence of the upper critical field $H_{c2}(T)$ was also determined from the resistive transition. Down to 1.2 K, a field of 4.5 T was available; in the dilution refrigerator range (below 1 K) the field was restricted to

0.25 T. The field was applied in the plane of the ribbon parallel to the long dimension. Temperature was measured by a calibrated carbon glass thermometer or calibrated Ge resistor according to the temperature range. Accuracy is of order 10 mK or better.

Interpretation of the data requires accurate knowledge of the resistivity and the density.[12] The density was measured by an Archimedes method with toluene as the medium, the accuracy ($\pm 0.75\%$) being limited by the amount of sample (about 60 mg) which could be weighed at any one time. The resistivity was found from the resistance of a one-meter length of ribbon together with the mass and the density. Because of the great homogeneity of sample dimensions we were able to obtain the resistivity to within $\pm 1.5\%$.

Magnetic susceptibility measurements were made at room temperature by a Faraday method with an estimated accuracy of 0.5%. Honda plots were necessary for Co- and Fe-rich samples, the correction being small. The susceptibility of both Fe-Zr and Co-Zr was also examined as a function of temperature in a vibrating sample magnetometer down to 4 K. No significant temperature dependences to the susceptibility were seen in any sample showing superconductivity, from which we conclude that there is no measurable local magnetic moment in these samples. (Samples containing more than 40 at. % Fe were ordered ferromagnetically and of course showed a strong temperature dependence to the susceptibility.)

Finally it should be mentioned that all samples were measured "as made." We have previously noted in Cu-Zr that a very substantial ($\sim 20\%$) decrease in T_c occurs if the sample is thermally relaxed by annealing at 200 °C for 2 h. In order to be able to have access to as wide a composition range of each alloy system as possible, we used unrelaxed samples. This underscores the need to maintain the samples at 80 K, since, even at room temperture, samples will thermally anneal over a period of some months.[13]

III. RESULTS AND DISCUSSION

Figure 1 shows the magnetic susceptibility and the superconducting transition temperature for the entire series of alloys. The susceptibility is the room temperature *valence* susceptibility X_v, the core susceptibility having been subtracted. For Zr, Cu, and Ni this presents no problem; for Fe and Co we have no simple way of knowing the core susceptibility. We have used the value for Ni as representative. Thus there is some uncertainty in the valence susceptibility of both Fe-Zr and Co-Zr. However, since

TABLE I. Measured parameters for Cu-Zr, Ni-Zr, Co-Zr, and Fe-Zr metallic glasses.

Composition	Density d (g/cm^3)	Resistivity ρ ($\mu\Omega$ cm)	T_c (K)	$\dfrac{dH_{c2}}{dT}\Big|_{T_c}$ (kOe/K)	χ_v (10^{-6} emu/mole)
$Cu_{25}Zr_{75}$	6.85±0.04	158±2	3.180	31.0±0.2	133.7
$Cu_{30}Zr_{70}$	6.89	162	2.780	28.6	125.9
$Cu_{33}Zr_{67}$	6.95	165	2.380	28.2	118.9
$Cu_{35}Zr_{65}$	7.00	166	2.250	27.7	116.0
$Cu_{40}Zr_{60}$	7.07	169.5	1.750	26.2	108.5
$Cu_{45}Zr_{55}$	7.14	171.5	1.250		96.64
$Cu_{50}Zr_{50}$	7.25	177	0.920		91.4
$Cu_{55}Zr_{45}$	7.34	180	0.650	23.2	84.47
$Cu_{60}Zr_{40}$	7.37	183	0.310	22.0	77.0
$Ni_{20}Zr_{80}$	6.80	160	3.970	29.7	152.8
$Ni_{24}Zr_{76}$	6.88	165.5	3.590	27.1	150.9
$Ni_{29}Zr_{71}$	6.93	169	3.240	30.1	145.1
$Ni_{33}Zr_{67}$	7.06	168	2.885	28.6	140.7
$Ni_{36.5}Zr_{63.5}$	7.10	173	2.560	28.8	136.8
$Ni_{40}Zr_{60}$	7.17	176	2.350	29.0	131.0
$Ni_{45}Zr_{55}$	7.32	185	1.830	27.9	124.35
$Ni_{50}Zr_{50}$	7.50	183.5	1.400	26.7	117.4
$Ni_{55}Zr_{45}$	7.63	180.0	1.100	21.4	110.8
$Ni_{60}Zr_{40}$	7.81	175.5	0.600	20.6	107.15
$Ni_{63.7}Zr_{36.3}$	7.96	172.0	0.300	18.4	104.7
$Ni_{67}Ni_{33}$	8.05	168.0	0.130		101.1
$Co_{20}Zr_{80}$	6.90	162	4.001	34.3	162.8
$Co_{25}Zr_{75}$	7.00	164	3.691	30.0	156.2
$Co_{30}Zr_{70}$	7.00	173	3.291	31.8	151.6
$Co_{33}Zr_{67}$	7.12	176	3.002	32.7	149.8
$Co_{35}Zr_{65}$	7.20	175	2.758	31.4	149.1
$Co_{40}Zr_{60}$	7.35	180	2.050	31.5	158.6
$Co_{45}Zr_{55}$	7.40	183.5	1.070	32.9	166.0
$Co_{47}Zr_{53}$	7.63	176.5	0.700	30.6	174.2
$Fe_{20}Zr_{80}$	6.75	162	3.300	37.1	198.3
$Fe_{24}Zr_{76}$	6.78	165	2.100	34.0	215.1
$Fe_{25}Zr_{75}$	6.80	166	1.820	35.7	223.5
$Fe_{27}Zr_{73}$	6.84	166.5	1.300	35.3	231.0
$Fe_{28}Zr_{72}$	6.85	167	0.600	33.9	240.0

their susceptibility is rather larger than Ni-Zr and Cu-Zr and, since, also the alloys are Zr rich, the error remains insignificant. T_c was determined in the usual way as the midway point on the R vs T transition. Apart from one or two samples at the extreme high—Zr-concentration limit of the glass-forming range, all the transitions were very sharp; the temperature difference between the 90% and 10% points of the resistance change is typically less than 20 mK for Cu-Zr, Ni-Zr, and Co-Zr, and 35 mK for Fe-Zr. The experimental data are summarized in Table I.

It will be noticed that both T_c and χ_v essentially converge towards one value at pure Zr but that otherwise the behavior of each of the four alloy systems is entirely different. Superconductivity is far more rapidly suppressed as one moves away from Zr in the alloys containing Co and Fe than those with Ni and Cu. This we interpret as the result of much stronger spin fluctuations in Co-Zr and Fe-Zr. Spin fluctuations tend to stabilize parallel spin configuration and to act as pair breakers. Their presence is clearly reflected in the dramatic increase in susceptibility in Fe-Zr and Co-Zr. Equally significant perhaps is the contrast in the behavior of dT_c/dx, x being the Zr concentration, which increases with x for Cu-Zr, is constant for Ni-Zr, and diminishes with x for Co-Zr and Fe-Zr. The collapse of superconductivity is particularly spectacular in Fe-Zr, where it would appear that dT_0/dx may actually diverge close to $x=0.71$, T_c being 0.6 K for $x=0.72$ and less than 0.06 K for $x=0.71$. This collapse
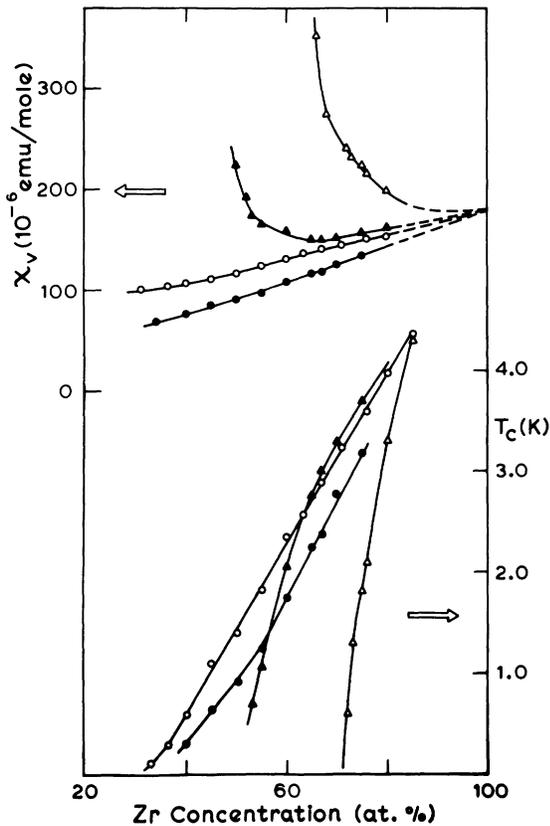
FIG. 1. The valence magnetic susceptibility and the superconducting transition temperature for Zr-based metallic glasses. ● = Cu-Zr; ○ = Ni-Zr; ▲ = Co-Zr; and △ = Fe-Zr.

occurs as one would expect at the point where the susceptibility begins to increase strongly.

Although Fig. 1 strikingly illustrates the influence of spin fluctuations in superconductivity, a quantitative assessment of the effect is harder to obtain.

Various authors[16,17] have suggested that the influence of spin-fluctuations may be included by modifying the McMillan equation[18] as follows:

$$T_c = \frac{\Theta_D}{1.45} \exp\left[- \frac{1 + \lambda_{ep} + \lambda_{sf}}{\lambda_{ep} - \lambda_{sf} - \mu^*} \right], \tag{1}$$

where λ_{ep} and μ^* are the electron-phonon and Coulomb interaction parameters in the usual McMillan equation, and λ_{sf} is the spin-fluctuation mass enhancement given in the early treatment of spin fluctuations[19]:

$$\lambda_{sf} = \frac{9}{2} \bar{I} \ln\left[1 + \frac{P_1^2}{12} \frac{1}{1 - \bar{I}} \right]. \tag{2}$$

$\bar{I}$ is the familar Stoner enhancement factor in the valence magnetic susceptibility which is[20]

$$\chi_v = \frac{\mu_B^2 N^b(0)}{1 - \bar{I}}, \tag{3}$$

and P_1 is the momentum cutoff for spin fluctuations expressed as a fraction of the Fermi momentum. Equation (1) may be obtained from the McMillan equation by letting

$$\lambda_{ep} \rightarrow \lambda_{ep} / (1 + \lambda_{sf})$$
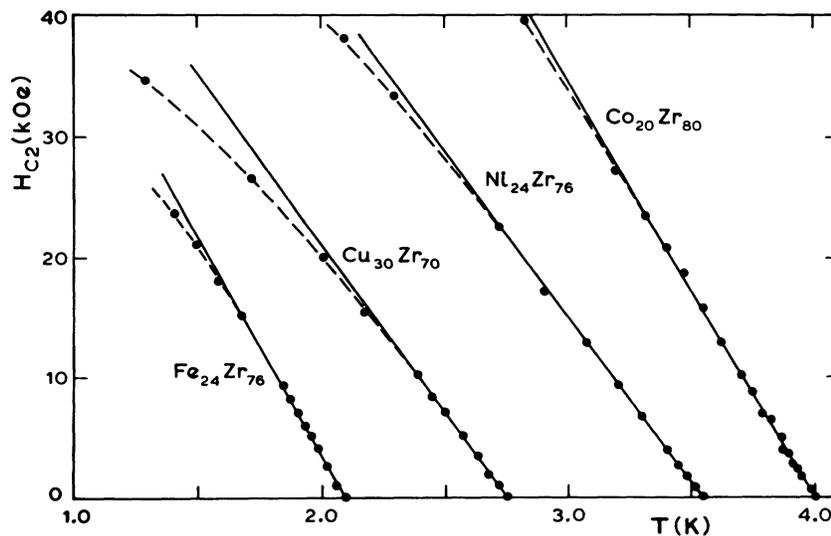
FIG. 2. The upper critical field against temperature for some representative Zr-based metallic glasses.

and

$$\mu^* \rightarrow (\mu^* + \lambda_{sf})/(1 + \lambda_{sf})$$

(Ref. 17), i.e., λ_{ep} is renormalized and μ^* is both enhanced and renormalized. Equation (1) shows that spin fluctuations cannot simply be handled by taking a new value of λ_{ep}. In (3), $N^b(0)$ is the bare density of electron states at the Fermi energy.[20] $N^b(0)$ is difficult to obtain directly from simple measurement. The closest is to find the "specific-heat" density of states, $N^\gamma(0)$, either from the electronic specific-heat coefficient γ or from the rate of change of H_{c2} with temperature at T_c. $N^\gamma(0)$ is larger than $N^b(0)$ by a mass enhancement factor

$(1 + \lambda_{ep} + \lambda_{sf})$. If $N^\gamma(0)$ is to be obtained from the slope of the upper critical field, the samples should be at "extreme dirty limit" where the coherence length is determined by the electronic mean free path. In this case the Ginsburg-Landau-Abrikosov-Gor'kov theory[21] gives

$$N^\gamma(0) = -(9.451 \times 10^{-10})\frac{M}{\rho d}\left[\frac{dH_{c2}}{dT}\right]_{T_c}. \quad (4)$$

The prefactor in the above equation is chosen so that $N^\gamma(0)$ comes out in states/eV atom, provided M the molecular weight is in grams, d the density in grams/cm^{-3}, and ρ the normal-state resistivity in

TABLE II. Derived parameters using Eqs. (1)–(4) for Cu-Zr, Ni-Zr, Co-Zr, and Fe-Zr metallic glasses. $N^\chi(0)$ is the "susceptibility density of states," i.e., $N^b(0)/(1-\bar{I})$. The remaining parameters are defined in the text.

Composition	States/eV atom $N^\chi(0)$	$N^\gamma(0)$	$N^b(0)$	$\bar{I}$	λ_{sf}	λ_{ep}
$Cu_{25}Zr_{75}$	4.32	2.05	1.044	0.758	0.145	0.818
$Cu_{30}Zr_{70}$	4.07	1.845	0.947	0.768	0.155	0.793
$Cu_{33}Zr_{67}$	3.84	1.80	0.963	0.749	0.137	0.732
$Cu_{35}Zr_{65}$	3.76	1.77	0.958	0.745	0.133	0.714
$Cu_{40}Zr_{60}$	3.43	1.57	0.867	0.747	0.135	0.675
$Cu_{45}Zr_{55}$	3.12	1.48[a]	0.858	0.725	0.117	0.608
$Cu_{50}Zr_{50}$	2.95	1.39[a]	0.826	0.720	0.114	0.568
$Cu_{55}Zr_{45}$	2.73	1.22	0.726	0.734	0.124	0.556
$Cu_{60}Zr_{40}$	2.55	1.11	0.681	0.733	0.123	0.507
$Ni_{20}Zr_{80}$	4.73	2.06	0.949	0.799	0.193	0.976
$Ni_{24}Zr_{76}$	4.67	1.96	0.912	0.8045	0.201	0.947
$Ni_{29}Zr_{71}$	4.49	1.84	0.885	0.806	0.203	0.910
$Ni_{33}Zr_{67}$	4.35	1.72	0.816	0.8125	0.214	0.893
$Ni_{36.5}Zr_{63.5}$	4.23	1.64	0.788	0.8136	0.215	0.866
$Ni_{40}Zr_{60}$	4.05	1.52	0.747	0.821	0.228	0.867
$Ni_{45}Zr_{55}$	3.85	1.37	0.656	0.8297	0.244	0.846
$Ni_{50}Zr_{50}$	3.63	1.245	0.613	0.835	0.255	0.824
$Ni_{55}Zr_{45}$	3.43	1.09	0.498	0.8498	0.289	0.841
$Ni_{60}Zr_{40}$	3.31	0.99	0.462	0.8604	0.318	0.824
$Ni_{63.7}Zr_{36.3}$	3.24	0.867	0.386	0.881	0.388	0.85
$Ni_{67}Ni_{33}$	3.13	0.82[a]	0.352	0.8818	0.391	0.825
$Co_{20}Zr_{80}$	5.26	2.35	0.987	0.8125	0.214	1.015
$Co_{25}Zr_{75}$	5.05	2.00	0.894	0.823	0.232	1.005
$Co_{30}Zr_{70}$	4.90	1.89	0.857	0.825	0.236	0.969
$Co_{33}Zr_{67}$	4.84	1.855	0.853	0.8238	0.233	0.942
$Co_{35}Zr_{65}$	4.82	1.755	0.795	0.835	0.255	0.952
$Co_{40}Zr_{60}$	5.13	1.67	0.728	0.858	0.311	0.982
$Co_{45}Zr_{55}$	5.37	1.61	0.709	0.868	0.341	0.930
$Co_{47}Zr_{53}$	5.63	1.57	0.673	0.8805	0.386	0.948
$Fe_{20}Zr_{80}$	6.14	2.47	1.124	0.817	0.221	0.981
$Fe_{24}Zr_{76}$	6.66	2.284	1.009	0.8485	0.286	0.978
$Fe_{25}Zr_{75}$	6.92	2.30	1.014	0.854	0.300	0.974
$Fe_{27}Zr_{73}$	7.20	2.285	1.008	0.860	0.317	0.950
$Fe_{28}Zr_{72}$	7.42	2.14	0.942	0.873	0.358	0.913

[a]Interpolated values.

Ω cm. dH_{c2}/dT should be expressed in Oe K^{-1}. Typical data for one alloy in each system is shown in Fig. 2. The validity of Eq. (4) in amorphous superconductors has been verified in a number of systems, and in the present case we find that the values of $N^{\gamma}(0)$ we obtain in Cu-Zr and Ni-Zr (see Table II) are in good arrgement with specific-heat data.[15,22,23] Equations (1)–(3) have been used together with specific-heat data, to analyze superconductivity in $A15$ compounds.[5] Values obtained for Nb and V were consistent with numerical calculations[14] starting from the Eliashberg equations.

In order to apply Eqs. (1)–(4) to our data we need to know the three parameters Θ_D, μ^*, and P_1^2. Values of Θ_D for some Cu-Zr compositions and $Ni_{24}Zr_{76}$ have been given by various authors.[15,23,24] There is some scatter in the data, but a best fit to the data yields

$$\Theta_D = 360 - 250x \text{ K} ,$$

which we have taken as representative. No figures are available for Co-Zr and Fe-Zr; we have used the same values as for Cu-Zr and Ni-Zr. We do not believe serious errors result from this. There is no independent means of estimating μ^* and, as has been

FIG. 3. Variation of the electron-phonon parameter λ_{ep} and the spin-fluctuation parameter λ_{sf} for Zr-based metallic glasses. ● = Cu-Zr; ○ = Ni-Zr; ▲ = Co-Zr; and △ = Fe-Zr.

generally done in the past, we take a value of 0.13 and observe only that the most of the data fitting is not too sensitive to the exact value of μ^*. The choice of P_1^2 presents a much harder problem since there is no *a priori* value of P_1^2 for glassy systems. However, rather than leave it as a fitting parameter for each composition, we have tried to arrive at one value of P_1^2 for all four alloy systems in such a way that, as shown below, the results are internally as well as externally consistent. Such a value turns out to be $\frac{1}{6}$. The data may now be uniquely analyzed, leading to the parameters listed in Table II.

The most important parameters to appear in Table II are λ_{ep} and λ_{sf}. They are also illustrated graphically in Fig. 3 where we see how, for the particular P_1^2, μ^*, and Θ_D used, the two converge on a single set of values for pure Zr. A larger value of P_1^2 causes the various curves of λ_{sf} to cross over and not to converge, and, even more alarmingly, causes λ_{ep} to *increase* with decreasing Zr concentration in Ni-Zr, Co-Zr, and Fe-Zr, in contrast to the bare density of states, $N^b(0)$, which decreases in all three systems. Such behavior seems quite unphysical since it would imply a very large increase in the electron-phonon interaction as the Zr concentration is reduced. A further check comes from comparing our values of $N^b(0)$ with calculated values[25,26] (see Table III). In four out of the six cases where comparisons are possible the agreement is excellent. In the remaining two ($Cu_{30}Zr_{70}$ and $Ni_{30}Zr_{70}$ from Ref. 25), examination of the original paper shows $N^b(0)$ to be very sensitive to the precise value taken for the Fermi energy, so the discrepancies are not significant. A final check may be provided by the behavior of the electron mass enhancement factor $(1 + \lambda_{ep} + \lambda_{sf})$. Once again this is sensitive to P_1^2; with a value of $\frac{1}{6}$, the factor turns out to lie between 1.7 and 2.3. A larger value of P_1^2 causes λ_{sf} to increase dramatically as one moves towards Ni, Co, and Fe, with corresponding effect on the mass enhancement. For example, in $Ni_{67}Zr_{33}$ the mass enhancement becomes 3.89 for $P_1^2 = \frac{1}{4}$. Corresponding figures for $Fe_{28}Zr_{78}$ and $Co_{47}Zr_{53}$ are 3.56 and 3.72, respectively. We do not believe such large values are reasonable and they are also at variance with the behavior of the thermoelectric power $S(T)$. According to Jäckle[27] and Gallagher and Greig[28] the ratio of S/T at low temperatures to that at high temperatures is in fact just the mass enhancement factor. Figures for this ratio are shown in Table III taken from published[28,29] and unpublished[30] data. The results do not suggest a strong increase at the Ni-, Co-, and Fe-rich end, rather the reverse. The figures are in fact in reasonable agreement with those obtained using $P_1^2 = \frac{1}{6}$.

The physical significance of P_1^2 is not clear. Generally it is accepted that, for crystalline materials P_1
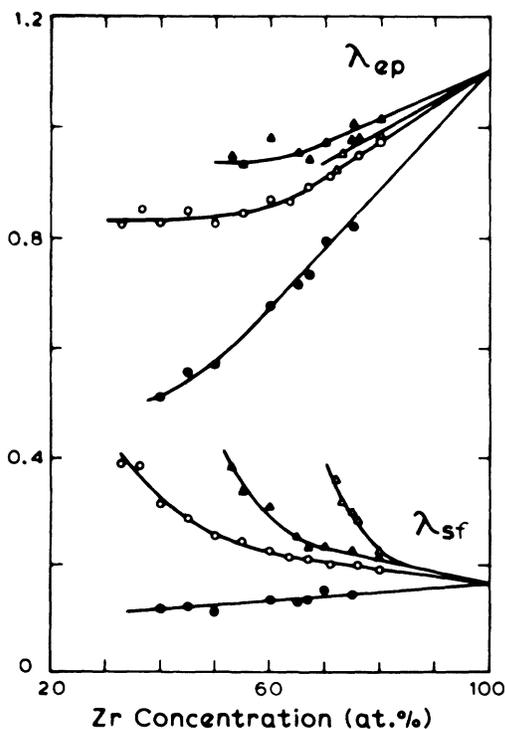
TABLE III. Comparisons of experimental and theoretical values for bare electronic density of states (upper table) and comparisons of electron mass enhancement with thermopower data (lower table; see text).

| Composition | $N^b(0)$ (States/eV atom) | | |
	Ref. 26	Ref. 25	This work
$Cu_{30}Zr_{70}$	1.23		0.95
$Cu_{33}Zr_{67}$		0.9	0.96
$Cu_{60}Zr_{40}$		0.78	0.68
$Ni_{30}Zr_{70}$	1.07		0.89
$Co_{30}Zr_{70}$	0.83		0.86
$Fe_{30}Zr_{70}$	0.96		0.94 (for $Fe_{28}Zr_{72}$)
	$(S/T)_{low}/(S/T)_{high}$	$(1+\lambda_{ep}+\lambda_{sf})$	
$Cu_{25}Zr_{75}$[a]	1.85±0.2	1.95	
$Cu_{60}Zr_{40}$[a]	1.82±0.2	1.63	
$Ni_{20}Zr_{80}$[b]	2.4 ±0.3	2.17	
$Ni_{63.7}Zr_{36.3}$[b]	2.18±0.2	2.23	
$Co_{20}Zr_{80}$[c]	2.26±0.2	2.23	
$Co_{47}Zr_{53}$[c]	1.87±0.4	2.33	
$Fe_{20}Zr_{80}$[c]	2.01±0.2	2.20	
$Fe_{28}Zr_{72}$[c]	> 1.39	2.27	

[a]Reference 28.
[b]Reference 29.
[c]Reference 30.

should be of order unity, and in describing the A15 compounds, Orlando and Beasley[15] used $P_1^2 = \frac{1}{2}$, which, as explained, gives quite impossible parameters here. Perhaps the relatively low value of the cutoff momentum (and hence energy) is a result of the disordered structure. But much more study of spin fluctuations in a disordered material is required before any useful conclusions may be drawn.

A few other points should be made about the parameters in Table II. In Fe-Zr the Stoner parameter increases strongly with increasing Fe, as one would expect. If the plot is continued, it *suggests* that ferromagnetism would set in somewhere between 35 and 40 at.% Fe. We have in fact examined two samples of $Fe_{40}Zr_{60}$ and $Fe_{33}Zr_{67}$, respectively, and have indeed found that the former undergoes a paramagnetic to ferromagnetic transition at about 200 K, while the latter remained paramagnetic to 4.2 K. Such a result gives some support to the analysis, though it must be pointed that the validity of Eq. (2) in alloys is not established.

Finally we can see from our results why Cu-Zr could apparently be well described without requiring the inclusion of spin fluctuation. The reason is that spin fluctuations are weak in Cu-Zr and grow weaker as one moves towards the Cu-rich end, in contrast to the other three systems. Nonetheless such a fit yields an incorrect value for λ_{ep}, as is shown by the mass enhancement determined by thermopower.

IV. CONCLUSION

The behavior of the Zr-based glasses illustrates very clearly the influence of spin fluctuations on superconductivity. In Cu-Zr the influence diminishes as one moves away from the Zr-rich end; in the other three systems it increases with decreasing Zr. Also at fixed Zr concentration it increases as one moves from Cu towards Fe. This much is directly evident from the data.

Quantitative analysis may be consistently handled using a modified form of the McMillan equation yielding parameters which are both internally consistent and in agreement with outside evidence. Nonetheless such a fitting can only be regarded as a first step and a great deal more study is required.

Ideally the problem should be tackled by numerical solution of the Eliashberg equations which are known to give numerically reliable estimates of T_c in crystalline materials. However, for this a much more detailed and reliable knowledge of the lattice vibrational spectrum is required than is currently available. Such information does not appear to be immediately forthcoming. In the meantime three sets of experiments would clearly add valuable information. One is to study closely the influence of thermal relaxation which is known to change λ_{ep} but not λ_{sf}.[8] The second is to carry out superconducting tunneling experiments so as to obtain more

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