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Influence of configurational changes on the superconducting transition temperature of an amorphous zirconium-nickel alloy

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The reversible thermal relaxation found in various amorphous materials has been observed in the glassy metal-metal alloy $Zr_{76}Ni_{24}$. The superconducting transition temperature, T_c, can increase reversibly in this alloy with increasing temperature of anneal T_a for $T_a \leq 300\,^{\circ}\mathrm{C}$. At $T_a \geq 300\,^{\circ}\mathrm{C}$ an irreversible decrease in T_c occurs. The effect of plastic deformation on T_c appears to be identical to the effect of heat treatment. It is speculated that high temperatures need not be produced during deformation, but rather that stress fields encourage the same atomic-scale relaxation processes which are active in thermal annealing.

I. INTRODUCTION

Glassy metallic alloys are produced by quenching from the melt using very fast cooling rates ($\sim 10^6$ K/s). The resulting material resides in a metastable state at room temperature. Annealing the glassy metal at temperatures well below the crystallization temperature causes the alloy to traverse a continuum of ever more stable metastable states. Concurrent with this thermal relaxation the various properties of the alloy, such as mass density or electrical resistivity, also change and thus these properties may be used to monitor the relaxation process.

Generally the relaxation process is irreversible and tends toward eventual crystallization of the sample. However, it has been demonstrated that, for some glassy alloys, it is possible to move *reversibly* between metastable states created at different annealing temperatures. It was the purpose of the work reported here to obtain additional information on reversible relaxation in glassy alloys, and to compare this information with that obtained for configurational changes caused by irreversible relaxation and by mechanical deformation.

The properties which have been used to study reversible relaxation in glassy alloys include the magnetic anisotropy[1,2] and Curie temperature,[3] the electrical resistivity,[4,5] the velocity of sound,[6] and calorimetric response.[7,8] All measurements have been on essentially high-temperature properties, and most of these measurements have been on magnetic materials containing "glass formers" such as B, P, or Si. It was our intent to extend the list of properties showing reversible behavior by monitoring the low-temperature phenomenon of superconductivity in a nonmagnetic alloy containing only metallic constituents. The binary metal-metal alloy $Zr_{76}Ni_{24}$ was selected since the details of its formation and stability have been documented,[9,10] and since the superconducting transition[11] occurs within the convenient experimental range of 2–4 K. The superconducting transition temperature T_c can be measured precisely, and therefore T_c itself was chosen as a monitor of relaxation behavior.

Reversible relaxation is not confined to glassy alloys, but also occurs in oxide glasses[12] and in polymers.[13] It is possibly a feature which is common to amorphous systems.

II. EXPERIMENTAL TECHNIQUES

The $Zr_{76}Ni_{24}$ alloy was prepared by arc melting. Portions of this alloy were then quenched from the melt using an arc-hammer technique.[14] No crystalline phases could be detected by x-ray diffraction. Samples cut from the splats were roughly square, 1–2 mm on a side, with a mass of $\sim 4\times 10^{-4}$ g. All samples cut from the same splat had the same superconducting transition temperature, $T_c = 3.40$ K, to within 30 mK, attesting to the homogeneity of the splats. Furthermore, identical thermal treatments produced the same changes in T_c to within 10 mK.

Heat treatments were performed in evacuated, thin-wall Pyrex capsules backfilled with pure Ar to 250 Pa to provide thermal contact between sample and walls. Yttrium powder was placed within the capsule to getter oxygen. All anneals were carried out at $T_a \leq 330\,^{\circ}\mathrm{C}$, which is below the crystallization temperature of $\sim 362\,^{\circ}\mathrm{C}$ measured in a differential scanning calorimeter at a rate of 20 K/min. After heat treatment the samples were cooled rapidly by moving the capsule directly from furnace to water. We found it necessary to give the Zr-Ni alloy a standardization anneal prior to any sequence of anneals performed in search of reversibility, otherwise only irreversible relaxation was evident. There was no attempt to optimize the standardization procedure.

Some samples were deformed by cold rolling between stainless-steel foils in a four-high rolling mill using tungsten carbide work rolls. No pin holes or other macroscopic defects appeared in the samples even for a reduction in thickness by a factor of 5.

The superconducting transition was detected by the modified induction method shown schematically in Fig. 1. A Zr-Ni sample was placed within a secondary coil with the plane of the Zr-Ni foil oriented perpendicular to the axis of the coil. The size of the square samples, 1 – 2 mm, was much smaller than the diameter of the primary coil. For the thickness of the present Zr-Ni foils (7 – 35 μm), the output of the bridge was independent of foil thickness but proportional to area. Hence, the superconducting property being detected was more closely related to an effective critical field H_E than to the critical current. The source of the 3ω signal is shown by Fig. 2(a). The solid line depicts the magnitude of the current I induced in the normal sample by the primary circuit during one-half of a cycle. The resistivity in the normal state is large and so I is small. The dashed line represents the current induced in the superconducting sample; I is now sufficiently large to exclude the alternating magnetic measuring field. The dotted line occurs if the measuring field exceeds the critical field $H_E(T)$ at temperature T. The 3ω component in the signal is caused by the depression in I from the maximum.

A plot of the output signal from amplifier A_3 is shown in Fig. 2(b) as a function of temperature. The transition temperature T_c is well defined. For a homogeneous type-I superconductor with critical field H_c, the slope and width of the curve immediately below T_c should be determined by $(dH_c/dT)_{T_c}$. This conclusion was checked by measurements on a sample of In. The field at the position of the sample is not known accurately, but using an estimate gives a measured $(dH_c/dT)_{T_c} \approx 2\times10^{-2}$ (T/K), which is in reasonable agreement with the value of 1.7×10^{-2} (T/K) obtained from the literature.[15] The Zr-Ni samples are, however, type-II superconductors. The effective critical field H_E for these measurements probably[16–20] lies between H_{c1} and H_c. Therefore, although the qualitative shape of the output curve for a Zr-Ni sample is similar to that for a type-I sample, the critical temperature T_c is the only quantitative information that is readily available from the inductive measurement technique of Fig. 1. A factor-of-10 change in measuring field changes the observed T_c by less than $\frac{1}{3000}$.

During a cryogenic run, one Zr-Ni sample was placed in each of the two secondary coils of Fig. 1. One of the two samples was left in place for all succeeding runs and served to provide a precise, fixed temperature relative to which small changes in T_c (caused by annealing or by deformation) of

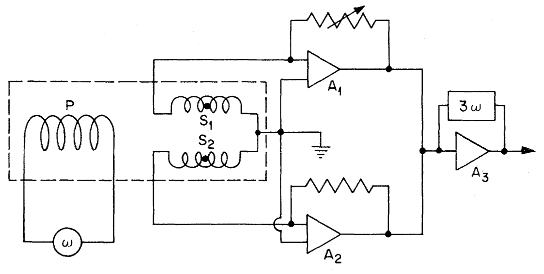

FIG. 1. Circuit used to detect the superconducting transition. A_1,A_2,A_3—amplifiers; S_1,S_2—samples placed within the two secondary coils. The secondary coils are placed side by side within the primary coil P. Amplifier A_3 is narrow banded at frequency 3ω (750 Hz); the gain of A_1 is adjusted initially to null the 3ω component in the signal. The portion of the circuit within the dashed line is contained in a copper block and immersed in liquid helium. The block also contains a calibrated germanium resistance thermometer not shown here.

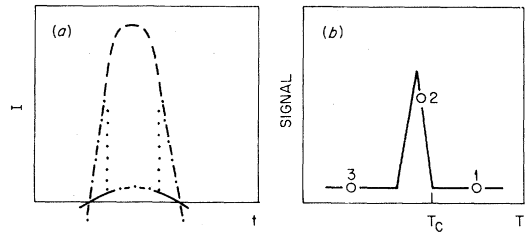

FIG. 2. (a) Amplitude vs time plot, for one-half cycle, of the current induced in a sample by the magnetic field produced by the primary coil P of Fig. 1. Solid line, sample in high-resistance normal state; dashed line, sample in superconducting state; dotted line, measuring field exceeds a critical field of the sample during a portion of the ac oscillation. (b) Sketch of the magnitude of the third-harmonic output of the bridge as a function of temperature. The superconducting transition temperature T_c is precisely established. Point 1 corresponds to the solid line of part (a), point 2 to the dotted line, and point 3 to the dashed line.

the second sample could be measured. A temperature scale was provided by a calibrated germanium resistance thermometer. The thermometers, coils, and samples were contained within a thick-walled copper vessel which allowed entry of liquid helium; the samples were in direct contact with the liquid helium. Only if the temperature of the helium bath was changed very rapidly could a temperature gradient be detected within the copper vessel.

Figure 3 is an example of the output of the bridge using a measuring field of 5×10^{-4} T rms. In this example the sample *A* was as-quenched Zr-Ni while sample *B* had been heat treated for 21 h at 272 °C. The heat treatment reduced T_c by 10%.

III. RESULTS AND DISCUSSION

The results of heat treatment are discussed first, as this information will then be used in an attempt to understand the effects of deformation.

A. Heat treatment

The behavior shown in Fig. 3 is typical of superconducting glassy alloys.[19–21] As the sample is held at some fixed annealing temperature T_a for a sufficiently long period of time, the superconducting transition temperature nearly saturates or stabilizes. With increasing T_a, T_c decreases. However, the response of glassy Zr-Ni to anneals of short duration is quite different. Four samples were subjected to a sequence of 10-min isochronal anneals. The results are shown in Figs. 4 and 5. The T_c in the portion of each T_c vs T_a curve lying between ~200 and 300 °C *increases* with increasing T_a. Furthermore, T_c in this portion of the curve varies reversibly as a function of T_a. The effect of thermal history on the T_c of these samples will now be discussed in detail.

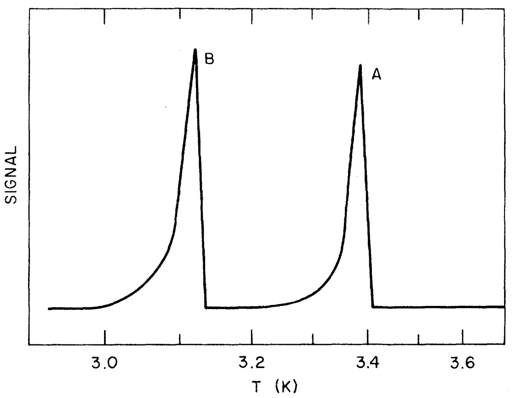

FIG. 3. Data obtained when a glassy Zr-Ni sample is placed in each of the two secondary coils of Fig. 1. A, virgin sample; *B*, sample from same splat, but annealed 21 h at 272 °C. The instrumentation noise level was ~1% of the peak amplitudes at *A* or *B*, and therefore was not reproduced in this tracing. The horizontal scale is linear in the resistance of the germanium thermometer, and thus is nonlinear in temperature.

In Fig. 4 the two samples were standardized at a temperature of 270 °C for 21 h, then annealed at 220 °C for 1 h. A sequence of 10-min isochronal anneals was then carried out at the temperatures indicated. Reversibility is evidenced by the agreement between the filled and open symbols, the filled symbols having been obtained prior to the isochronal sequence. For 10-min anneals, heat treatment at temperatures above ~300 °C caused a large and irreversible[22] decrease in T_c as shown in Fig. 4. Whereas the shape of the signal [Fig. 2(b)] remained unchanged for all reversible anneals at $T_a < 300$ °C, irreversible relaxation at $T_a \geq 300$ °C did change the shape with $(dH_E/dT)_{T_c}$ always decreasing[23] with decreasing T_c. The T_c could be reduced irreversibly to 2.3 K with no x-ray evidence for crystallization.

The sample of Fig. 5 represented by open circles was given a standardization anneal of 45 h at 200 °C, then subjected to a sequence of 10-min isochronal anneals as shown. A large irreversible decrease in T_c occurred at $T_a = 331$ °C. This sample was then annealed again at 200 °C for 24 h, fol-

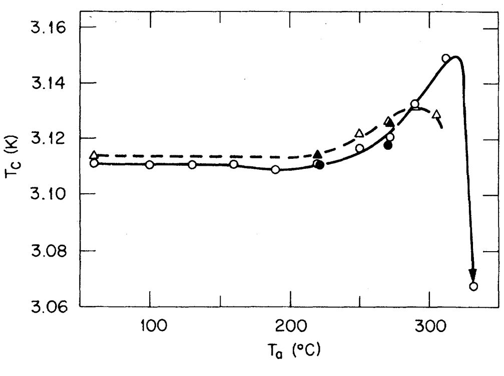

FIG. 4. Variation of superconducting transition temperature T_c as a function of annealing temperature T_a for two glassy Zr-Ni samples cut from the same splat. Those data obtained after the samples had been given a standardization treatment of 270 °C for 21 h, and after a further anneal at 220 °C for 1 h, are shown by filled symbols. The open symbols represent a sequence of 10-min isochronal anneals. Both samples were subjected to the same sequence of anneals below 250 °C, but a complete set of data was obtained only for one sample. The uncertainty in T_c, and in T_a, is roughly the size of the data points.

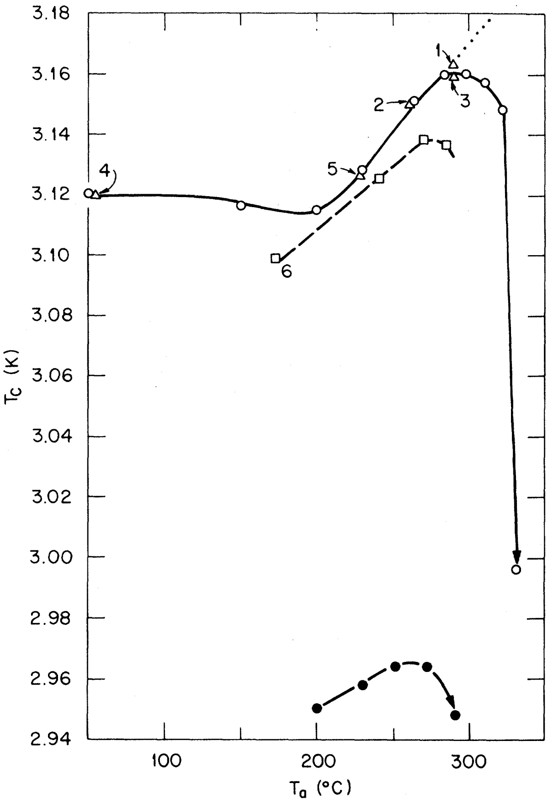

FIG. 5. Variation of T_c vs T_a for two glassy Zr-Ni samples cut from the same splat. ○, sequence of 10-min isochronal anneals following standardization at 200 °C for 45 h; ●, continuation of 10-min isochronal anneals for the same sample following the irreversible anneal at 331 °C and a 24-h stabilization at 200 °C; △, second sample subjected to the following sequence: (1) 20-min standardization at 290 °C, (2) 10 min at 262 °C, (3) 10 min at 290 °C, (4) 10 min at 50 °C, (5) 10 min at 230 °C, (6) 264 h at 173 °C followed by three 10-min isochronal anneals indicated by □.

lowed by another set of 10-min isochronal anneals, and these data are shown by the filled circles of Fig. 5. The reversible portions of the T_c-T_a plots, i.e., the portions with positive slope, are rather short. If we nevertheless measure this slope, that for the open circles appears to be $\sim 6\times 10^{-4}$ (the same as in Fig. 4). Following the intentional irreversible relaxation, the filled circles indicate a smaller slope of $\sim 2.5\times 10^{-4}$. This suggests that the reversible relaxation process is influenced by the history of irreversible relaxation.[24] It would be interesting to measure, at fixed values of T_a, the rate of approach of T_c to the reversible portion of the curves. This information would provide a value for the effective activation energy of the reversible process. However, such measurements are best carried out using techniques considerably more efficient in time.[4,5]

The response to annealing of another sample is also shown in Fig. 5, and the data are labeled in the sequence in which they were obtained. Initially the sample was given a 20-min standardization treatment at 290 °C, giving point 1. This point lay very close to an extrapolation of the reversible curve (the dotted line) for the previous sample. Point 2, which was obtained after a 10-min anneal at 262 °C, also lies on this curve. Another 10 min at 290 °C (point 3) caused an irreversible relaxation of −0.004 K. This unintentional decrease of 0.004 K is now added as a correction to the next two 10-min anneals,[25] namely point 4 and point 5. We thus see in Fig. 5 that two nearly identical T_c-T_a curves are obtained for two samples, even though their thermal histories are not the same. The two standardization anneals, 20 min at 290 °C and 45 h at 200 °C, produced essentially the same irreversible relaxation from the as-quenched state.

It would be helpful if the reversible portions of the T_c-T_a curves could be extended. At higher T_a this might be accomplished by shorter anneals and faster quench rates. At lower T_a the annealing time would have to be extended. We tried this between data points 5 and 6 of Fig. 5. A first anneal of 45 h at 123 °C indicated that, at 123 °C, an inconveniently long anneal would be required. Therefore, 173 °C was tried, first for 96 h to check on progress, then to a total of 264 h which produced point 6. This point was rather close to an extrapolation of the equilibrium curve, so a sequence of 10-min isochronal anneals was carried out to determine if the sample was indeed on the same curve. The dashed line shows that the sample had been altered, that some irreversible relaxation had occurred during the total of 309 h in the furnace. Thus, it is not possible, for Zr-Ni, to extend the reversible portion of the T_c-T_a curves to significantly lower temperatures.

Two additional relaxation phenomena were observed. First, it will be noted that the two samples of Fig. 4 were nearly identical in their behavior *except* in the rate at which irreversible relaxation entered near 300 °C. Based on experience with other samples, the two samples of Fig. 4 could be expected again to attain nearly the same T_c after a long-term anneal at some temperature near 300 °C. Hence, even though the samples were nearly identical in many respects, the kinetics of irreversible relaxation differed. This made it difficult to plan a set of heat treatments for the reversible portion of the T_c-T_a curve as it was not known *a priori* where irreversible relaxation would commence. Second, from the data of Fig. 5 represented by circles, it may be seen that irreversible behavior sets in at lower T_a as the irreversible process progresses. The open circles show irreversible behavior at $T_a \geq 298\,°\text{C}$, whereas for the filled circles irreversibility occurs at $T_a \geq 270\,°\text{C}$. This effect, combined with the decrease in slope of the reversible portion of the T_c-T_a curve, makes it more difficult to detect reversible behavior in Zr-Ni as the amount of irreversible relaxation increases.

It should be emphasized that the word "reversible" is used for convenience. The continuum of states or configurations of the sample represented by the reversible portion of the T_c-T_a curve are only in metastable equilibrium. A sufficiently long anneal at any temperature on this curve will cause irreversible relaxation. As an example, one glassy Zr-Ni sample was standardized at 300 °C for 21 h, then given a sequence of long isochronal anneals of 30-min duration. Contrary to the data of Figs. 4 and 5, the T_c decreased continuously by a total of 20 mK between 100 and 300 °C except in the region from 210—260 °C where T_c was essentially independent of T_a.

The relaxation behavior of the glassy Zr-Ni alloy can be explained by the simplified energy function dU sketched in Fig. 6 where z is a generalized configurational coordinate. Here dU is the potential energy of a local region of sample having a volume dV. An ensemble of similar curves would represent the entire sample. At low temperatures of ~200 °C, following standardization, the material contained in dV might lie in the energy minimum at A. As the temperature is increased to 270 °C, there would be an increased probability of finding dV in minimum B. A rapid quench as in the present measurements could leave dV with insufficient thermal energy to surmount barrier C and return to the minimum of lower energy at A. Increasing the temperature still further, to ~300 °C, would permit dV to surmount barrier D, but then the thermal energy would also permit a transition over barrier E to a region of still lower potential energy. The probability of surmounting barrier F, on the other hand, is much smaller. To move a significant distance toward positive z would require remelting of the sample.

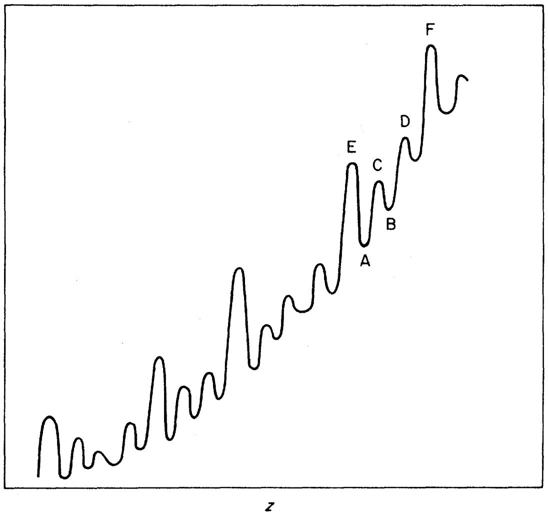

FIG. 6. Schematic representation of the potential energy dU, of a small volume of a glassy Zr-Ni sample, as a function of a generalized configurational coordinate z. Other elements of volume would have similar curves, but different in detail.

The metastable positioning of dV among the minima situated between a pair of large peaks in Fig. 6 corresponds to the reversible behavior of the T_c-T_a curve.[26] An excursion over a large barrier represents an irreversible relaxation process. Note that, even if the material in dV is located at minimum A, there does remain a small but finite probability of thermally surmounting barrier E towards smaller values of z. This is consistent with our observation that irreversible relaxation occurs even on the reversible portion of the T_c-T_a curve provided sufficient time is provided at a specified T_a. We had mentioned previously that irreversible behavior sets in at lower T_a as the irreversible process progresses (see Fig. 5). This suggests that the difference in size, between the low- and high-potential barriers of Fig. 6, decreases as the curve is followed to the left toward more stable atomic configurations.

It has been suggested[3] that reversible relaxation (which we associate with the smaller barriers in Fig. 6) is related to a compositional or chemical short-range ordering, while the irreversible relaxation (via the large barriers of Fig. 6) may be associated with a topological short-range order. The present measurements contribute little to this question. It has been reported[6] that irreversible relaxation in a glassy metal does lead to a significant increase in mass density, whereas any density change associated with reversible relaxation is too small to measure ($<0.01\%$). We also attempted to detect a density change by measuring the length of the sample. To the 0.01% resolution available, no change could be observed over the reversible por-

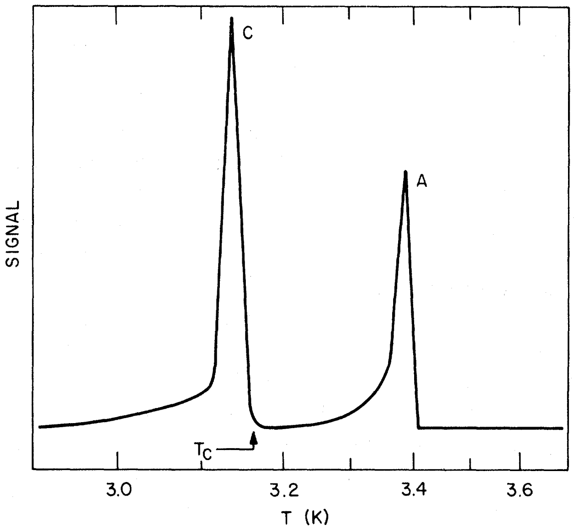

FIG. 7. Output signal for two glassy Zr-Ni samples measured during the same cryogenic run. *A*, virgin sample used to provide a reference temperature; *C*, sample from same splat annealed for 21 h at 270 °C, then reduced in thickness ~12% by cold rolling. The vertical scale is arbitrary, but is the same as in Fig. 3.

tion of the T_c-T_a curve of Fig. 5.

We do not know why T_c changes with T_a. It has been shown[6] that the velocity of sound decreases reversibly with increasing T_a in the glassy alloy $Co_{58}Fe_5Ni_{10}B_{16}Si_{11}$. If the same phonon softening should occur in glassy Zr-Ni, this fact alone might account for the reversible increase in T_c with increasing T_a. To summarize this section we note by the change in T_c that a reversible thermal relaxation process does occur in the glassy metal-metal alloy $Zr_{76}Ni_{24}$.

B. Deformation

The effect of cold rolling a glassy Zr-Ni sample is shown in Fig. 7 by curve *C*. Sample *C* had been standardized for 21 h at 270 °C prior to a reduction in thickness of ~12%. Comparison with sample *B* of Fig. 3, which received the same standardization, shows that the 12% deformation caused no *major* change in the T_c nor in the shape of the curve. Samples which had not been standardized prior to deformation produced signals similar to that of the as-quenched sample *A* of Figs. 3 or 7. In brief, the effect of cold rolling is qualitatively independent of the preanneal cycle. Also, the effect of deformation did not depend on whether the samples had been deformed by rolling in only one direction, or in two perpendicular directions.

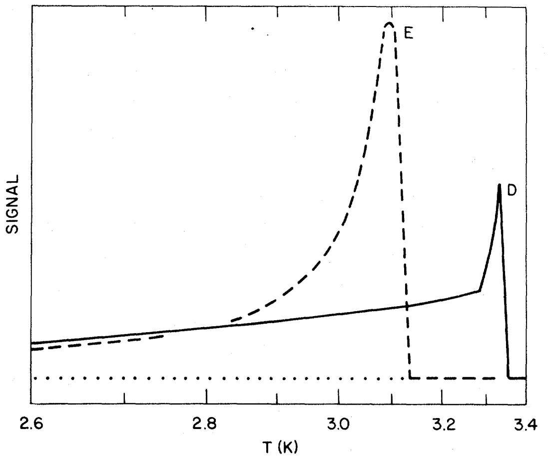

FIG. 8. Output signal for a glassy Zr-Ni sample reduced by cold rolling to one-fifth of the original thickness. *D* (solid curve), cold rolled with no pre- or postanneal; *E* (dashed curve), same sample following a postanneal of 22 h at 270 °C. The dotted line indicates zero output signal. Cold rolling increased the area of the foil; the sample used here had been recut to a size similar to other undeformed samples. The vertical scale has been amplified by a factor of 2 relative to Figs. 3 and 7 to exhibit more clearly the low-temperature tail. This tail continued downward in temperature to ~2.3 K.

Deformation does alter the detailed behavior of superconducting glassy Zr-Ni. In one fraction of the sample T_c is increased slightly by ~1%. In another fraction T_c can be reduced by as much as 30%. The reduction in T_c will be discussed first.

By comparing Figs. 3 and 7 it may be noted that, following deformation, a small low-temperature "tail" appears on curve *C*. The magnitude of this tail increases with increased deformation. An extreme example at 80% reduction is shown by curve *D* in Fig. 8. Whereas the peak at 3.33 K scales linearly with the ac magnetic measuring field, the tail is a much stronger function of the measuring field. A simple explanation is available for this behavior. Deformation of glassy alloys near room temperature is generally inhomogeneous. Indeed, microscopic examination of sample *D* (Fig. 8) revealed deformation bands separated by ~2 μm. Thus the peaks in Figs. 7 or 8, which remain after deformation, may be attributed to the three-dimensional islands of material which have not undergone significant deformation. The tail at lower temperatures may be due[27] to highly strained material lying within the deformation bands and having a lower T_c. The strong field dependence of the tail could arise because of the difficulty of moving magnetic flux in and out of the sample, during each one-half cycle of the measuring field, through the narrow "webbing" of deformation bands between the superconducting islands. Qualitatively it appears from these measurements that increased deformation does decrease the amount of lightly strained material, and increases the portion of highly strained material, present in the sample.

Note that deformation does not produce a tail extending to temperatures higher than the original T_c, but only to lower temperatures. In brief, deformation produces the same qualitative effect as annealing. This conclusion is supported by curve *E* of Fig. 8, which is the same sample as curve *D* but following an anneal at 270 °C for 22 h. The T_c is reduced to that of curve *C* in Fig. 7, i.e., T_c is nearly the same independent of whether the sample was deformed then annealed, or annealed then deformed. In addition, from Fig. 8, the tail that did exist above 3.13 K has been eradicated, while that lying below ~ 2.8 K remains essentially unchanged by the 270 °C anneal. Thus, the portions of the sample having a local T_c less than 2.8 K have, *in effect,* been "annealed" by the deformation process at a temperature larger than 270 °C. The surviving portion of the tail will not be eradicated until the sample is actually annealed thermally at a temperature > 270 °C. One possible interpretation of this behavior is that the material in the deformation bands has actually been heated to high temperatures (but less than T_{melt}) during deformation. An alternative explanation is presented below.

Deformation also increases the T_c of some fraction of the sample by a small amount, $\sim 1\%$. This fraction may be associated with the islands of lightly strained material. Sample *C* of Fig. 7 had been preannealed to reduce T_c. The reduced T_c permitted use of a reference sample (*A* of Fig. 7) during the same run, and hence allowed a precise determination of small changes in T_c. The small increase in T_c with increasing deformation is shown in Fig. 9. The uncertainty in measuring the average deformation $\Delta d/d$ was larger for small deformation. The overall change in T_c could be linear as indicated by the dashed line. Referring to Figs. 4 and 5, this increase in T_c with deformation could be attributed to a significant rise in temperature of the entire sample during deformation (to ~ 300 °C), followed by rapid cooling. However, such a temperature rise is unlikely. Rather, the effect of stress is probably to readjust the relative depths of the minima in the potential energy curve of Fig. 6 and thereby permit thermal hopping (over the barriers) which would otherwise not occur with finite probability near room temperature. Likewise we speculate that the heavily deformed material in the deformation bands, that producing the tail of Fig. 8, may not truly be raised in temperature to well above 300 °C. Rather, the concentrated local stress in the deformation bands may modify the curve of Fig. 6 until the higher barriers can be surpassed statistically even at a moderate increase in temperature.[28]

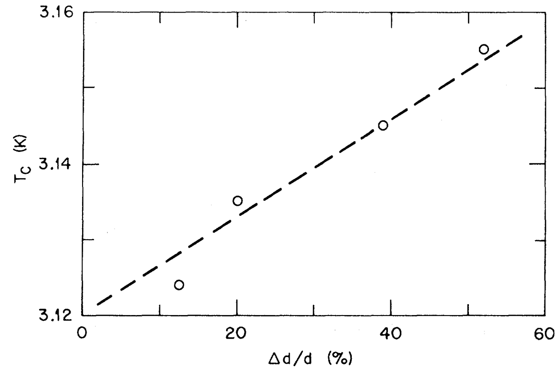

FIG. 9. Increase in the superconducting transition temperature T_c of Fig. 7 as a function of the reduction in thickness *d* with cold rolling.

Irrespective of the temperature attained during deformation, one can argue that the effects of deformation and of heat treatment on glassy Zr-Ni are similar in character because both are associated with the same basic mechanisms of atomic-scale motion or reconfiguration.

IV. SUMMARY

The reversible annealing behavior found in various amorphous materials also occurs in the glassy metal—metal alloy $Zr_{76}Ni_{24}$. For 10-min isochronal anneals at temperature T_a, we find the superconducting transition temperature T_c to increase reversibly with increasing T_a for $T_a \leq 300$ °C. For $T_a \geq 300$ °C, an irreversible decrease in T_c occurs.

Inhomogeneous deformation of glassy $Zr_{76}Ni_{24}$ by cold rolling alters the superconducting transition in two ways. The T_c of one fraction of the sample is increased slightly by $\sim 1\%$ while in an interspersed fraction of the same sample the T_c is reduced by as much as 30%. Our data suggest that the large decrease in T_c may occur in the deformation bands. Both effects of deformation appear to be indistinguishable from the effects of heat treatment. It is not suggested that high temperatures are present during deformation, but rather that stress fields encourage the same atomic-scale relaxation processes which are active in thermal annealing.

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[14] D. M. Kroeger, W. A. Coghlan, D. S. Easton, C. C. Koch, and J. O. Scarbrough, J. Appl. Phys. 53, 1445 (1982).

[15] See, for example, D. E. Mapother, Phys. Rev. 126, 2021 (1962).

[16] This suggestion can be tested by computing the Ginzburg-Landau parameter κ (Refs. 17 and 18) from our data and comparing this value with independent measurements. Since $H_{c2}=\sqrt{2}\kappa H_c$ near T_c, $(dH_{c2}/dT)_{T_c}=\sqrt{2}\kappa(dH_c/dT)_{T_c}$. Using as an estimate (Ref. 19) $(dH_{c2}/dT)_{T_c}\approx 3$ (T/K) and assuming $(dH_c/dT)_{T_c}=(dH_E/dT)_{T_c}$ with $(dH_E/dT)_{T_c}\approx 5\times 10^{-3}$ T/K as measured, we find $\kappa=400$ as an upper limit. For a lower limit use $H_{c1}=(H_c/\sqrt{2}\kappa)\ln\kappa$, thus $dH_{c2}/dT\approx\kappa^2 dH_{c1}/dT$. Assuming now that $(dH_{c1}/dT)_{T_c}=(dH_E/dT)_{T_c}$ we find $\kappa\approx 24$ as a lower limit. Finally, κ can be computed directly from the expression $\kappa=7.5\times 10^3\rho\gamma^{1/2}$ using the measured electrical resistivity (Ref. 11) ($\rho=167\times 10^{-6}\ \Omega\,\mathrm{cm}$) and specific-heat coefficient (Ref. 20) ($\gamma\approx 5600$ erg/cm^3 K^2) for $Zr_{76}Ni_{24}$ to give $\kappa=94$. This value does lie between our limits of $\kappa=24$ and 400 found above.

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[22] Irreversible relaxation of $Zr_{76}Ni_{24}$ at $T_a\geq 300\,^\circ\mathrm{C}$ has also been observed in internal friction measurements by A. DasGupta (private communication).

[23] A 17-h anneal at 288 °C continued the irreversible relaxation of Fig. 4, reducing T_c to 2.84 K and producing a net decrease of a factor of ~ 7 in $(dH_E/dT)_{T_c}$.

[24] It is reported in Ref. 5 that the reversible portions of resistance versus T_a curves for glassy $Fe_{40}Ni_{40}P_{14}B_6$ do not change slope after irreversible relaxation until crystallization does, or is about to, commence.

[25] A long and, in retrospect, unnecessary stabilization anneal of 45 h at 200 °C was given to this sample between points 3 and 4.

[26] Figure 6 is consistent with the reversible calorimetric behavior discussed in Ref. 8.

[27] The possibility of a change in surface barrier or a reduction in flux pinning has been considered, but it is unlikely that such effects would contrive to produce the annealing behavior reported here.

[28] It would be useful to compare the present deformation results with x-ray measurements in an attempt to determine the atomic nature of the deformation process, see for example, Y. Waseda, K. T. Aust, and T. Masumoto, Scr. Metall. 13, 187 (1979) and Y. Calvayrac, M. Harmelin, A. Quivy, J. P. Chevalier, and J. Bigot, *ibid.* 14, 895 (1980). Such a comparison is difficult because of the inhomogeneous nature of the deformation combined with the fact that x-ray measurements average over the entire sample. No attempt has been made to deconvolute the relative atomic displacements occurring in deformation bands from those in the weakly strained islands.