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Amorphous superconducting Zr_xCu_{1-x}: Electronic properties, stability, and low-energy excitations

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Amorphous Zr_xCu_{1-x} alloys $(0.50 \leq x \leq 0.74)$ prepared by melt-spinning are investigated by means of electrical and thermal measurements. The negative temperature coefficient of the electrical resistivity suggests that the criterion $2k_F \approx k_p$ is always fulfilled in this system [k_F is the Fermi wave number, k_p is the position of the first maximum of the structure factor $S(k)$]. The high density of states $N_\gamma(E_F)$ as inferred from specific-heat measurements originates from the d electrons of Zr. The bare density of states [determined from $N_\gamma(E_F)$ with the aid of the electron-phonon coupling constant λ] is 3 times higher than that calculated from the free-electron model and almost independent of the Zr concentration. Phonon-electron scattering as determined by thermal-conductivity measurements shows a similar deviation from free-electron behavior. A *decisive* test of the Nagel-Tauc condition for high (meta-) stability of the metallic glasses is not possible due to the apparent failure of both free-electron and rigid-band models. All samples investigated are superconducting and belong to the extreme-type-II superconductors. Fluctuation-induced paraconductivity extends up to $1.5T_c$. An analysis of the electron-phonon coupling constant λ as determined from T_c indicates that the electron-ion matrix element $\langle I^2 \rangle$ varies strongly across the Zr_xCu_{1-x} series. The size of λ, the jump of the specific heat at T_c, and its drop at low temperatures show that Zr-Cu alloys are weak- to intermediate-coupling superconductors. The relatively high T_c values of the Zr-rich metallic glasses allow the observation of a linear specific-heat term for $T \ll T_c$ in all these samples which is due to localized low-energy excitations. These excitations are also seen—via strong phonon scattering— in the thermal conductivity.

I. INTRODUCTION

Amorphous superconductors were studied 30 years ago by Buckel and Hilsch[1] in quench-condensed films of alloys of simple metals. Liquid-quenched amorphous metals, which are usually called metallic glasses, were first studied by Duwez.[2] More recently, the rather easy preparation of amorphous ribbons by the melt-spinning technique opened the field for various applications of these metallic glasses, which explains the tremendous interest herein.[3-11] Originally most of the available metallic glasses contained about 80 at. % transition metals and about 20 at. % metalloids. In the past few years metallic glasses containing only transition metals have become known which, in favorable cases, were not restricted to a small concentration range close to a eutectic concentration. One of these metallic glasses, which in addition becomes superconducting, is the Zr_xCu_{1-x} system, whose properties on the high-Zr-concentration side $(0.50 \leq x \leq 0.74)$ are the subject of the present investigation. The interest in this amorphous superconducting metal stems from three major points.

(i) The wide glass-forming range in this system allows one to look for a possible contribution of the electronic properties of metallic glasses to the relative stability of the metastable noncrystalline phase. Such a contribution of the conduction electrons was proposed by Nagel and Tauc,[12] where "good stability" was expected when the Fermi wave vector k_F obeys the condition $2k_F \approx k_p$ (k_p is the position of first maximum of the structure factor). Low-temperature specific-heat measurements yield the concentration-dependent electronic density of states at the Fermi level. Measurements of the crystallization temperature, on the other hand, lead to a reliable measure of the stability. Hence both quantities can be compared with each other in order to check the above idea, because the temperature dependence of electrical resistance suggests that $2k_F \approx k_p$ is indeed valid for glassy ZrCu.

(ii) The superconducting properties of amorphous transition metals[13,14] seem to differ widely from those of amorphous simple metals.[15] The simple metals are mostly strong-coupling superconductors with electron-phonon coupling constants $\lambda > 1$. Their electronic properties are well described by the free-electron model.[16] For amorphous transition metals the validity of the free-electron model is not expected because of partially occupied d states. Therefore, a detailed comparison between the measured density of states (renormalized by virtue of the electron-phonon interaction with the aid of T_c measurements) and the free-electron density of states appears worthwhile. In addition, measurements of the thermal conductivity allow a determination of the phonon-electron scattering coefficient in amorphous metal which can be compared to the free-electron-model coefficient. The electron-phonon coupling constant λ can be further analyzed on the basis of McMillan's factorization,[17] and the physical origin of the concentration dependence of λ is discussed on similar grounds, as previously done for amorphous La–noble-metal alloys.[18]

(iii) The superconductivity of amorphous Zr_xCu_{1-x} allows us (for $T \ll T_c$) to corroborate the existence of configurational low-energy excitations in amorphous metals[19,20] and to look for their concentration dependence. These excitations can be described as two-level systems (TLS). The main difference with respect to amorphous insulators lies in the additional coupling to the conduction electrons in amorphous metals.[21] Amorphous superconductors are the obvious choice to investigate the contributions of two-level systems to the thermal conductivity κ and specific heat C, because well below T_c the electronic contributions to κ and C and also the TLS electron coupling can be neglected. In view of the unresolved microscopic origin of the low-energy excitations, measurements of the specific heat well below T_c can clarify whether two-level systems are in fact of intrinsic nature. Measurements of the thermal conductivity below T_c yield information about the coupling of TLS to phonons.

The possibility of dealing with these three major points of interest in a single metallic-glass system which can be produced in a wide concentration range is very intriguing. The Zr_xCu_{1-x} system of the present detailed investigation is such a system. Preliminary reports of some aspects of this work have already appeared.[22–26]

This paper is organized as follows. Section II contains the experimental methods. The results of the measurements are presented in Sec. III. Section IV is devoted to a discussion of the three major aspects outlined in the above Introduction. Finally, the most important conclusions of our work are summarized in Sec. V.

II. EXPERIMENTAL DETAILS

A. Sample preparation and resistance measurements

The Zr_xCu_{1-x} alloys for the present investigation are prepared by arc-melting the appropriate amounts of the constituents (99.999% pure Cu and 99.98% pure Zr) under high-purity argon. Amorphous ribbons are then produced by the centrifugal melt-spinning technique: The alloy is melted inductively in either a quartz or a BN tube and then pressed through a circular orifice of 0.2–0.3-mm diameter by He gas onto the inside of a convexly shaped rotating Cu drum. The polished inner surface (diameter ~8 cm) of the drum has a maximum orbital velocity of 33.5 m/s. The whole process is done in a He atmosphere to reduce oxidation and to assure a smooth ribbon geometry. All the ribbons have an average thickness of 20 μm and an average width of about 1 mm.

The amorphous structure of the samples is always checked immediately after quenching by x-ray analysis (Cu$K\alpha$ radiation). The Debye-Scherrer diagrams show no indication of sharp rings. The composition of a $Zr_{0.60}Cu_{0.40}$ sample was checked by neutron-activation analysis at the Kernforschungsanlage (KFA) Jülich where the Zr and the Cu concentrations were determined independently. No deviation from the nominal concentration could be detected within the uncertainty of measurements of 1 at. %.[27]

The *electrical resistance* of the samples is measured with a standard four-probe technique as a function of temperature from 30 mK up to 1000 K with the use of different devices. At temperatures below 4.2 K, a demagnetization cryostat with an additional superconducting solenoid operating up to 7 T is used for measurements of the *superconducting transition temperatures* T_c and the *upper critical field* H_{c2}. H_{c2} is determined from the resistive transition with the field oriented parallel to the ribbon. The transition temperature is chosen as that temperature at which the resistance has decreased to 50% of the residual resistance. Between 4.2 and 300 K the measurements are performed in a liquid-He vessel with a Si diode as thermometer. Above room temperature the resistance is measured in a highly evacuated quartz tube heated electrically. A Ni-NiCr thermocouple is used to measure the temperature. The electrical resistance is measured generally with a lock-in amplifier at low frequencies. At low temperatures silver paint and above room temperature clamp contacts of Pt are used to establish electrical lead connection. The accuracy of the *resistance* measurement is better than 1%. Electrical resistivities are calculated from the measured dimensions of the ribbons. The uncertainties in the *resistivity* arise mainly from the uncertainties in the measurements of the ribbon thickness and are only accurate to 15–20%.

B. Thermal-conductivity and specific-heat measurements

The *thermal conductivity* κ is measured between 0.5 and 20 K in a He^3 cryostat using the standard four-terminal steady-state technique with one heater and two thermometers. Owing to the poor diffusivity of the samples, the times necessary to acquire steady heat flow are extremely long. Therefore, for each measurement 20–30 strips of the ZrCu alloys are clamped together with four copper clamps which carry heater and thermometers and provide the thermal anchoring, respectively (see the inset of Fig. 6 for details). In this way, the thermal shunt by the electrical leads (NbTi or Manganin) is reduced to less than 2% of the thermal conductance of the sample. For further details of the κ measurement of samples of poor diffusivity, see, e.g., Ref. 28. The resolution of the thermal-conductivity measurements is about 2%. However, absolute values of κ are certain only within 15–20%, again because of the uncertainty in the determination of the sample geometry.

The specific heat of the amorphous ribbons is measured between 0.1 and 7 K in two different calorimeters. A standard He cryostat is used for measurements between 1.5 and 7 K. Owing to the small heat capacities of the samples and the long internal relaxation time, a modified heat-pulse technique was employed.[29,30] The amorphous ribbons with masses ranging from 0.5 to 1.5 g are tightly wound on a small coil form. Only the last layer is fixed with 0.3 to 0.5 mg of Ge 7031 varnish. The coil form is machined from CuBe and carries a strain gauge as heater and a carbon resistor as thermometer. This thermometer is calibrated in a separate run against a calibrated Ge resistance thermometer which is mounted on a copper block providing a constant-temperature reservoir.

The calibration is checked each run at liquid-He temperature. The electrical contacts are made with single-core NbTi superconducting wires which are thermally connected to the constant-temperature reservoir. These wires provide the main thermal link to the bath.

The background heat capacity of the addenda—including sample holder, thermometer, heater, leads, etc.—is determined in a separate run. At $T=1.5$ K the heat capacity of the addenda is about 20% of the total heat capacity. Owing to the high portion of the addenda and in order to check the apparatus for systematic errors, an independent measurement of the heat capacity of high-purity copper was performed. The deviation of the data from values of literature[31] is less than 1% for the Sommerfeld constant γ and less than 6% for the Debye temperature Θ_D.

The measurements of the heat capacity from 0.1 K up to 3 K are made in a He^3-He^4 dilution refrigerator. A "quasiadiabatic" heat-pulse technique is employed.[32] The sample holder consists of a 0.2-mm-thick Si plate which carries on one side an evaporated Au heater and a doped Si thermometer. The ZrCu samples (usually 20 strips with a total weight of about 40 mg) are attached to the other side with a small amount ($\sim 1-2$ mg) of Apiezon *N* grease. The Si plate is thermally coupled weakly to the mixing chamber with thin nylon threads and the heat capacity is determined from the initial temperature rise following a heat pulse.

The heat capacity of the sample holder, thermometer, heater, leads, etc., and the specific heat of Apiezon *N* grease[33] are determined in separate runs. The addenda heat capacity amounts to only 5×10^{-9} J/K at 0.1 K and rises to 1.5×10^{-7} J/K at 1 K. The ratio of the heat capacities of the ZrCu samples and of the addenda is typically ~ 0.5 between 0.1 and 0.3 K and rises to 5 at 1 K. Again, an independent check of the calorimeter with 40 mg of high-purity copper foil was done separately. The deviation from literature data is less than 10% in the whole temperature range. In the temperature region below 0.5 K, agreement between the measured specific heat and the copper reference specific heat[31] is better than 3%. Further details of the measuring method are planned to be published elsewhere.[34]

III. RESULTS

A. Resistance measurements

The temperature dependence of the electrical resistance R of all amorphous $\mathrm{Zr}_x\mathrm{Cu}_{1-x}$ $(0.50 \leq x \leq 0.74)$ alloys is shown in Fig. 1. R is normalized to its value at 10 K for the sake of comparison. Between 10 and 300 K, R always decreases with increasing temperature, the total variation being $\sim 4\%$. At low temperatures all $R(T)$ plots are slightly curved and only above 150 K nearly linear. The negative temperature coefficient of the resistance $-\alpha = -R^{-1}dR/dT$, evaluated for $T > 150$ K, is plotted as function of the Cu content in the inset. A maximum of α at 30 at. % Cu is visible. The value of the electrical resistivity ρ of these metallic glasses is about 200 $\mu\Omega$ cm. Because of the uncertainty of 15–20% for the absolute values of ρ (see Sec. II B) we refrain from indicating the data for each concentration.

For all $\mathrm{Zr}_x\mathrm{Cu}_{1-x}$ glasses investigated we observe superconductivity. The superconducting transition temperatures T_c of the as-quenched samples are shown in Fig. 2 where some data of other authors[35–38] are included. Very recently, Altounian *et al.*[39] reported on T_c measurements in a series of amorphous ZrCu alloys, which agree well with our data. T_c drops with increasing Cu content with a roughly linear slope $dT_c/dc = -0.095$ K/at. % Cu. (For clarity, c denotes the Cu concentration in at. % while x indicates the molar fraction of Zr.) A wide extrapolation of these data predicts a $T_c \approx 5.6$ K for the hypothetical case of "amorphous pure Zr." The transition width ΔT_c from 10% to 90% of the residual resistance is smaller than 20 mK for all samples (see inset of Fig. 3 as an example). These sharp T_c values hint at rather good homogenities of these metallic glasses. We note, however, that a current-voltage measurement always records the first superconducting current path through the sample. The transition widths resulting from specific-heat and thermal-conductivity experiments which measure bulk properties are clearly larger. Also, T_c as determined from these bulk properties is up to 0.1–0.2 K smaller than T_c obtained from the resistive transition. In this context special interest should be devoted to annealing effects below the glass temperature of amorphous alloys, which can modify their physical properties without crystallization. Preliminary measurements of T_c of ZrCu alloys show a decrease of ~ 0.2 K for $\mathrm{Zr}_{0.65}\mathrm{Cu}_{0.35}$ and $\mathrm{Zr}_{0.74}\mathrm{Cu}_{0.26}$ when annealed at 200 °C for several hours, while the electrical resistance changes only slightly during the annealing procedure. Further details are planned to be published elsewhere.[40] In this paper, we report only on as-quenched samples unless otherwise indicated.

The high normal-state residual resistance together with the small superconducting transition width permit the observation of superconducting fluctuations above T_c. The normalized electrical resis-

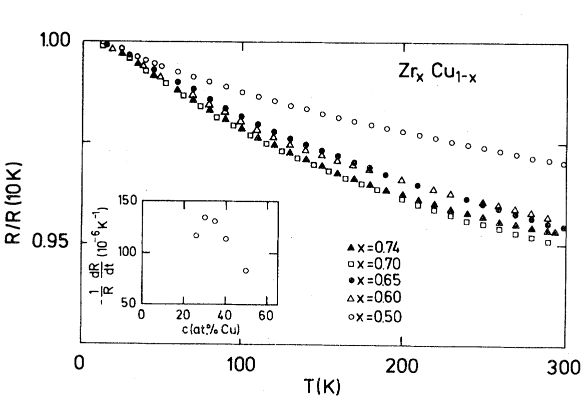

FIG. 1. Electrical resistance R (normalized to its value at 10 K) as a function of temperature T for various amorphous $\mathrm{Zr}_x\mathrm{Cu}_{1-x}$ alloys. Inset shows the linear temperature coefficient of R (taken at 250 K) as a function of the Cu concentration c.

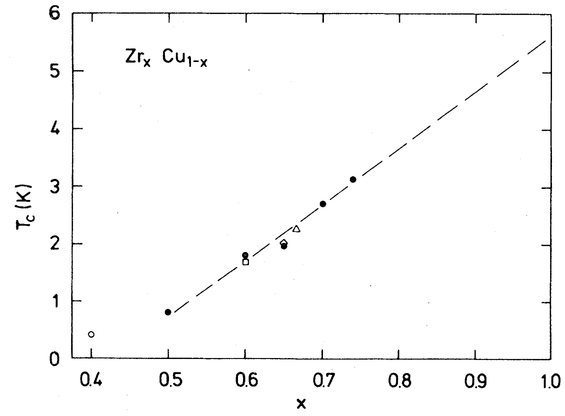

FIG. 2. Superconducting transition temperature T_c of amorphous ZrCu alloys as a function of the Zr concentration x (closed circles). Open symbols indicate data of other workers [diamond (Ref. 35), triangle (Ref. 36), square (Ref. 37), and circle (Ref. 38)]. Dashed line serves as visual guide.

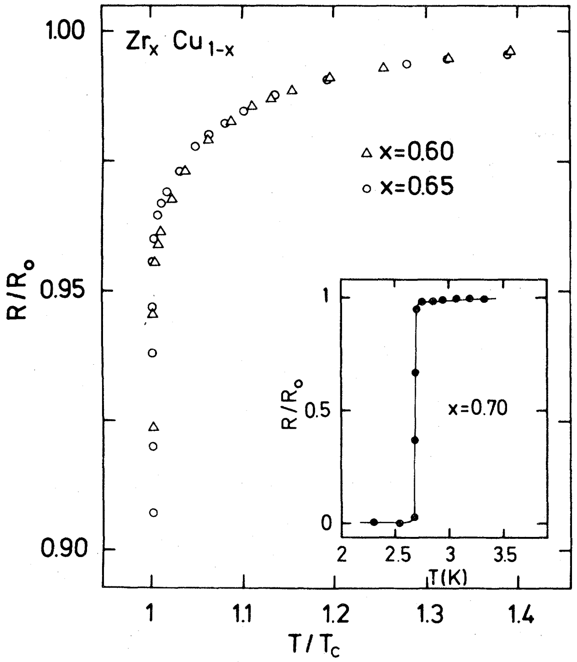

FIG. 3. Electrical resistance R (normalized to its maximum value R_0) as a function of temperature T (normalized to its superconducting transition temperature T_c) for $Zr_{0.65}Cu_{0.35}$ and $Zr_{0.60}Cu_{0.40}$. Inset shows the full transition of a $Zr_{0.70}Cu_{0.30}$ glass.

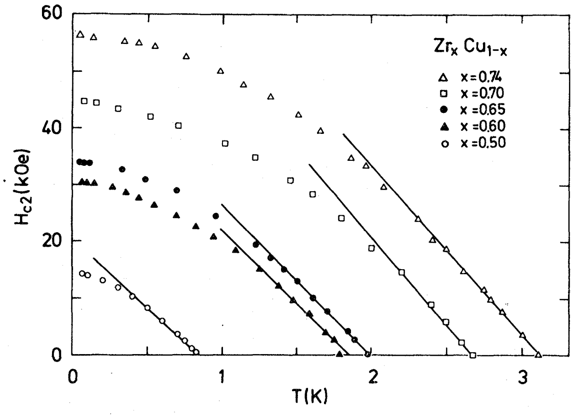

FIG. 4. Upper critical magnetic field H_{c2} of amorphous Zr_xCu_{1-x} as a function of temperature T for various x. Solid lines indicate a linear temperature dependence of H_{c2} near T_c.

tance R/R_0 of two ZrCu glasses as a function of the reduced temperature T/T_c is shown in Fig. 3. R_0 is the resistance value at the shallow maximum in $R(T)$ which occurs because of the negative temperature coefficient of the electrical resistivity. From Fig. 3, one infers that superconducting fluctuations extend up to $T/T_c \approx 1.5$. No difference between the two glasses is observed. The inset shows the full transition of $Zr_{0.70}Cu_{0.30}$ for comparison.

Figure 4 shows the upper critical field H_{c2} as function of temperature for all ZrCu glasses investigated. All $H_{c2}(T)$ curves are of approximately parabolic form. In the vicinity of T_c H_{c2} varies linearly with temperature as indicated by the solid lines. The slope $(dH_{c2}/dT)_{T_c}$ is about -28 kOe/K for all concentrations. Preliminary measurements indicate that annealing effects have no influence on the parabolic behavior of $H_{c2}(T)$ and on the slope near T_c while the T_c value itself is affected as mentioned above. With the Gorkov-Goodmann relation for the Ginzburg-Landau parameter κ,

$$\kappa = \kappa_0 + 7.5\times 10^3 \rho\gamma^{1/2}$$

(where ρ is the electric resistivity in Ω cm; γ is the Sommerfeld constant in erg/cm^3 K^2), and the results of the specific-heat measurement [see Sec. III C, item (i)], we estimate the Ginzburg-Landau (GL) parameter $\kappa > 80$, where κ_0 is the GL parameter of the pure material. As the density of ZrCu we take $\rho_d = 7.39$ g/cm^3.[41] This indicates that amorphous ZrCu alloys belong to the extreme-type-II superconductors as do other amorphous metals.[13]

All ZrCu glasses begin to crystallize above room temperature. The crystallization temperatures T_K are determined from the first significant deviation from the slightly negative temperature dependence of the electrical resistance. X-ray analysis of the heat-treated samples confirms that this determination of T_K is reliable. The crystallization temperature depends on the heating rate, which therefore is kept in all experiments at about 70 K/min. The first deviation of the electrical resistance is positive for some concentrations, e.g., $Zr_{0.60}Cu_{0.40}$ and negative for $Zr_{0.50}Cu_{0.50}$. Hence the electrical resistance seems to depend on the phase mixture into which the glassy metal crystallizes. Figure 5 shows the strong increase of T_K with Cu content. Measurements of the glass temperature T_g show even a linear dependence.[42] The absolute values of T_K differ in literature, which might be due to different quenching techniques, heating rates, and oxygen contamination.[43,44] However, the general trend of T_K with Cu concentration is unambiguous.

B. Thermal conductivity

The thermal conductivity κ for four Zr_xCu_{1-x} alloys ($0.50 \le x \le 0.74$) is shown as a function of

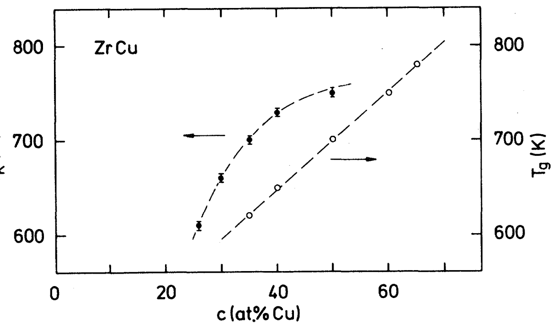

FIG. 5. Crystallization temperature T_K and glass temperature T_g for liquid-quenched ZrCu alloys as a function of Cu concentration. The T_g data are taken from Ref. 42. Dashed lines serve as visual guides.

temperature in Fig. 6. κ increases monotonically with T in the normal state, exhibiting a slight leveling off at higher temperatures, as seen most clearly for $x=0.5$. The increase of κ when the samples become superconducting indicates that phonons are the dominant heat carriers: Their thermal conductivity κ^{ph} is enhanced below T_c because of the progressive condensation of quasiparticles which act as scattering centers for phonons. (Throughout this paper the superscript to κ denotes the type of heat carrier and the subscript the scattering process. For example, κ_e^{ph} is the phonon thermal conductivity as limited by electron scattering only. Note that the addition of thermal resistivities for different scattering processes implies the use of the dominant phonon approximation.) From the high electrical resistivity ($\rho \approx 200\ \mu\Omega\,\text{cm}$) one indeed estimates a minor electronic contribution κ^e to the total thermal conductivity: $\kappa^e=(L/\rho)T=1.2\times10^{-4}T$, where $L=2.45\times10^{-8}\ \text{W}\,\Omega/\text{K}^2$, and κ^e is expressed in W/cm K. Hence κ^e/κ is about 20% to 30% at T_c. Of course, this ratio rapidly vanishes for $T \ll T_c$, hence $\kappa \equiv \kappa^{ph}$ sufficiently below T_c.

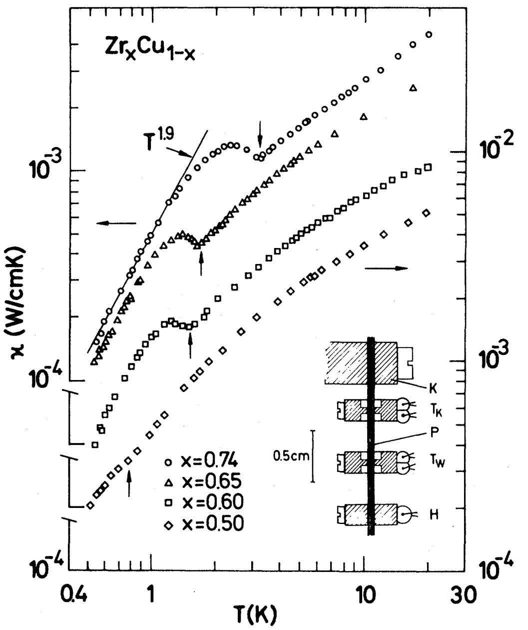

FIG. 6. Thermal conductivity κ of amorphous Zr_xCu_{1-x} as a function of temperature T in a double-logarithmic plot for various x. For clarity, each curve is shifted upward by a factor of 2. Vertical arrows indicate the superconducting transitions. Solid line represents the $T^{1.9}$ dependence of κ below 1 K for $Zr_{0.74}Cu_{0.26}$. Inset show the experimental arrangement for measurements of κ. K is the low-temperature reservoir. P denotes the sample, H the heater, and the temperature difference is measured between T_w and T_k.

Well below T_c, where both electron heat transport and phonon scattering by electrons are negligible, κ varies as T^m with $1.7 \le m \le 2$, e.g., $m=1.9$ for $x=0.74$ as indicated in Fig. 6. This T dependence and also the absolute magnitude of κ are characteristic of phonon scattering by low-energy excitations as observed in insulating[45] and metallic glasses.[19,20] The phonon thermal conductivity in amorphous ZrCu is limited by this "intrinsic" thermal resistivity $(\kappa_i^{ph})^{-1}$ and in addition near and above T_c, by $(\kappa_e^{ph})^{-1}$. Both scattering processes can be unambiguously separated by application of an overcritical magnetic field below T_c.[26] For a discussion of κ_e^{ph} and κ_i^{ph} we refer to Secs. IV B and IV C, respectively.

C. Specific heat

The specific heat C divided by the absolute temperature T, measured between 1.5 and 7 K, is shown in Fig. 7 as a function of T^2 for all ZrCu alloys. The straight lines represent best fits to the familiar specific-heat equation in the normal conducting state at low temperature ($T<\Theta_D/25$ where Θ_D is the Debye temperature):

$$C=\gamma T+\beta T^3\ . \tag{1}$$

The measured Sommerfeld constant γ for the metallic glasses increases monotonically with Zr concentration x and exceeds the values for the pure crystalline constituents considerably [Cu: $\gamma=0.7$ mJ/(mole K^2); Zr: $\gamma=2.8$ mJ/(mole K^2) (Ref. 46)].

For a first evaluation of the vibrational specific heat, we assume the Debye model (see, however, Sec. IV C) to express the coefficient β in terms of Θ_D. Θ_D of the ZrCu alloys (see Table I) is less

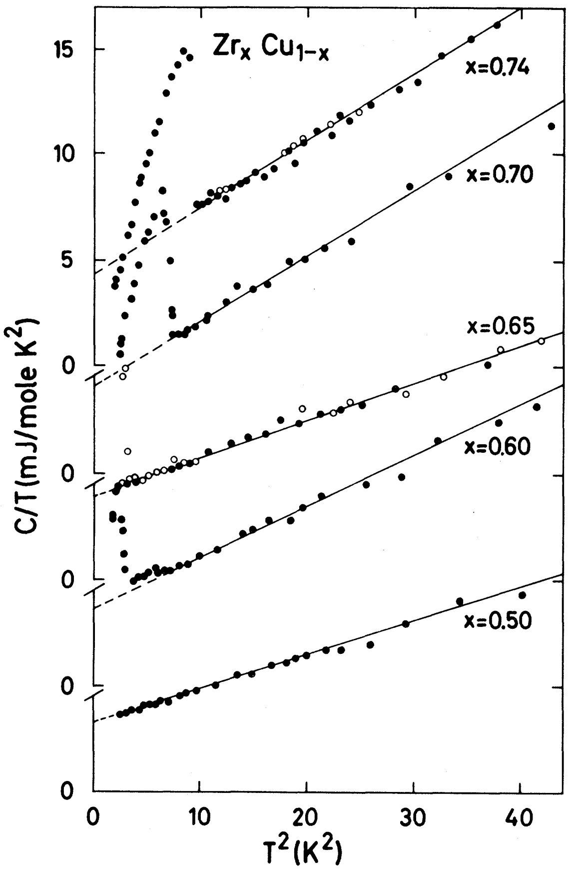

FIG. 7. Specific heat C divided by temperature T of amorphous Zr_xCu_{1-x} as a function of T^2 for various x. Each curve is shifted upward by 5 mJ/(mole K^2) for clarity. Solid lines indicate a best fit of $C = \gamma T + \beta T^3$ to the experimental data. Dashed lines are extrapolations of the fit to temperatures below T_c.

than the values for Cu ($\Theta_D = 343$ K) and Zr ($\Theta_D = 291$ K).[46] Deviations from Eq. (1) towards higher powers of T (i.e., T^5), as found for example in amorphous $Pd_{0.775}Si_{0.165}Cu_{0.06}$,[47] are not found in our ZrCu samples within the accuracy of the measurement.

For the samples with high Zr concentration the superconducting transition is observed with this experimental setup. The jump ΔC of the electronic specific heat at T_c will be analyzed together with the data obtained at lower temperatures (see also Table I). The specific heat of $Zr_{0.65}Cu_{0.35}$ has been measured twice. This seemed to be necessary because of the very different slope in the C/T vs T^2 plot. The second measurement, done after a new calibration of the system, shows no deviation from the first one. In addition, $Zr_{0.74}Cu_{0.26}$ was investigated twice to test the contribution of the addenda and to look for a possible effect of room-temperature anneal. More details of the annealing effects at elevated temperatures will be published elsewhere.[40]

The specific heat C for four Zr_xCu_{1-x} alloys (measured in the dilution refrigerator) is shown in Fig. 8 as a function of temperature. The data are presented on a log-log plot to facilitate the large variation of C with T in the superconducting state and thus to make the contributions to C at the lowest temperatures clearly visible. In the high-temperature region of overlap (1.4 to 2.5 K) the data taken with the two different experimental setups agree within about 10%.

Three main conclusions can be drawn from the data already at this point. They are supported by appropriately plotting the data, as done in Figs. 9(a)–9(c) for the example $Zr_{0.70}Cu_{0.30}$.

(i) Figure 9(a) shows the electronic specific heat C_e divided by T (βT^3 subtracted from total specific heat) near T_c. With the usual argument of equal entropies, the measured specific-heat jump is replaced by an ideal jump ΔC keeping the areas under the C_e/T vs T curves constant. For $Zr_{0.70}Cu_{0.30}$, $\Delta C/\gamma T_c = 1.79$, which is somewhat higher than the BCS value of 1.43. Values between 1.42 and 1.80 are obtained for the Zr_xCu_{1-x}

TABLE I. List of experimentally determined parameters for Zr_xCu_{1-x} metallic glasses. The symbols are explained in the text.

x	T_c (K)	Θ_D (K)	λ	$\frac{\Delta C}{\gamma T_c}$	ϵ	$N_\gamma(E_F)$ (at.$^{-1}$eV^{-1})	$N_{H_{c2}}(E_F)$ (at.$^{-1}$eV^{-1})	$N_b(E_F)$ (at.$^{-1}$eV^{-1})	$\frac{m_t^*}{m_0}$	a (10^{-5} J/mole K^2)
0.50	0.83	231	0.45	1.57	1.71	1.39	1.24	0.95	3.02	
0.60	1.79	201	0.54	1.46	1.68	1.52	1.40	0.98	2.98	4.7
0.65	1.97	221	0.54	1.42	1.57	1.65	1.41	1.07	3.17	6.2
0.70	2.68	184	0.61	1.79	1.44	1.69	1.52	1.05	3.04	6.3
0.74	3.13	182	0.64	1.71	1.45	1.85	1.71	1.12	3.21	4.1

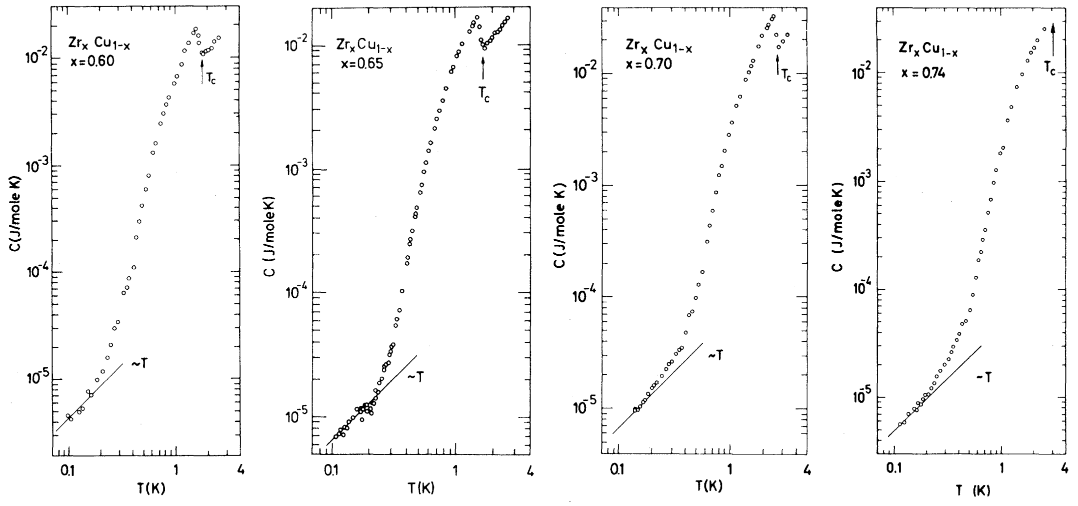

FIG. 8. Specific heat C of as-quenched amorphous Zr_xCu_{1-x} as a function of temperature T in a double-logarithmic plot for various x. Arrows indicate the superconducting transition temperatures T_c. Solid lines represent the linear contribution $C \sim T$ for $T \ll T_c$.

series (cf. Table I) indicating weak to intermediate coupling in this system, as previously found in $Zr_{0.70}Pd_{0.30}$ (Ref. 48) and as opposed to the strong-coupling simple amorphous metals.

(ii) This conclusion can be checked by an analysis of the electronic specific heat in the superconducting state C_{es} by plotting $C_e/\gamma T_c$ vs T_c/T [cf. Fig. 9(b)]. The temperature dependence of the energy gap precludes a simple exponential, i.e., a straight line in this plot over the whole T range below T_c. For $T \rightarrow 0$ the BCS expression for C_{es} is approximated by

$$\frac{C_{es}}{\gamma T_c} \approx 9.17 \exp(-\epsilon T_c/T) , \qquad (2)$$

where $\epsilon = 1.5$. Figure 9(b) and Table I show that Eq. (2) is indeed obeyed with ϵ between 1.45 and 1.68.

(iii) As C_{es} vanishes exponentially, the T^3 term and also the quasilinear term due to low-energy excitations become important as already apparent from Fig. 8 (in Sec. IV C we will show that the explanation in terms of intrinsic low-energy excitations is indeed the most likely one). Figure 9(c) shows C/T vs T^2 for $Zr_{0.70}Cu_{0.30}$. A linear dependence is observed for $0.02\ K^2 \leq T^2 \leq 0.12\ K^2$. The coefficient $\beta = 3.11 \times 10^{-4}$ J/(mole K^4) of the T^3 term agrees perfectly with that obtained from data above T_c, $\beta = 3.10 \times 10^{-4}$ J/(mole K^4). Good agreement is also obtained for $Zr_{0.74}Cu_{0.26}$. (For the other samples with lower T_c the T^3 coefficient cannot be reliably extracted because of the rapidly rising quasiparticle contribution C_{es}.)

The main point of Fig. 9(c) is the clear determination of a linear contribution to the specific heat, $C = aT$. Such a contribution is found in all investigated Zr_xCu_{1-x} samples (see Table I), ZrCu being the second system found[22] after ZrPd (Ref. 48) which shows this behavior. This lends further credence to the general occurrence of low-energy excitations in amorphous metals, as pointed out previously.[24] Meanwhile, it appears that these excitations are presented in metallic glasses quenched from the melt, in quench-condensed amorphous films and in sputtered amorphous metals.[20] In the latter a T dependence of the specific heat less than linear is observed[29] (see Sec. IV C for a discussion).

IV. DISCUSSION

The results presented in Sec. III will be discussed under the three main aspects mentioned in the Introduction. A possible influence of the electronic structure of glassy metals on the stability (better: metastability) of these alloys will be discussed in Sec. IV A. In Sec. IV B the superconducting properties and especially the electron-phonon coupling constant will be analyzed. Section IV C deals with the low-energy excitations in amorphous ZrCu.

A. Stabilization of the glassy state by the electronic structure

In crystalline materials the success of the electron theory in explaining transport properties is

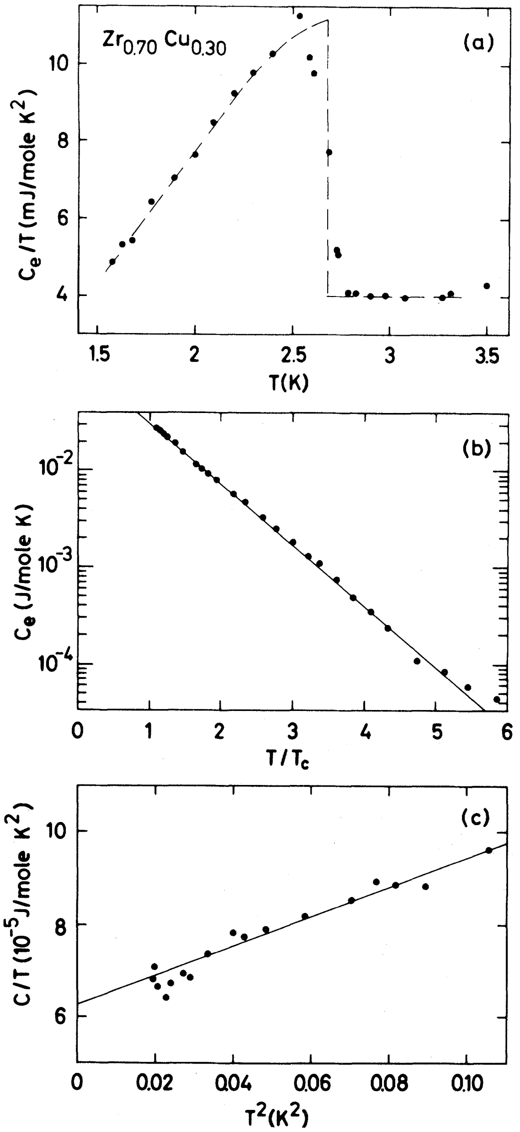

FIG. 9. (a) Electronic specific heat C_e divided by temperature T as a function of T near the superconducting transition temperature T_c for amorphous $\mathrm{Zr}_{0.70}\mathrm{Cu}_{0.30}$. Dashed line serves as visual guide indicating an idealized jump ΔC at T_c. (b) Electronic specific heat C_e vs temperature T (normalized to T_c) in a semilogarithmic plot for $T < T_c$ for $\mathrm{Zr}_{0.70}\mathrm{Cu}_{0.30}$. Solid line represents a best fit of $C_e \sim \exp(-\epsilon T_c/T)$ to the experimental data. (c) Specific heat C divided by temperature T vs T^2 for $\mathrm{Zr}_{0.70}\mathrm{Cu}_{0.30}$ at temperatures $T \ll T_c$. Solid line serves as visual guide for a linear dependence of C/T vs T^2.

largely based on the periodic order of the atoms and the resulting feasibility of band-structure calculations. In the noncrystalline state, long-range order is absent and the theory of Bloch cannot be used. Instead, the Ziman theory or extensions of it give good agreement with the experimental data for many liquid and amorphous metals.[50] In particular, the temperature dependence of the electrical resistivity ρ can be explained very well. Glassy metals show only a weak positive or negative temperature dependence of ρ. In the extended Faber-Ziman theory the sign of the T dependence of $\dot{\rho}$ is governed by the ratio of the position of the first maximum in structure factor k_p and of the doubled Fermi wave vector $2k_F$. All noncrystalline ZrCu alloys investigated here show a negative temperature coefficient α of the electrical resistivity in the temperature range from 10 K up to crystallization temperature. This means in terms of the extended Faber-Ziman theory that the condition $2k_F \approx k_p$ is always fulfilled. The value of α has been calculated in this model for $\mathrm{Zr}_{0.40}\mathrm{Cu}_{0.60}$ with the assumption that Zr has two valence electrons per atom and Cu one.[41] The agreement of α in sign and absolute value with experimental data is very good. With increasing Zr concentration the Fermi wave vector k_F should increase (at least in a free-electron model), while k_p as measured by partial x-ray diffraction decreases[51] in apparent contradiction to the fact that α is always negative in glassy ZrCu. An independent measurement of k_F would be necessary to clarify this point.

Nagel and Tauc proposed a possible contribution of the electronic properties of glassy metals to the high metastability.[12] In the case $2k_F \approx k_p$ the electronic density of states at the Fermi energy $N(E_F)$ should be reduced in the amorphous state compared with the crystalline state.

A direct experimental manifestation of this reduction is lacking. Indeed, an experimental comparison of $N(E_F)$ in the glassy and crystalline state seems to be difficult. Firstly, the glass-forming range of simple metals lies mostly in the neighborhood of the eutectic composition, which means that in the crystalline state one would measure the $N(E_F)$ of a phase mixture. For some noncrystalline transition metals, however, one can compare the glassy state with an intermetallic phase, e.g., $\mathrm{Zr}_{0.66}\mathrm{Cu}_{0.33}$ (Ref. 36) and $\mathrm{Zr}_7\mathrm{Cu}_{10}$ (Ref. 52). But even in these favorable cases another problem arises: The effective mass of the electrons can change upon crystallization due to a possible change of the electron-phonon interaction (see Sec. IV B). In this case the $E(k)$ dependence in a spherical shell of thickness $\hbar\omega_D$ around E_F will be changed after crystallization. In the simple free-electron model the density of states at E_F decreases with decreasing effective mass m^*. If there is any stabilization effect due to the electronic structure, this effect could be masked by a change of the electron-phonon interaction with crystallization. Therefore we do not attempt to make a comparison between the crystalline and amorphous state but instead look for the concentration dependence of $N(E_F)$ in the glassy state. This has been done already by Mizutani *et al.*[53] for PdSiCu, i.e., a metallic glass of the form $T_{80}M_{20}$ (T denotes transition metal, M denotes metalloid). In this system the concentration can be varied only in a small range, and a well-defined maximum in $N(E_F)$ is observed. But, as pointed out by the authors themselves, the temperature coefficient of the electrical resistivity is positive in this system, which in terms of the Ziman theory means that the criterion $2k_F \approx k_p$ is not fulfilled.

Glassy ZrCu can be obtained in a very broad concentration range and does not contain any metalloids. From the Sommerfeld constant γ as determined from specific-heat measurements (see Sec. III C) the electronic density of states $N_\gamma(E_F)$ is calculated in the independent-particle model:

$$N_\gamma(E_F)=3\pi^{-2}k_B^{-2}\gamma \, .$$

(Nonelectronic contributions to the linear term in the specific heat such as low-energy excitations, which will be discussed in Sec. IV C amount to only 2% of the electronic part and are negligible for the present argument.) Figure 10 shows the $N_\gamma(E_F)$ values as a function of the Cu concentration c together with some results of other authors on Cu-rich ZrCu glasses.[54–56] The magnitude of $N_\gamma(E_F)$ is comparable to $N_\gamma(E_F)$ of pure crystalline Zr [$N(E_F)=1.3$ eV^{-1} atom^{-1}] and much higher than $N_\gamma(E_F)$ of pure crystalline Cu. This indicates that the electronic density of states of glassy ZrCu is dominated by the Zr atoms. The concentration dependence is only weak. With increasing Cu concentration $N_\gamma(E_F)$ decreases linearly. There is no indication of a minimum of $N_\gamma(E_F)$ vs c.

To discuss the relative stability of a metallic glass correctly we must look for the difference in the Gibbs free energy G between the crystalline and amorphous state. Unfortunately, there is not a simple relation between the quantity G and the easily measurable crystallization temperature or glass temperature. Nevertheless the crystallization temperature T_K is a useful index for the relative stability. Our results (Fig. 5) therefore suggest that the stability increases as T_K with increasing Cu concentration. This is supported by measurements of the heat of crystallization of ZrCu which decreases linearly with increasing Cu concentration.[57] We note that there is no concentration with a particularly high crystallization temperature in ZrCu. But if there is any correlation with the electronic properties then the electronic density of states decreases with increasing "stability." For a comparison of the $N_\gamma(E_F)$ measurements with UPS results on glassy ZrCu,[60] we must renormalize the dressed $N_\gamma(E_F)$ as determined from the specific heat with the electron-phonon enhancement factor. This can be done with the aid of the T_c measurements (see Sec. IV B). Ultraviolet photoemission spectroscopy (UPS) measurements show, like the calorimetric results, the strong relation of $N(E_F)$ to the Zr d states and, in addition, a second maximum at higher binding energies, which originates from the Cu d states. The concentration dependence of $N(E_F)$ is only weak, as shown in Fig. 10 and Table I, whereas the position of the second maximum decreases only slightly to lower binding energies and its width increases with increasing Cu concentration. Such a behavior is not expected in a rigid-band model. Therefore, we suggest that neither the rigid-band model, which is assumed to be valid for the stability criterion, nor the free-electron model (as will be discussed in more detail in Sec. IV B) seem to be appropriate for the noncrystalline ZrCu system.

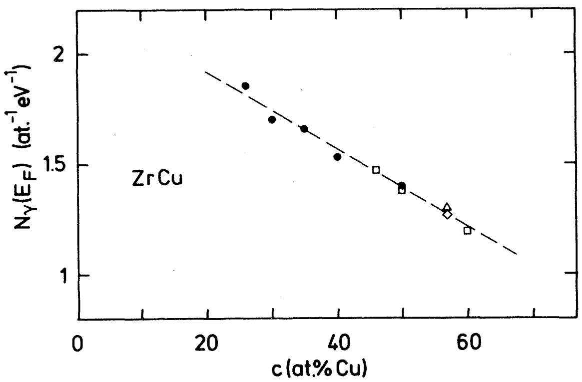

FIG. 10. Electronic density of states $N_\gamma(E_F)$ (determined from calorimetric measurements) as a function of Cu concentration c for the glassy ZrCu system (closed circles). Open symbols indicate data of other workers [triangle (Ref. 54), squares (Ref. 55), and diamond (Ref. 56)]. Dashed line indicates a linear dependence of $N_\gamma(E_F)$ on concentration.

B. Superconducting properties and electron-phonon interaction

The superconducting transition temperature T_c of the as-quenched ZrCu glasses decreases roughly linearly with increasing Cu concentration as shown in Fig. 2. The slope dT_c/dc amounts to nearly -0.1 K/at. % Cu, which is of the same magnitude as for other Zr glasses.[14,58,59] For fixed Zr concentration, the absolute values of T_c seem to increase with decreasing horizontal separation from the alloying element in the Periodic Table (ZrCu-ZrNi-ZrCo). This might be due to the decreasing *d*-band splitting in the valence-band spectra as studied by photoemission,[60] because with vanishing *d*-band splitting the electronic density of states at the Fermi energy should increase. For a more comprehensive discussion we restrict ourselves to the glassy ZrCu system for which many of the relevant parameters are known.

For a T_c calculation the numerical solution of the Eliashberg equations by McMillan[17] is commonly accepted. For that calculation, a measurement of the phonon spectrum $F(\omega)$ and the knowledge of the electron-phonon matrix element $\alpha(\omega)$ is needed to determine the electron-phonon coupling constant

$$\lambda=2\int_0^\infty \alpha^2(\omega)F(\omega)d\omega/\omega\ .$$

A precise determination of λ for glassy ZrCu must await the availability of good tunneling data. As long as the quantity $\alpha^2(\omega)F(\omega)$ is not known, McMillan's expression for T_c provides a way to estimate λ:

$$\lambda=\frac{1.04+\mu^*\ln(\Theta_D/1.45T_c)}{(1-0.62\mu^*)\ln(\Theta_D/1.45T_c)-1.04}\ , \qquad (3)$$

where μ^* is the effective Coulomb coupling constant which is usually set up to $\mu^*=0.13$. The decision to evaluate Θ_D from the cubic term in the specific-heat implicitly assumes the validity of the Debye model at low temperatures to describe the low-energy part of the vibrational spectrum in amorphous solids. There is evidence for extra structural excitations in amorphous metals.[19,20] In fact, a comparison between specific-heat and sound-velocity measurements in ZrCu suggests that the apparent Θ_D values obtained from the T^3 specific-heat term are ~20% too low (see Sec. IV C). As Θ_D enters Eq. (3) only logarithmically this might lead to a (minor) systematic error in λ.

The electron-phonon coupling constant λ evaluated with Eq. (3) is listed in Tabel I. λ increases from 0.45 to 0.65 with increasing Cu concentration. The magnitude of λ indicates that amorphous ZrCu is a weak-to-intermediate coupling superconductor as reported previously for LaGa.[61] λ is significantly smaller than the value observed for the simple (nontransition) amorphous superconductors ($\lambda\approx 2$).[16] This corroborates the experimental findings concerning the electronic specific-heat jump $\Delta C/\gamma T_c$ at T_c [cf. Fig. 9(a) and Table I] and the exponential drop (with a coefficient ϵ) of the specific heat to lower temperatures [cf. Fig. 9(b) and Table I]. The values of both $\Delta C/\gamma T_c$ and ϵ indicate weak-to-intermediate coupling in ZrCu as already mentioned in Sec. III C. The value of the density of states at the Fermi level determined (as in Sec. IV A) from the coefficient γ of the linear term in the specific heat for a weak-coupling metal is enhanced ("dressed") by the electron-phonon interaction. This enhancement can be described by the factor $(1+\lambda)$. For a comparison with calculations or measurements of the density of states which do not include electron-phonon interactions (e.g., UPS experiments), the "bare" density of states

$$N_b(E_F)=N_\gamma(E_F)/(1+\lambda) \qquad (4)$$

is given in Table I. For glassy ZrCu, $N_b(E_F)$ is close to 1 states/(eV atom) for both spin directions and increases only slightly with increasing Zr concentration. $N_b(E_F)$ for many of the simple (nontransition) amorphous metals is predicted accurately by the free-electron model.[16] This model is not expected to apply to amorphous transition metals which are mainly influenced by large *d* band effects. Hence, $N_b(E_F)$ is much larger than the free-electron density of states $N^{(f)}(E_F)$. The enhancement can be expressed in terms of the effective-thermal-mass ratio

$$\begin{aligned} m_t^*/m_0 &= N_b(E_F)/N^{(f)}(E_F) \\ &= N_\gamma(E_F)/[(1+\lambda)N^{(f)}(E_F)]\ , \end{aligned} \qquad (5)$$

which is listed also in Table I. $N^{(f)}(E_F)$ is calculated with the assumption that each Zr atom contributes two free electrons and each Cu atom one free electron, as used for the analysis of the temperature dependence of the electrical resistivity. The effective thermal mass is nearly independent of the Zr concentration and amounts to $m_t^*/m_0\approx 3$ for all samples.

The effective-mass enhancement can also be inferred from the analysis of the thermal conductivity.[22,26] In the normal conducting state of a metal, heat is carried by electron and phonons. The electronic thermal conductivity κ^e can be expressed by assuming the validity of the Wiedemann-Franz law $\kappa^e=(L/\rho)T$. When the metal becomes superconducting κ^e decreases and the phonon thermal conductivity $\kappa^{\rm ph}$ increases because of the condensation of quasiparticles. For $T \ll T_c$, $\kappa_s^e \ll \kappa^{\mathrm{ph}}$ and the phonon mean free path is limited by scattering from low-energy excitations as discussed in Sec. IV C; hence $\kappa_s \equiv \kappa_s^{\mathrm{ph}} \equiv \kappa_l^{\mathrm{ph}}$. In the same temperature range the normal-state phonon conductivity κ_n^{ph} can be separated from total conductivity, $\kappa_n^{\mathrm{ph}} = \kappa - \kappa_n^e$, either in magnetic field exceeding H_{c2} or with the aid of a second ZrCu glass which has a lower T_c due to a different Zr concentration. In the first case we assume κ_n^{ph} to be independent of the magnetic field, as indeed observed for $T > T_c$; in the second case we assume κ_n^{ph} to be independent of concentration, which is also seen for $T > T_c$. With κ_n^{ph} known and assuming the validity of Matthiesens's rule for phonons,

$$\kappa_n^{\mathrm{ph}} = [(\kappa_l^{\mathrm{ph}})^{-1} + (\kappa_e^{\mathrm{ph}})^{-1}]^{-1} , \tag{6}$$

we can evaluate the phonon conductivity as limited by scattering from electrons only, κ_e^{ph}, and its temperature dependence. In the low-temperature region we get a linear variation, $\kappa_e^{\mathrm{ph}} = D_e^{-1} T$, where D_e is the phonon-electron scattering coefficient. For the two types of analysis, the experimentally determined values are $D_e = 2.1 \times 10^3$ cm K^2 W^{-1} (Ref. 26) and 1.4×10^3 cm K^2 W^{-1} (Ref. 22) for ZrCu. The temperature dependence of κ_e^{ph} is in agreement with that obtained in the free-electron model for $T \ll \Theta_D$ (Refs. 62 and 63)

$$\kappa_e^{\mathrm{ph}} = 1.82 \times 10^{-3} \rho \Theta_D A n_0^{-2/3} T = T / D_e^{(f)} , \tag{7}$$

where A is the average mass number, n_0 is the average number of electrons per atom, and ρ is expressed in Ω cm to yield κ_e^{ph} in W/cm K. However, $D_e^{(f)} = 2.8 \times 10^2$ cm K^2 W^{-1}; i.e., the enhancement factor in the scattering coefficient $D_e / D_e^{(f)}$ amounts to 5–7. The high value of D_e is very likely attributable to the high electronic density of states at the Fermi level.

With the knowledge of $N_b(E_F)$, the coupling constant λ can be analyzed further. As $\alpha^2(\omega)F(\omega)$ is unknown, this can only be done with McMillan's factorization of λ (Ref. 17):

$$\lambda = N_b(E_F) \langle I^2 \rangle / M \langle \omega^2 \rangle ,$$

where $\langle I^2 \rangle$ is the average squared electron-ion matrix element, M the ionic mass, and $\langle \omega^2 \rangle$ the mean-square phonon frequency. As shown in Table I, λ increases with increasing Zr concentration in glassy ZrCu, while the bare density of states is nearly constant. Therefore the quantity $\langle I^2 \rangle / M \langle \omega^2 \rangle$ must also increase. Bennemann[64] suggests that $1/M\langle \omega^2 \rangle$ in transition metals is proportional to the melting temperature and estimates a very weak e/a dependence of $1/M\langle \omega^2 \rangle$ for amorphous metals. If this is valid for ZrCu, our data indicate a strong variation of $\langle I^2 \rangle$ with alloying.

A strong $\langle I^2 \rangle$ variation is also inferred from T_c measurements on amorphous La–noble-metal alloys, where the main influence of $\langle I^2 \rangle$ on T_c with alloying could be estimated with the aid of band-structure calculations of crystalline La.[18,65]. There, the variation of $\langle I^2 \rangle$ can be explained by an increasing hybridization between f and d states.

In the case of glassy ZrCu the hybridization should occur between $s(p)$ and d states of Zr atoms as a consequence of a decrease of the average atomic distance of neighboring Zr atoms with decreasing Cu concentration. Another way to reduce the average distance of neighboring Zr atoms in glassy ZrCu is to apply external pressure. In this case, T_c should increase which indeed has already been found experimentally.[37,66] In brief, the fact that $N_b(E_F)$ is nearly constant in the $\mathrm{Zr}_x\mathrm{Cu}_{1-x}$ amorphous alloys allows one to trace the T_c (and λ) variation back to a variation of $\langle I^2 \rangle$. In crystalline transition-metal alloys an interpretation along these lines should not be valid because $\langle I^2 \rangle / M \langle \omega^2 \rangle$ can depend on $N_b(E_F)$ and/or is roughly constant within a given d band.[67]

In Sec. III A we estimated the Ginzburg-Landau parameter to $\kappa > 80$ which shows that amorphous ZrCu is an extreme-type-II superconductor as other amorphous metals as expected.[13] This is directly seen in the magnitude of the upper critical field H_{c2} (cf. Fig. 4). The temperature dependence of H_{c2} is nearly linear for $T \lesssim T_c$ and parabolic for lower temperatures. Deviations from the parabolic curve can be estimated from the usual plot of $[H_{c2}(T)/H_{c2}(T=0)] - [1-(T/T_c)^2]$ vs $(T/T_c)^2$. The observed deviations are smaller than 5%. The parabolic behavior of $H_{c2}(T)$ can be successfully described by Maki's theory.[13,68]

For an isotropic strong-coupling superconducter the density of states can be estimated from the slope of H_{c2} near T_c with the relation[16]

$$\frac{dB_{c2}}{dT} = \eta 4 k_B e \pi^{-1} N_{H_{c2}}(E_F) \rho , \tag{8}$$

where ρ is the electrical resistivity and η is an enhancement factor which has been calculated numerically by Rainer and Bergmann, $\eta \approx 1$.[69] The values for $N_{H_{c2}}(E_F)$, as determined from Eq. (8), are listed in Table I. They are in good agreement with the values of $N_\gamma(E_F)$ determined from the specific-heat measurements, but they are systematically lower. This might be due to the systematic error in the geometry factor entering the electrical resistivity. Therefore, the uncertainty in $N_{H_{c2}}(E_F)$ is considerably higher than in $N_\gamma(E_F)$.

Recent measurements[39] indicate a relation between $\ln T_c$ and the inverse magnetic susceptibility χ^{-1} in ZrCu. However, a direct comparison of χ and $N_b(E_F)$ is not possible because of Stoner enhancement.

As a final point of this section on superconducting properties, we note that in amorphous superconductors the small coherence length leads to an immense increase of the fluctuation region which is very small in pure crystalline bulk superconductors. For glassy ZrCu the fluctuation region is observed up to several degrees above T_c (cf. Fig. 3). The product of the BCS coherence length ξ_0 and the mean free path of the electrons l can be calculated with the slope of H_{c2} near T_c:

$$(dH_{c2}/dT)_{T_c}=\phi_0/(4.54\xi_0 l)1/T_c \ , \tag{9}$$

where ϕ_0 is the flux quantum. For the dirty limit $l/\xi_0 \ll 1$ we estimate for $Zr_{0.65}Cu_{0.35}$ with the Ginzburg-Landau-Abrikosov-Gor'kov (GLAG) theory

$$\xi_0 l \approx 1.64\times 10^4 \text{ Å}^2 \ .$$

The Ginzberg-Landau coherence length ξ_{GL} is given by

$$\xi_{GL}(T)=0.85(\xi_0 l)^{1/2}[T_c/(T_c-T)]^{1/2} \ , \tag{10}$$

which leads for $T=0$ to $\xi_{GL}(0)=108$ Å for ZrCu. Close to T_c the coherence length ξ_{GL} increases tremendously, but even at $T_c-T\approx 10$ mK it is small compared with the dimensions of the samples. Therefore the fluctuation formula for a three-dimensional superconductor would be appropriate. A more quantitative discussion which was given for $Zr_{0.75}Rh_{0.25}$ (Ref. 70) is not possible because of the uncertainty in the shape factor of our samples.

C. Low-energy excitations in Zr_xCu_{1-x}

After having dealt in some length with the electron-phonon interaction and its effect on superconductivity in amorphous Zr_xCu_{1-x} we now discuss the low-energy excitations and their interaction with phonons and electrons. A detailed treatment of these interactions in terms of the tunneling model where the low-energy excitations are considered as two-level systems has been given in recent reviews[19,20] and will not be repeated here. Of course, in the superconducting state well below T_c, we are left with only low-energy excitations and phonons, and that simplies the matter.

As far as the very existence of low-energy excitations is concerned, it has been demonstrated in a variety of amorphous metals, as mentioned already in Sec. III C. In the following we will briefly discuss two objections to the intrinsic nature of these excitations that are often raised when dealing with low-temperature anomalies in amorphous superconductors. (i) Normal-state inclusions within the superconducting matrix which would lead to $C\sim T$ for $T \ll T_c$ are unlikely to be produced at such a similar rate over a wide range of T_c's. Furthermore, they should become superconducting by the proximity effect if their radius does not exceed the coherence length ξ_{GL} of ~ 100 Å for $T\rightarrow 0$. This conjecture is supported by the fact that mild heat treatment leaves the linear term in amorphous ZrCu unchanged[40] or even reduces it,[71] while heat treatment resulting in partial crystallization yields an enhancement of this term which indeed is indicative of normal-state crystalline inclusions.[72] (ii) Gaseous impurities could also give rise to low-temperature anomalies in the heat capacity as known, for example, for hydrogen trapped by interstitial impurities, like oxygen or nitrogen, in crystalline Nb. In this configuration, H is a tunneling system as evidenced by the strong isotope effect.[73] From specific-heat measurements alone, it cannot be ruled out that hydrogen unintentionally introduced during preparation (and perhaps trapped by oxygen) produces a contribution to C in amorphous ZrCu and other superconducting amorphous metals. However, because of the small H mass the tunneling splitting is rather large. This should lead to a rapid decrease of C in the low-temperature range of the present investigation, i.e., near 0.1 K, as observed in the Nb-N-H and Nb-O-H systems.[73,74] Furthermore, thermal-conductivity measurements indicate that phonon scattering by H impurities in Nb (Refs. 75 and 76) (with a H concentration that would lead to a contribution to C of the same magnitude as that observed in amorphous Zr_xCr_{1-x}) is much weaker than the observed phonon scattering in this material. Hence specific heat and thermal conductivity together convincingly support the intrinsic nature of low-energy excitations in ZrCu.

While our measurements do indicate a *linear* term in the specific heat, $C=aT$, it is possible that deviations from this simple T dependence could occur when extending the measurements to temperatures well below 0.1 K, just as in very pure vitreous silica (Suprasil *W*) where $C \sim T^{1.22}$ down to 25 mK was found.[77] We did check if our data are compatible with a $T^{0.5}$ dependence of the extra contribution by plotting $C/T^{0.5}$ vs $T^{2.5}$. This, however, gave no satisfactory fit. Thus our data rule out a $T^{0.5}$ contribution to C recently reported for sputtered amorphous superconducting Zr alloys.[49]

Turning to the concentration dependence of the linear term aT of C in $\mathrm{Zr}_x\mathrm{Cu}_{1-x}$, we note that roughly the same value of a is observed considering the relatively large error of 10–15 % which is due to the very small heat capacity of our samples for $T \ll T_c$. In particular, no general relation between a and the glass transition T_g is observable. T_g decreases with increasing Zr concentration from 660 K ($x=0.6$) to 600 K ($x=0.74$),[42] and, on the other hand, a varies nonmonotonically with x (see Table I). The simple relation $a \sim T_g^{-1}$ has been suggested in the frame of the free-volume theory of the glass transition.[78] Experimentally, $a \sim T_g^{-1}$ was found in some insulating-glass systems.[79] The possible reasons for the lack of this observation in $\mathrm{Zr}_x\mathrm{Cu}_{1-x}$ as follows. (1) The change of a expected from a 10% change of T_g could be masked by the relatively large error in a. (2) Composition-dependent short-range ordering in metallic glasses is currently discussed which could inhibit a simple $a \sim T_g^{-1}$ law and which could account for the nonmonotonic dependence of a on x.

The next point concerns an excess T^3 contribution to C. In insulating glasses it generally exceeds the Debye contribution $b_D T^3$, i.e., $C=\beta T^3 =(b_D+b)T^3$.[80] However, in metallic glasses no direct hint for such an extra contribution has been found yet.[47,81] Very recent sound-velocity measurements on $\mathrm{Zr}_{0.40}\mathrm{Cu}_{0.60}$ yield $v_l=4.3\times10^5$ cm/s and $v_t=2.1\times10^5$ cm/s for longitudinal and transverse waves, respectively.[82] In the Debye model this results in $\Theta_D=272$ K. This value is considerably higher than that obtained from our specific-heat measurements on $\mathrm{Zr}_{0.50}\mathrm{Cu}_{0.50}$ and from those on $\mathrm{Zr}_{0.40}\mathrm{Cu}_{0.60}$ (Ref. 55) which both give $\Theta_D \approx 230$ K. This indicates a T^3 contribution exceeding $b_D T^3$ with $b=6.2 \times 10^{-5}$ J/(moleK^4) which is very close to the excess T^3 contribution in vitreous silica.[80] Simultaneous measurements of v_l, v_t, and C on other metallic glasses should be carried out to check if the bT^3 term occurs there also. These experiments should be particularly interesting since the origin of this term even in insulating glasses remains to be established.

We now turn to the interaction of low-energy excitations with phonons as probed with the thermal-conductivity measurements of the present work. In the tunneling model, the phonon thermal conductivity as limited by resonant scattering from two-level systems (TLS) is given by[19]

$$\kappa_i^{\mathrm{ph}}=\frac{\rho_d k_B^3}{6\pi\hbar^2}\left[\sum_\nu \frac{v_\nu}{\bar{n}_0 M_\nu^2}\right]T^2\,, \tag{11}$$

where ν indicates the phonon polarization mode (l or t), $\bar{n}_0$ is the density of states of TLS strongly coupled to phonons, and M_ν the off-diagonal TLS-phonon coupling constant. With $\bar{n}_0 M_t^2=1.8$ J/cm^3 [obtained from the logarithmic variation of the sound velocity with T, $\Delta v/v \sim \ln T$, in $\mathrm{Zr}_{0.40}\mathrm{Cu}_{0.60}$ (Ref. 38)] and setting $\bar{n}_0 M_t^2=2\bar{n}_0 M_1^2$, Eq. (11) yields $\kappa_i^{\mathrm{ph}}=3.1\times10^{-3}$ W/cm K at $T=1$ K, while the experimental values for $\mathrm{Zr}_x\mathrm{Cu}_{1-x}$ are between 5 and 7.7×10^{-4} W/cm K for $0.5 \leq x \leq 0.74$ at that temperature. This indicates a TLS-phonon coupling is 3–4 times larger than obtained from the ultrasonic measurements. This large discrepancy is surprising because the two measurements were carried out on samples well below their respective transition temperature, so that the additional complication of the TLS-electron interaction[19,20] can be neglected. Hence the case should be analogous to insulators where good agreement is obtained.[83] In fact, quite satisfactory agreement has been found for $\bar{n}_0 M_t^2$ in superconducting $\mathrm{Zr}_{0.70}\mathrm{Pd}_{0.30}$ determined from three different measurements (ultrasonic absorption, $\Delta v/v$, and κ).[84]

As has been pointed out before,[20] the reduced transverse sound velocity in amorphous metals with respect to insulating glasses gives rise to a greatly enhanced TLS-phonon relaxation rate ($\sim v^{-5}$), thereby increasing the relaxational absorption for $\omega T_1 \gg 1$, where T_1^{-1} is the total TLS relaxation rate. This should be particularly noticeable in superconductors where the TLS-electron relaxation rate is largely reduced. However, since the sound velocities in amorphous ZrPd and ZrCu are close, this cannot account for the different behavior observed, which at present therefore must remain unexplained.

A final remark is concerned with the intrinsic phonon thermal conductivity of amorphous metals κ_i^{ph} above 1 K, which is obtained from

$$(\kappa_l^{ph})^{-1}=(\kappa^{ph})^{-1}-(\kappa_e^{ph})^{-1}$$

with an extrapolation of $\kappa_e^{ph}=T/D_e$ to $T>T_c$ (see Sec. IV B). It has been shown for two different ZrCu alloys where κ_e^{ph} was determined differently (i.e., by application of a magnetic field below T_c or by comparison of a normal-conducting and a superconducting alloy), that a plateau in κ_l^{ph} occurs.[20,26] This shows that a plateau in the phonon thermal conductivity is present in amorphous metals when the phonon-electron scattering can be determined and subtracted from the thermal resistivity (as in ZrCu) or is only weak [as in PdSiCu (Ref. 85)]. This ubiquitous plateau (it has been observed in virtually all amorphous solids) has been related to the deviations from the Debye specific heat in two different ways (see Ref. 20 for a discussion): (i) by assuming that the excess over b_DT^3 is due to tunneling two-level systems (with quadratic energy density of states) which scatter phonons,[86] (ii) by assuming that the excess specific heat (often visible as a maximum in a plot of C/T^3 vs T) is due to localized phonons which interact with Debye phonons and thus limit heat transport.[87] While our measurements cannot distinguish between these two possibilities, it is reassuring that the plateau in κ_l^{ph} indeed coincides with an enhanced T^3 specific heat.

V. CONCLUSIONS

A systematic study of a large number of properties of the liquid-quenched metallic glass Zr_xCu_{1-x} has been presented. All ZrCu glasses investigated show a negative temperature dependence of the electrical resistivity which can be explained with the extended Ziman theory in the case $2k_F \approx k_p$. The electronic density of states at the Fermi level $N_\gamma(E_F)$—as determined from specific-heat measurements—depends linearly on the Zr concentration. A direct correlation of $N_\gamma(E_F)$ to the measured crystallization temperature which is a reliable measure of stability, or a pronounced minimum of $N_\gamma(E_F)$ as proposed for high stability of metallic glasses is not found. This could have its origin in the invalidity of a rigid-band model which is inferred from our specific-heat measurements in conjunction with UPS measurements by other workers.

Superconducting amorphous ZrCu alloys are extreme-type-II superconductors with a Ginzburg-Landau parameter $\kappa>80$. Measurements of the jump of specific heat at T_c and an estimation of the electron-phonon coupling constant λ show an intermediate-to-weak coupling behavior in contrast to the simple (nontransitional) amorphous metals which characteristically do exhibit strong-coupling superconductivity. For our ZrCu samples the determination of $N(E_F)$ from upper-critical-field measurements is nearly as good as the calorimetric determination. Both methods yield the dressed density of states which can be converted to $N_b(E_F)$ by the factor $(1+\lambda)^{-1}$. In contrast to simple amorphous metals the bare density of states $N_b(E_F)$ of glassy ZrCu is about 3 times larger than the free-electron density of states. This large influence of partially occupied d states can also be seen in the difference between the phonon-electron scattering coefficient as determined from thermal-conductivity measurements, and the coefficient in the free-electron model. An analysis of the electron-phonon coupling constant λ in terms of the McMillian factorization leads to a concentration-dependent electron-ion matrix element $\langle I^2 \rangle$, which might have its physical origin in the increasing hybridization of s and d states with increasing Zr concentration.

Measurements of the specific heat and the thermal conductivity down to lowest temperatures give further evidence for the existence of configurational low-energy excitations. The coefficient a of the roughly linear specific heat found for temperatures well below T_c, while being of roughly the same size for all Zr concentrations x, varies nonmonotonically with x. Hence a $a\sim T_g^{-1}$ behavior, as found in some amorphous insulators, is not observed in glassy ZrCu. This is perhaps due to compositional short-range ordering in amorphous ZrCu. In order to investigate this point in more detail, a study of annealing effects on the low-temperature properties of glassy ZrCu is under way.

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