PHYSICAL REVIEW B VOLUME 37, NUMBER 13 1 MAY 1988

Annealing effects on the sound velocity and internal friction in the superconducting and normal states of the $Cu_{30}Zr_{70}$ amorphous alloy

P. Esquinazi and J. Luzuriaga
Centro Atômico Bariloche, Instituto Balseiro, 8400 Bariloche, Argentina

(Received 10 August 1987)

By means of the vibrating-reed technique we have measured the evolution upon low-temperature annealing of the internal friction Q^{-1} and sound velocity v of the $Cu_{30}Zr_{70}$ amorphous alloy between 0.1 and 10 K. With an applied magnetic field of 5.6 T we measured also the normal-state behavior of both properties. Upon annealing, the internal friction and the slope of the logarithmic temperature dependence of v in the superconducting state decrease, in agreement with the standard tunneling model. Our results indicate that with thermal treatments, the coupling constant between tunneling systems (TS's) and phonons decreases, and the density of states of the TS remains constant or decreases, at most 25%, in the fully relaxed state, which is in agreement with published specific-heat results in these materials. From our data we conclude that the coupling constant between the TS and phonons should be very sensitive to the relaxed state of the disordered structure. The sound-velocity behavior strongly indicates that relaxation processes up to 10 K involve the interaction with the TS. A well-defined change of slope in v at the superconducting critical temperature T_c is observed in the as-quenched and the first relaxed state, which cannot be explained with the standard tunneling model and the Korringa-like relaxation rate between the TS and electrons. Several features observed in the superconducting and normal states lead to the conclusion that the TS-electron interaction problem remains unsolved.

I. INTRODUCTION

Properties of metallic and insulating glasses have been intensively studied in the past 20 years.[1,2] These materials are important for their technologically interesting properties,[3,4] and also for their almost universal behavior at low temperatures which is a fascinating problem in basic research.[5,6]

The well-known tunneling model[7] (TM) has been very successful in explaining a wide variety of low-temperature properties of amorphous materials by assuming the existence of low-energy excitations or tunneling systems (TS's) with a wide distribution of energies and relaxation times in glasses or in highly disordered crystals.[1,2] The main aspects of the low-temperature specific heat, thermal conductivity, sound attenuation, etc., are quantitatively explained by the model,[1,2,5,8] however, the microscopic nature of the TS remains unclear. It is often stated that it is an atom or a "small" group of atoms which tunnels between two almost equivalent positions in the amorphous structure. Theoretical models much more sophisticated than this have been proposed and attempts to correlate the TS with "voids" (liquidlike clusters),[9] "polymorphism",[10] "disclination loops",[11] and "critical potentials" in certain local structures,[12,13] and also to special features observed in computer-generated structural models,[14–16] have been made, but in spite of the insight gained from complementary and sometimes even contradictory approaches and the partial successes these efforts can claim, no definitive assessment for the nature of the tunneling systems has been given.

Through thermal conductivity measurements, changes of the interaction between phonons and the TS's have been seen with annealing, and in Zr-based amorphous alloys a reduction of the product $P\gamma^2$ has been reported.[17–20] Here P is the density of states of the TS and γ is the average deformation potential or coupling constant between the TS's and phonons. The meaning of this change is still somewhat controversial since measurements show a rather constant specific heat upon annealing,[19,20] indicating that P remains fairly constant. Since a decrease in P was expected, among other reasons due to the decrease in $P\gamma^2$, a qualitative explanation given was that the relaxation spectrum of the TS was changing,[19] that is, the amount of the TS was increasing or decreasing according to their tunneling or energy splitting in such a way as to change the thermal conductivity but keeping the specific heat constant. An alternative explanation would be that it is only γ that is changing at constant P. Since acoustic measurements can, in principle, determine P and γ independently (unlike thermal conductivity which is sensitivity to the product $P\gamma^2$), one of the goals of the present paper is to clarify this situation; the results seem to favor the second explanation.

Recently published acoustic measurements[21,22] on two Zr-based amorphous alloys have revealed several shortcomings of the standard TM when the TS-electron interaction based on a Korringa-like relaxation time[5,23,24] is assumed. The interaction of the TS-electron-phonon system is still an open question. Some ideas proposed include the formation of highly correlated oscillations of the conduction electrons around the TS leading to some sort of "bound state" which could reduce the effective density of states for the TS interacting with phonons,[25] and that the coupling constant between the TS and electrons depends on the electronic density of states or, in superconductors, on the amount of Cooper pairs. It is hoped that more experimental data can help clarify the situation. To our knowledge no low-temperature experiments, where acoustic properties are measured at different stages of annealing in superconducting glasses, have been reported, although they could yield data on the variation of the couplings in the TS-electron-phonon system for different states of relaxation of the amorphous material. Measurements in the normal and the superconducting state also give the possibility of gaining additional information by comparing the same material with and without normal electrons at low temperatures.

We present here the results of low-frequency measurements of acoustic properties as a function of annealing in the $Cu_{30}Zr_{70}$ metallic glass. The alloy is superconducting with $T_c = 2.6$ K. Applying a magnetic field of 5.6 T, the material could be driven normal.

The organization of the paper is as follows. Section II presents a short review of the main changes produced by heat treatments on several properties of the $Cu_{30}Zr_{70}$ amorphous alloy. Section III gives a few details of the sample preparation and experimental arrangement. In Sec. IV sound-velocity and internal friction results are presented, the discussion of the results corresponds to Sec. V, and Sec. VI is a summary where the main conclusions of the paper are outlined.

II. ANNEALING BEHAVIOR

It is well known that annealing amorphous metals below the crystallization temperature produces changes in the topological (and also possibly chemical) short-range order through local atomic rearrangements without changing the amorphous nature of the structure.[3,26,27] It is believed a more relaxed amorphous structure is reached, with a lower concentration of "extrinsic" defects. Properties such as low-temperature thermal conductivity,[17–20] specific heat,[19,20,28] sound dispersion,[29,30] internal friction,[31] and pinning forces,[32] have been reported to change with annealing.

Because we are interested in the $Cu_{30}Zr_{70}$ amorphous alloy and in the correlation between the state of disorder and the low-energy excitations (TS), we think it may be useful to review here the main structural relaxation effects in this system. The evolution of amorphous $Cu_{30}Zr_{70}$ has been extensively studied in our laboratory; electrical resistivity,[18,33] superconducting critical temperature,[18,34] critical field B_{c2},[34] low-field penetration depth $\lambda(T)$,[35] pinning forces,[36] elastic coupling (Labusch constant) of the vortex lattice to the pinning centers,[37] and thermal conductivity κ,[18] have been measured.

In all the experiments mentioned above the heat treatments have been made at constant temperature between 423 and 523 K for a specific annealing time. The glass transition temperature of amorphous $Cu_{30}Zr_{70}$ is 590 K and its crystallization temperature is 630 K.[38–40] From all the measured properties one can conclude that there are two well-defined regimes. The first regime where a homogenization of the material occurs, and the second regime where devitrification or microcrystallization sets in. In the first regime the resistivity remains practically constant (it systematically increases by approximately 1%) and T_c decreases roughly by 15%, see Fig. 1. One could think that the first structural relaxation regime corresponds to a local atomic regrouping leading to a homogenization of the material. Upon further annealing in the second regime, microcrystallization starts through long-range cooperative structural rearrangements (with possible phase separation).[3,27]

The information obtained from the penetration depth[35] and the evolution of the elastic coupling of the vortex lattice,[37] properties which are sensitive to the surface of the sample, indicates that some kind of surface phase segregation takes place before the beginning of the second regime where the resistivity decreases and T_c remains approximately constant. An analysis of the data[35,37] indicates that a small amount of a normal or superconducting phase (hundreds of Angstroms thick) with $T_c < 1$ K is growing at the surface, probably small amounts of ω-Zr [$T_c = 0.7$ K (Ref. 41)] embedded in a Cu-rich amorphous matrix. Nevertheless, normal x-ray analysis does not detect the presence of crystalinity.[35] One could ask if properties like the electrical resistivity, thermal conductivity, critical fields, and in our case internal friction and sound dispersion, are sensitive to this surface phase separation before the crystallization. Analysis of the experimental data leads to the conclusion that these properties are rather insensitive to the surface segregation.

III. EXPERIMENTAL DETAILS

The sample, in the form of a ribbon about 10 cm long, 17 μm thick, and 1 mm wide was made using the melt spinning technique described in Ref. 42. From this long ribbon two short pieces were cut. One of the pieces was used to characterize the sample by measuring the electrical resistivity temperature dependence and the superconducting transition. It has been observed that these two properties are much more sensitive to the presence of microcrystalites and inhomogeneities in the amorphous matrix than normal x-ray analysis.[38,43] The sample had a negative temperature coefficient of resistivity (-0.05 between 4 and 300 K) with an absolute value for the residual resistivity of 180 $\mu\Omega$ cm. The superconducting transition measured with the standard four-probe technique was found to be at 2.806 K with a transition width $\Delta T_c = 32$ mK (determined from 10% and 90% of the resistive transition). This rather small width is indicative of a good degree of sample homogeneity and amorphicity. This sample was attached to the same holder as the vibrating reed in order to monitor the evolution of T_c; the resistive transition was measured after each heat treatment simultaneously with the internal friction and sound velocity.

The other piece of sample which was 3.20 mm long, 0.51 mm wide and 17±2 μm thick was used for the low-frequency measurements by means of the vibrating reed technique.[44] Our experimental setup was similar to that used in Refs. 21 and 22 and was described in more detail in Ref. 45. The sample, clamped with its main area perpendicular to the applied magnetic field, was made to oscillate at the resonance frequency ω (first normal mode) with a tracking circuit. From the relative change in the resonance frequency with temperature we obtain $\Delta v_E/v_E$, where v_E is the Young modulus (E_Y) sound velocity, $(E_Y/\rho_d)^{1/2}$ (ρ_d is the mass density which for our sample was 7.0 g/cm^3). Simultaneously, we measured the resonance amplitude u_m at different temperatures which gives the temperature dependence of $Q^{-1} \propto 1/u_m\omega^2$. The absolute value of Q^{-1} was obtained at several different temperatures from the resonance curve, obtained by sweeping the driving frequency while measuring the corresponding amplitude. Within our error ($\sim 2\%$), both methods gave the same T dependence for Q^{-1}. In the whole temperature range we used very low driving voltage so that the strain at the free end was estimated to be 1×10^{-8}.

Measurements were performed in a small dilution refrigerator. The sample was clamped between two well-polished and previously annealed (30 h at 300 °C) Cu plates. The distance between electrodes and the free end of the sample was $\cong 0.2$ mm. The sample holder was specially built to make possible heat treatments without removing the sample and the electrodes. We made coaxial electrodes with a ceramic core with 1-mm-i.d. Cu wire. Removing only the thermometers we annealed the assembled sample and holder in a low-pressure pure argon atmosphere. Special care was taken not to touch or move the electrodes between different experiments. In this way we kept constant the effective sample geometry and electrostatic corrections[31] [the sample is slightly tilted when the bias voltage (150 V) is applied, giving an estimated 1% correction to the absolute value of the Young modulus].

The temperature was measured with three previously calibrated thermometers. Two of these were different carbon resistors which showed 5% temperature deviation with a magnetic field of 5 T below K. The other thermometer was a field-independent carbon glass. The magnetic field, perpendicular to the main area of the sample, was provided by a superconducting solenoid operated in persistent mode.

IV. EXPERIMENTAL RESULTS

The three experiments reported in this work correspond to three different annealing stages: as-quenched, first anneal (15 min. at 200 °C), and second anneal (20 h at 200 °C). In the first anneal the sample showed a decrease in T_c and ΔT_c: $T_c = 2.715$ K, $\Delta T_c = 13$ mk; in the second anneal $T_c = 2.436$ K and $\Delta T_c = 26$ mK with 8.1% increase in ω ($\cong 17\%$ increase in E_Y). From the literature one expects that with our heat treatments the change in length, volume or mass density in our sample should be less than 1%.[39,46]

For the as-quenched sample we obtain $v_E = (2.8\pm0.3)\times10^5$ cm/s and a Young modulus $E_Y = (5.5\pm1)\times10^{11}$ dyn/cm^2, in agreement with published results.[47] According to data in the literature,[3,48] and as a characteristic of the ductile plastic deformation in metallic glasses, the estimated Poisson's ratio for our sample is ≤ 0.40. With this value the longitudinal and transversal sound velocity are $v_l \leq 1.27 v_E$ and $v_t \geq 0.60 v_E$.

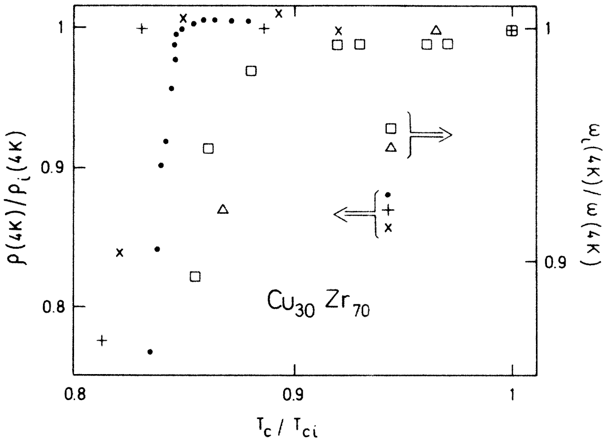

FIG. 1. Relative change upon annealing of the electrical resistivity ρ and resonance frequency ω at 4 K as a function of the relative value of the superconducting critical temperature T_c/T_{ci} (i means initial or as-quenched state). (+), Ref. 18; (×), Ref. 36; ●, Ref. 38; (□,△), this work.

The measurement of the evolution of the resonance frequency at 4 K with annealing provides an interesting result. Figure 1 shows $\omega_i(4\text{ K})/\omega(4\text{ K})$ (i denotes initial or as-quenched state) versus T_c/T_{ci} for two different Cu$_{30}$Zr$_{70}$ samples with different heat treatments. We observe that $\omega(4\text{ K})$ remains practically constant in the first regime up to a $T_c = 0.9 T_{ci}$, and upon further annealing it increases. Note that ω starts to increase before the resistivity decreases, i.e., there is an increase of the Young modulus E_Y before the beginning of crystallization. This behavior suggests that the elastic response of this amorphous alloy is sensitive to cooperative rearrangements or compositional fluctuations which occur before the crystallization to the stable phases (α-Zr+CuZr$_2$).[40] The increase of E_Y for $T_c > 0.87 T_{ci}$ is less than 17%, in agreement with the increase observed in different amorphous metals prior to crystallization.[3,27,46]

A. Sound velocity results

The relative change

$$\Delta v_E/v_E = [v_E(T) - v_E(T_0)]/v_E(T_0)$$

of the Young modulus sound velocity with respect to an arbitrary reference temperature T_0 is shown in Fig. 2 for the as-quenched sample and for the two different heat treatments. The field is zero and the arrows indicate the superconducting transition.

At the lower limit of our temperature range (see also Figs. 3–5) with an expanded scale), we observe the end of the sound-velocity maximum usually seen in amorphous materials and which coincides with the end of the internal friction "plateau" regime (see Refs. 22 and 45 in our Figs. 9-11). As the temperature is raised v_E decreases logarithmically until a temperature T_1 is reached. This temperature shifts in the same way as the superconducting critical temperature T_c upon annealing, so that T_1 is always approximately $T_c/6$. After T_1 there is a much

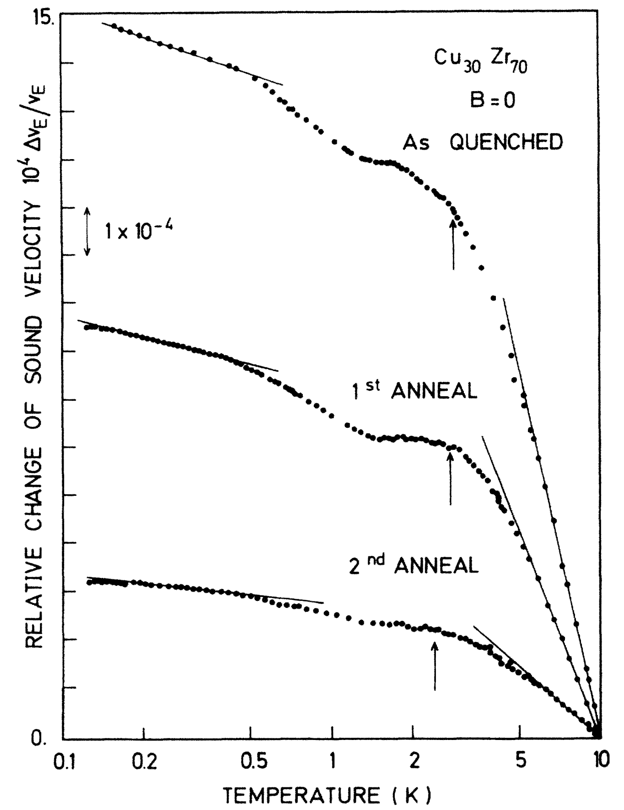

FIG. 2. Relative change of sound velocity $\Delta v_E/v_E$ as a function of temperature for three sample states. The arrows indicate the corresponding critical temperature $T_c = 2.806$, 2.715, and 2.436 K for the as-quenched, first anneal, and second anneal, respectively. The solid lines are only a guide to the eye. Observe that the relative decrease of the drawn slopes below 0.5 K and above 5 K is the same.

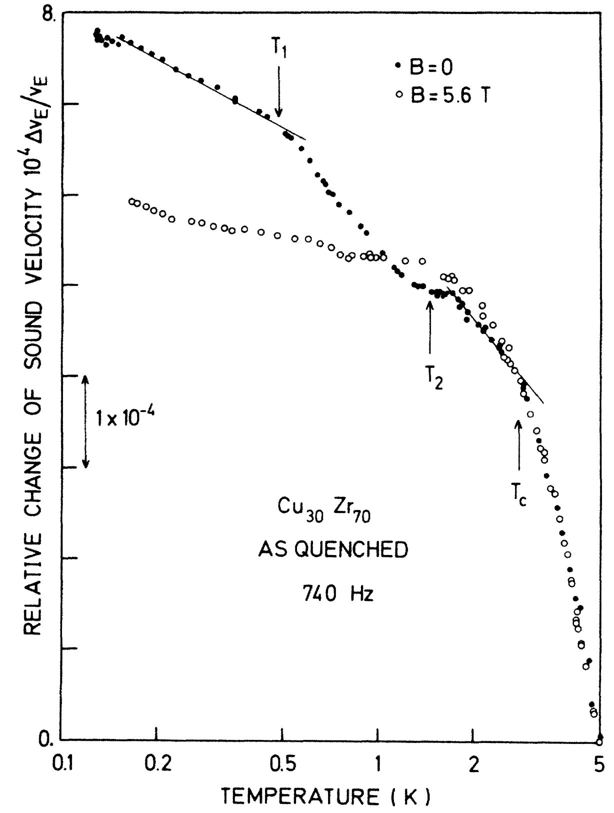

FIG. 3. Sound-velocity change vs temperature for the as-quenched state in the superconducting (●) and normal (○) states. $T_1 = 0.48$ K and $T_2 = 1.45$K . From the logarithmic slope below T_1 (solid line), and according to the tunneling model, we obtain $C = 1.6 \times 10^{-4}$. Note the change of slope below T_c.

faster decrease in v_E until at a temperature T_2, which also scales with T_c ($T_2 \cong T_c/2$), a well-defined kink is observed. Between T_2 and T_c the velocity still decreases but with a much smaller slope, and in the case of the first and second anneal it almost remains constant. There is a further change in slope at the superconducting critical temperature T_c, which is most noticeable in the first anneal (Fig. 4). At the highest temperatures we measure, between 5 and 10 K, the change in sound velocity can be expressed by a logarithmic function (Fig. 2). We want to note that precise low-frequency and ultrasonic measurements in $Cu_{30}Zr_{70}$ (Ref. 49) and SiO_2 (Suprasil W) (Ref. 50) up to 20 K indicate that there is no strictly linear T regime as was stated in Ref. 51.

Since at $T < T_c/6$ the amount of "normal electrons" (i.e., of quasiparticles excited across the energy gap) is negligibly small, they do not contribute to the relaxation mechanism and because we are in the temperature region where $\omega\tau_{\mathrm{ph}m} \ll 1$ ($\tau_{\mathrm{ph}m}$ is the minimum relaxation time due to the phonon interaction), the observed logarithmic temperature dependence can be understood in terms of the positive $+C$ contribution to the slope by the resonance process [52]and the negative $-3C/2$ contribution of the one-phonon relaxation.[53] The slope of $\Delta v_E/v_E$ in the logarithmic plot according to the TM then is equal to $-C/2$ where the parameter

$$C = P\gamma^2/\rho_d v^2 \,, \tag{1}$$

where P is the density of states of TS, γ the coupling parameter between phonons and TS, ρ_d the mass density, and v is the sound velocity. The numerical values of C obtained by fitting this slope are $C = (1.60 \pm 0.08) \times 10^{-4}$, $(1.14 \pm 0.07) \times 10^{-4}$, and $(0.30 \pm 0.035) \times 10^{-4}$. It should be noted that ρ_d changes less than 1% upon annealing and v less than 8%, so that changes in C reflect mainly the changes in the product $P\gamma^2$. The value of $P\gamma^2$ obtained in the as-quenched state is very similar to that obtained in other Zr-based glasses from low-frequency[22] and thermal conductivity[18–20] measurements. For example, Ref. 18 reports $P\gamma^2 = 1 \times 10^8$ erg/cm^3 obtained from thermal conductivity compared to $P\gamma^2 = 9 \times 10^7$ erg/cm^3 obtained here, an agreement that is remarkable if we take into account the difference in phonon frequencies and time relaxation spectrum probed by these two properties. When comparing C with that obtained in a sample that was annealed for one year at room temperature,[22] it can be seen that C in the as-quenched sample is larger by about a factor of 2. The T_c of the sample in Ref. 22 is 2.5

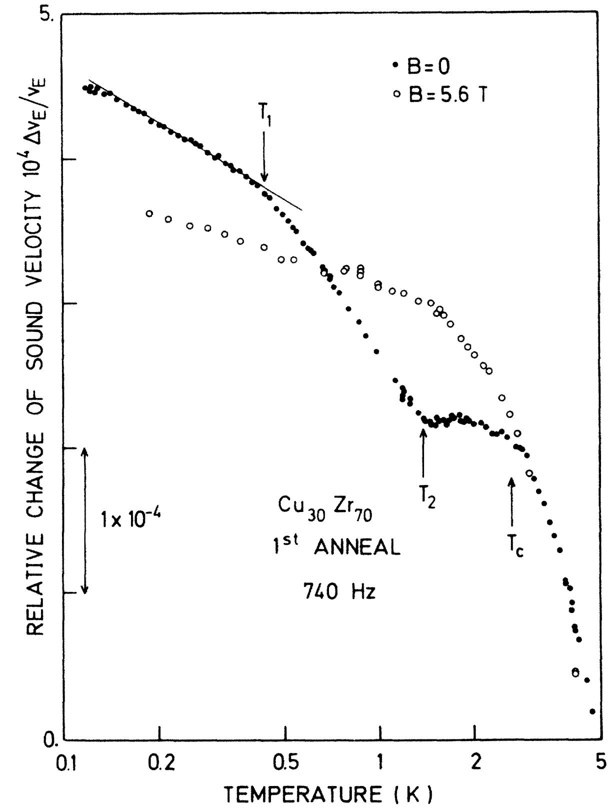

FIG. 4. Same as Fig. 3; $T_1=0.44$ K and $T_2=1.40$ K. From the data below T_1 we obtain $C=1.14\times10^{-4}$.

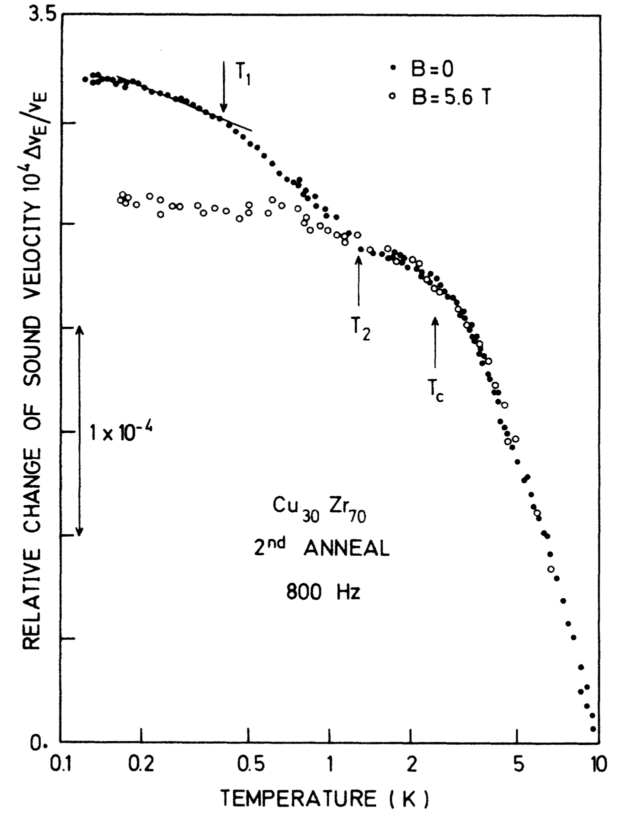

FIG. 5. Same as Figs. 3 and 4; $T_1=0.40$ K, $T_2=1.27$ K, and $C=3.0\times10^{-5}$. Note that there is no apparent difference between the normal and superconducting state between T_2 and T_c. Compare this result with that obtained for a room-annealed sample in Ref. 22.

K, 0.3 K lower than our as-quenched sample. The difference in C could be due entirely to the room-temperature annealing since a similar effect has been observed in thermal conductivity experiments[18] and is in agreement with changes observed for the shorter heat treatments at higher temperatures.

The behavior of v_E between T_1 and T_2 which shows a greater decrease than the logarithmic behavior due to the interaction of the TS and phonons must be due in some way to the contribution of the normal quasiparticles. But if one uses the standard Korringa-like interaction for the TS-electron relaxation rate, features such as the change in slope at T_c or the kink at T_2 cannot be explained. The scaling of T_1 and T_2 with the critical temperature upon annealing seems to indicate that the TS (electron mediated) relaxation time, independently of its temperature dependence, should scale with the reduced critical temperature $t=T/T_c$.

The decrease in v_E above T_c can be qualitatively understood by taking into account higher-order processes such as the two-phonon Raman process,[54] although it is not possible to get a good quantitative fit for the experimental data above 3 K if one uses the standard distribution function of the TS

$$P(E,u)dE\,du=P\,dE\,du/u(1-u^2)^{1/2}\ , \qquad (2)$$

where E is the energy splitting of the two levels and $u=\Delta_0/E$ with Δ_0 the tunneling splitting. A similar difficulty was encountered in Ref. 22. Corrections to $P(E,u)$ can improve the fitting substantially as was found in vitreous silica where the same type of corrections can fit the sound dispersion up to 10 K.[50]

Independent of the detailed process at $T>3$ K, if one fits a straight line to the data between 5 and 10 K in Fig. 2 (note the logarithmic scale), it can be seen that the relative change in slope upon annealing is, within a few percent, the same as the change in the C parameter obtained previously from the slope of the curves at low temperatures where one-phonon processes are dominant. This result strongly suggests that up to 10 K the phonons interact with TS through a high-order relaxation process which contributes to the summation of the TS relaxation rates. We think this correlation between the two regions is important and could help to understand the high-temperature ($T>3$ K) behavior of the sound velocity in amorphous materials, which still lacks an interpretation.[51]

By supressing the superconducting transition by means of a magnetic field of 5.6 T, measurements of the sound velocity where performed at low temperatures in the normal state (Figs. 3–5). The sound velocity has a negative slope up to the lowest temperatures measured, in spite of theoretical expectations of a maximum in v_E at around

1.5 K, which has been observed in $Pd_{78}Si_{16}Cu_6$.[45] The behavior is similar at all annealing stages and the approximately logarithmic change in v_E which is seen below 1 K can be fitted in a $\log T$ graph with a slope 2.5 times lower than that obtained for the superconducting state in the same temperature range. Within 20%, the relative change of this slope with respect to that of the as-quenched sample is the same as that of the superconducting state. As in the case of the high- and low-temperature slopes in the superconducting state this similarity could indicate also a proportionality with the parameter $C \propto P\gamma^2$ defined by Eq. (1).

In the normal state, and for a temperature range close below T_c, the sound velocity is larger than in the superconducting state as was observed in the $Pd_{30}Zr_{70}$ amorphous superconductor.[21,22] A new result of our measurements however is that heat treatments modify this behavior, i.e., in the second anneal v_E in the normal state is equal to v_E in the superconducting state within experimental uncertainty and we observe the maximum difference in the first anneal. Thus the different behavior[22] observed in this respect between $Cu_{30}Zr_{70}$ and $Pd_{30}Zr_{70}$ could be due to the fact that the Cu-Zr alloy was annealed for a year at room temperature and not to an intrinsic difference between both types of amorphous alloys.

B. Internal friction results

The internal friction (Q^{-1}) versus temperature plots are shown in Fig. 6. Data correspond to the three different heat treatments and were taken at zero applied field, so that below T_c the sample is superconducting. It can be seen that the absolute value of the internal friction decreases upon annealing indicating a decrease in C, as was seen from the sound-velocity results. To compare the evolution of Q^{-1} with that of v_E we use the value of Q^{-1} at $T=0.2$ K. At this temperature electrons are condensed into Cooper pairs and only phonons interact with the TS. The TM predicts that if the one-phonon process is responsible for the relaxation and if $\omega\tau_{\mathrm{ph}m} \ll 1$ holds (the well-known plateau regime in the phonon absorption) then

$$Q^{-1}=\pi C/2 \tag{3}$$

(due to the relatively low measuring frequency the resonant contribution is negligible). From Eq. (3) we find $C=(1.35\pm0.11)\times10^{-4}$, $(1.10\pm0.08)\times10^{-4}$, and $(0.39\pm0.11)\times10^{-4}$ for the as-quenched, first anneal, and second anneal, respectively. These values are consistent, within experimental uncertainty, with those obtained previously from the sound-velocity data.

The relative decrease of C with respect to the as-quenched value C_i is shown in Fig. 7; for both methods of obtaining C a good agreement is seen. Data of the relative change of the thermal conductivity (taken in the superconducting state at $T=0.5$ K from Ref. 18), with annealing are also plotted for comparison. The tunneling model predicts that the change in the ratio $\kappa_{\mathrm{ph}i}/\kappa_{\mathrm{ph}}$ at these low temperatures should be the same as C/C_i, if the sound velocity and mass density remain constant which is a good approximation in our case. The thermal conductivity ratio is seen to decrease less with annealing than the C/C_i ratio from the acoustic measurements, a result which could be explained because the samples are different, or by arguing that annealing produces different changes for different parts of the TS spectrum being tested by the two methods. Thermal conductivity probes frequencies of some 10^{10} Hz while the acoustic measurements were performed at 10^3 Hz. Another possibility, considered already in Ref. 22 is that the thermal conductivity is less sensitive to changes in $P\gamma^2$ because it probes mainly the high u-value region of the distribution function $P(E,u)$ while the internal friction is more sensitive to the small u values (for $\omega\tau_{\mathrm{ph}m} \ll 1$).

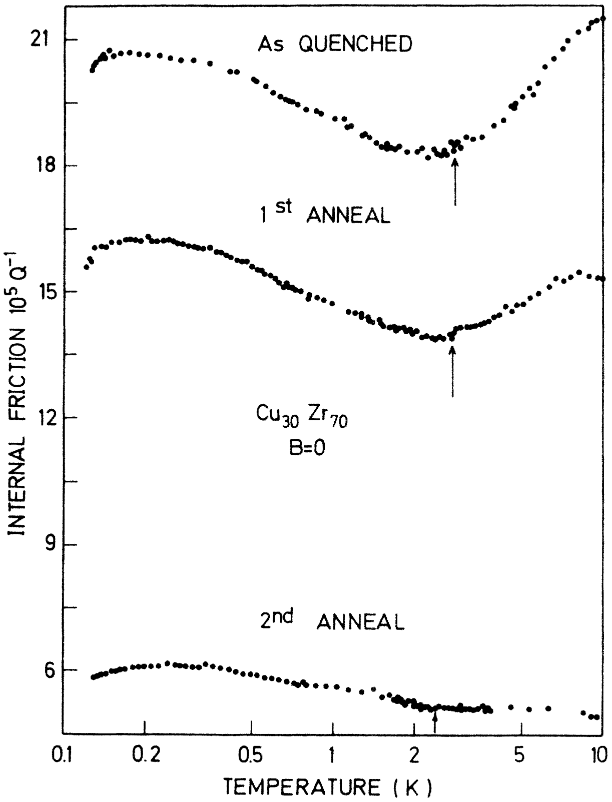

FIG. 6. Internal friction against temperature for the three sample states. The arrows indicate the superconducting critical temperature T_c.

The tunneling model predicts that the sound attenuation should have a plateau at low temperatures but in the superconducting state curves of Figs. 9–11 instead of a perfect plateau a rather broad maximum (marked at T_M) is observed. This is not due to the extra relaxation mechanism provided by the electrons, since these are condensed into Cooper pairs, but is rather an intrinsic result not obtained by use of the standard TM. It has been pointed out[50] that a broad maximum is a much more general property of amorphous materials than the seldom observed strictly temperature-independent plateau, and suggestions that a more rigorous treatment of the coupling constants between the TS and phonons could explain this have been proposed. A detailed discussion of

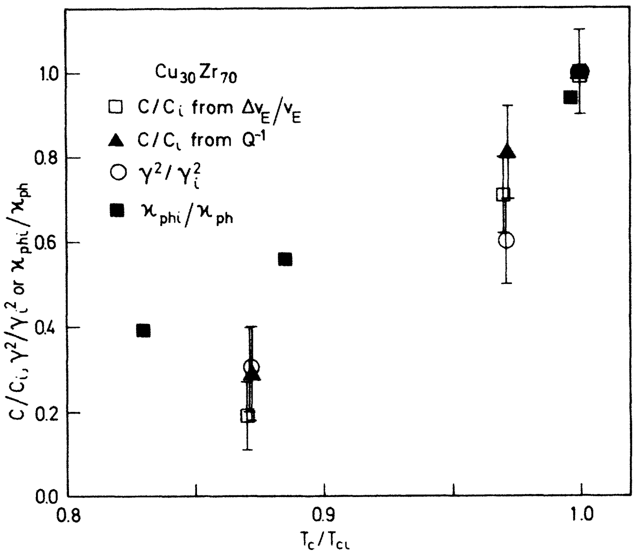

FIG. 7. Relative change upon annealing of the phonon thermal conductivity κ_{ph} obtained at 0.5 K from Ref. 18 (■) as a function of the critical temperature (i means initial or as-quenched). In the same figure we show the change of the C values obtained from the initial friction (▲) and sound velocity (□). The relative change of the coupling constant γ^2 obtained from the internal friction is also plotted (○).

this and other explanations that have been put forward is beyond the scope of this work and will be published elsewhere.[50] We do wish to point out here, however, that this broad maximum and the beginning of the plateau in the standard TM are related to each other.

The effect of changing the coupling between TS and phonons on Q^{-1} calculated numerically with the standard tunneling model is plotted in Fig. 8. The knee in the internal friction is at a temperature approximately coincident with the sound-velocity maximum,[22,45] which in our experiments falls below 0.1 K. For fixed frequency the position of the maximum depends only on the coupling constants and sound velocities through a prefactor A appearing in the TS relaxation rate due to phonons (one-phonon process)

$$\tau_{ph}^{-1}=Au^2E^3\coth(E/2kT) \tag{4}$$

and A is equal to

$$(\gamma_l^2/v_l^5+2\gamma_t^2/v_t^5)/2\pi\rho_d\hbar^4$$

where the indices l and t refer to the longitudinal and transversal phonon branches. Note that for a relative comparison of the parameters A and C the separation in two branches is irrelevant since it must be taken into account that, like the sound velocities, the coupling constants are related to each other. Curves a–d in Fig. 8 show the effect of changing A on the internal friction at a constant frequency of 740 Hz, while curve e is the same as d but changing the frequency to 800 Hz. The position of the point at which the plateau starts is seen to change with A and temperature according to the relation

$$AT^3=\text{const}\ , \tag{5}$$

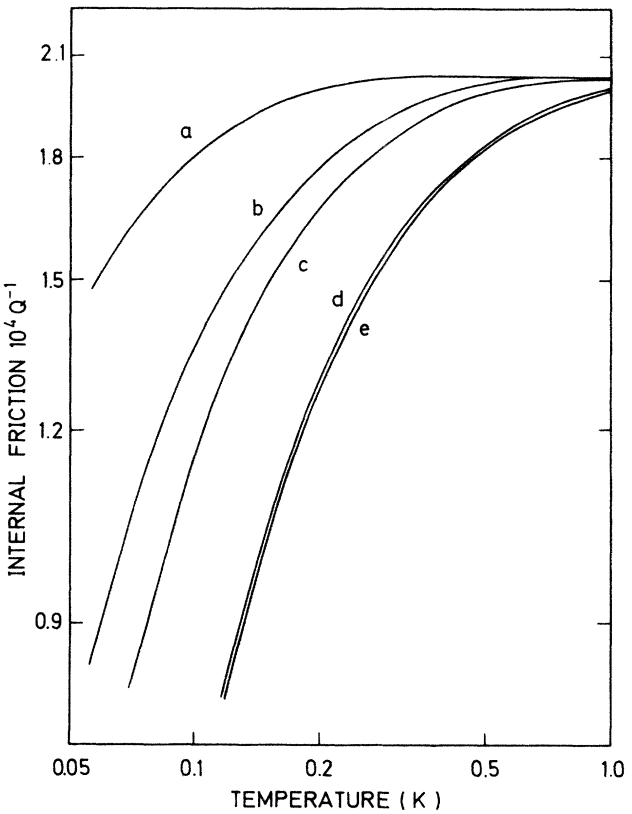

FIG. 8. Internal friction theoretical curves calculated with the tunneling model and taking into account the one-phonon relaxation process only. The contribution of the two-phonon (Raman) process, compatible with the sound velocity data, does not produce any notable change in the T dependence of Q^{-1} below 2 K. Curves a–d are calculated at 740 Hz with the parameter [see expression (4)] $Ak_B^3=(1\times10^8, 1\times10^7, 5\times10^6, 1\times10^6)$ $s^{-1}K^{-3}$. Curve e is obtained at 800 Hz with $Ak_B^3=1\times10^6$ $s^{-1}K^{-3}$.

where the T^3 dependence is obtained due to the energy dependence of τ_{ph}^{-1} in Eq. (4). Since the broad maximum observed experimentally must follow the scaling law given by Eq. (5), the relative change of the coupling constants upon annealing can be estimated. The point T_M corresponds to temperatures 0.16, 0.19, and 0.26 K (with an interpolation error of 10 mK) for the as-quenched, first anneal, and second anneal, respectively. From these values and taking into account the small change in relative frequency with annealing, the relative changes in the coupling constant are then $\gamma^2/\gamma_i^2=0.60\pm0.1$ for the first anneal and $\gamma^2/\gamma_i^2=0.32\pm0.1$ for the second anneal.

These relative changes in γ^2 are also plotted in Fig. 7 and it can be seen that within experimental uncertainty the change in γ^2 is the same as the change in $P\gamma^2$, indicating that P remains almost constant. The experimental error could mask at most a change of some 25% in P.

At temperatures higher than 0.4 K, while the sample is in the superconducting state, the internal friction versus temperature curves have a negative slope for all stages of annealing (Figs. 9–11). This behavior is unexpected within the standard TM; the internal friction should be independent of the relaxation mechanism when $\omega\tau_{\mathrm{ph}m} \ll 1$ holds. Another unexplained feature of the curves is that there is a minimum in Q^{-1} at a temperature just below T_c and not at T_c. When an applied field supresses the superconductivity, one can see that the curve corresponding to the normal state crosses the superconducting state curve once (Figs. 9 and 10). In Ref. 22 a still more complex behavior was observed. This anomaly of Q^{-1} at T_c could indicate two competitive electron dependent effects, for example in $P(E,u)$ and/or in the coupling constant between the TS and electrons.

The normal-state attenuation data (open circles in Figs. 9–11) show that at low temperatures Q^{-1} is always smaller in the normal than in the superconducting state. The difference in Q^{-1} at $T=0.2$ K is 20% for the as-quenched sample and the first anneal and 29% for the second anneal (around 50% if we subtract a constant background of approximately 2×10^{-5} which is the estimated contribution of the clamping to Q^{-1}).

An interesting feature is that in the as-quenched state and at $T>T_c$ the internal friction increases again having a maximum at approximately 15 K which can be partly seen in Fig. 9. A maximum in Q^{-1} has been already observed between 10 and 40 K in different amorphous metals: $Fe_{0.74}P_{0.16}C_{0.65}Al_{0.03}Si_{0.02}$,[31,55] $Pd_{81}Si_{19}$,[31] $Pd_{77.5}Si_{16.5}Cu_6$,[45,56] and $(Mo_xRu_{1-x})_{80}P_{20}$,[57] but to our knowledge there is no accepted explanation. Upon annealing we observe that the maximum shifts to lower temperatures and decreases its amplitude; in the fully relaxed state the maximum vanishes completely, see Figs. 6 and 11. Similar results with heat treatments have been obtained in the $Pd_{77.5}Si_{16.5}Cu_6$ (Ref. 56) amorphous alloy and also in the iron based amorphous compound $Fe_{0.74}P_{0.16}C_{0.65}Al_{0.03}Si_{0.02}$ (Ref. 31). The universality of these absorption peaks, also observed in a great variety of amorphous insulators,[2] leads to the question of whether these absorption peaks are related to the same defects which produce the TS. If this would be the case, the structural relaxation could produce a rapid and large increase in an accessible energy state. Some recent calculations[58] considering a virtual tunneling absorption through a third level of the two well potentials are promising and could contribute to the understanding of this unknown absorption mechanism.

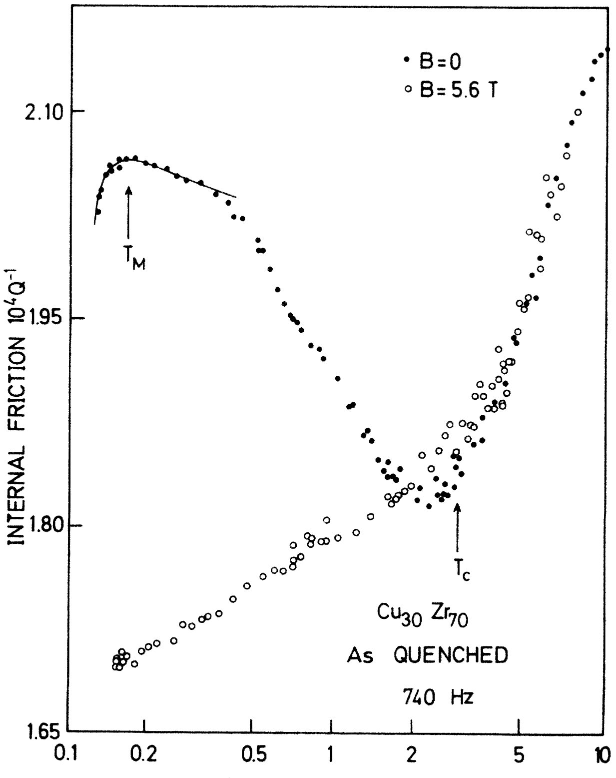

FIG. 9. Internal friction against temperature for the as-quenched sample. T_M denotes the beginning of the internal friction decrease on lowering T (or the maximum value); $T_M=0.16$ K and $T_c=2.806$ K.

V. DISCUSSION

We separate the discussion into two sections. In the first part we discuss some of our results in relation to the TS-electron interaction mechanism. The second part refers to the question of the stability of the density of the TS upon annealing.

A. Electron-TS interaction problem

Some of the experimental features observed confirm those already found in acoustic experiments on other Zr-based alloys.[22] The ones related to the heat treatment are new and should provide useful information on the TS and their evolution with the relaxation state of amorphous materials. Our main results can be summarized as follows.

(i) There is a well-defined change of behavior in the sound velocity at T_c which goes in the opposite way as that expected from theory.

(ii) In the region just below T_c the sound velocity is larger in the normal than in the superconducting state although the difference depends on the heat treatment and in the second anneal, for example, it is zero between T_2 and T_c.

(iii) The kinks observed in the sound velocity at T_1 and T_2 for the sample in the superconducting state scale with the superconducting critical temperature.

(iv) At all stages of annealing the sound velocity in the normal state shows no maximum, having a negative slope down to the lowest measured temperatures.

(v) The sound absorption is always less in the normal than in the superconducting state, except for the small temperature range just below T_c where the opposite behavior is systematically observed.

Numerical calculations of the sound velocity within the standard TM, taking into account the Korringa-like relaxation rate, the Raman two-phonon process and the one-phonon process (including the resonant process which is always present) invariably give a normal-state sound velocity with a positive slope if the temperature is below 1 K, in contrast with the negative slope observed in our experiment. Within the constraint of obtaining a reasonable qualitative fit for the superconducting state sound velocity, all changes in the parameters fail to change this behavior in the normal state. Even assuming an *ad hoc* linear increase of the coupling constant between the TS and electrons for the superconducting state relaxation rate, the normal state slope of the sound velocity below 1 K was positive, though surprisingly it was possible to give a good qualitative fit for the superconducting state sound velocity.

A striking result is obtained if we take into account only the phonon-TS interaction (i.e., only one- and two-phonon processes) in the above-mentioned calculation of v_E. A good qualitative fit is obtained for the normal state sound velocity if we increase by a factor of 3 or 4 the prefactor A in Eq. (4) with respect to the superconducting state value. This is striking because it would indicate that the conduction electrons increase the TS-phonon coupling. In other words, the electrons would effectively increase the relaxation rate of TS, but this fact becomes apparent through an enhancement of the phonon coupling. This is a very speculative hypothesis, in which one rules out an independent TS relaxation rate due to the conduction electrons, a process which has always been thought to be physically correct. The picture is not purely empirical, however, and some theoretical papers have addressed the possibility of some sort of enhancement of the TS-phonon interaction.

Vladar and Zawadovsky[25] proposed a new strong coupling interaction between electrons and TS. Below a certain temperature T_k they found that the new coupling constants between TS and electrons increase rapidly. This transition temperature T_k between a weak and strong coupling regime depends strongly on the high-temperature values for the coupling constants. They obtained a relaxation rate for the TS that depends on the two T-dependent coupling constants. But besides this important difference, its final form resembles that obtained from the Korringa-like interaction. This means that, because the coupling increases on lowering temperature, we would obtain a larger positive slope in the sound velocity in contradiction to our results.

The strong coupling between the TS and conduction electrons proposed could also lead to a reduction of the effective density of states of the TS through a reduction of the tunneling splitting Δ_0. How much $P(E,u)$ would be reduced depends on the coupling constants and the ratio between the asymmetry Δ and the tunneling splitting.[25] A reduction of the tunneling splitting with conduction electrons has also been proposed for hydrogen tunneling in niobium.[59] Recently, a preliminar approach based on the electron polaron effect[60] has been made to explain the observed internal friction behavior,[61] but more theoretical work has to be done to introduce this effect into the framework of the TM and calculate also the sound dispersion. The sound velocity is much more sensitive to the relaxation rates than the internal friction in the regime $\omega\tau_m \ll 1$ (τ_m is the minimum relaxation time of the TS due to phonons or electrons).

As in Ref. 22, the good qualitative agreement with theory in the superconducting state and the failure in the normal indicates the necessity of measurements of both electronic states. Because with low-frequency measurements we expand the temperature region where several electron-related features are observed ($\omega\tau_m \ll 1$ holds at $T > 0.1$ K), ultrasonic measurements alone are not a severe enough test for the theory.[62,63] In fact, low-frequency measurements in $Cu_{60}Zr_{40}$ also showed unexpected features below T_c in the internal friction and sound velocity[45] which are in clear conflict with the very good agreement with the theory found in Ref. 64 for high frequency.

The change of behavior in the sound velocity at T_c is an interesting and important result that requires a more detailed discussion. A similar change of slope in measurements with a vibrating reed was observed in the superconducting layered dichalcogenide 2H-$NbSe_2$.[65] The authors partially explained this anomaly with thermodynamic arguments as follows: At a second-order phase transition it was shown[65] that the discontinuity in the Young modulus for an isotropic solid is given by

$$\frac{\Delta E_Y}{E_Y} = -\frac{1}{9}\left[\frac{dT_c}{dP}\right]^2 E_Y \frac{\Delta C_P}{T_c}\ , \tag{6}$$

where P is the pressure and ΔC_P is the specific-heat jump at T_c. Taking the pressure dependence of T_c obtained for $Cu_{40}Zr_{60}$ (Ref. 66) and ΔC_P from Ref. 19, we obtain $\Delta E_Y/E_Y \cong -5.8\times10^{-7}$ ($\Delta v_E/v_E$ is just one-half of this value). The experimental values give a much larger difference in $\Delta v_E/v_E$ than this calculation provides.

There are several facts which indicate that the observed sound velocity behavior is due to the interaction between the TS and electrons and cannot be explained by Eq. (6): at $T > T_c$ our results indicate that the TS are responsible for the sound velocity T dependence (see Fig. 2). The change in v_E is not restricted to the transition point but extends between T_c and T_2 in a relatively wide temperature range. Furthermore, we obtain in the fully relaxed state (second anneal) a negligible difference in v_E between both electronic states. Because neither ΔC_P nor dT_c/dP should depend so much on the structure (e.g., compare these values with those obtained for pure Zr) it seems difficult to explain the observed features with expression (6).

The change in the behavior obtained in v_E for $2H$-$NbSe_2$ below T_c, induced us to look for a similar interaction between phonons and electron-dependent entities in related materials. To our surprise, in a related compound ($2H$-$TaSe_2$) two pseudospin configurations (ionic motions between two degenerated states) were proposed to explain the thermal conductivity at high temperatures.[67] This ionic motion would also imply some kind of correlation with the conduction electrons. Low-frequency measurements in the normal state of 2H-$NbSe_2$ are planned to clarify the sound-velocity behavior.

A decrease in P or γ with the decrease of quasiparticles just below T_c could explain the internal friction behavior. But a decrease in γ should increase the sound velocity when the temperature is increased. On the other hand, we could think that a decrease in γ could be totally compensated by a certain temperature dependence of the TS-electron coupling. At the stage of the recent theoretical developments, even a simple qualitative comparison with the experimental results is not possible. It seem that there were three new nondetermined temperature- and/or electron-dependent variables within the TM: the density of states of TS,[25] the coupling constant between phonons and TS,[68] and the coupling constants between electrons and TS.[25]

Another striking result we think important is observed in the normal state internal friction in the first and second anneal, see Figs. 10 and 11. Note the well-defined plateaus below 4 K. In the standard TM the beginning of the plateau in the low-temperature region should be at $\omega\tau_{em} \cong 1$ ($\omega\tau_{em}$ is the minimum relaxation time due to electrons). Because it is expected that $\omega\tau_{em} << \omega\tau_{\mathrm{ph}m}$ at temperatures below 1 K, we should have the beginning of the plateau at much lower temperatures, much lower than T_m in the superconducting state. It is possible that if $P(E,u)$ were temperature dependent, it could decrease on cooling due to an increase of the coupling constants between the TS and electrons,[25] explaining in this way the decrease in the attenuation which would be not only related to the relaxation times. But curiously, the relative increase upon annealing of the temperature where this plateau begins, is approximately the same as the increase in T_m, implying also that there is a correspondence of this beginning of the plateau and the coupling constant between phonons and TS.

According to the literature it seems that only in Zr-based superconducting amorphous alloys we can observe features contradicting the theoretical expectations. In fact, to our knowledge there are no published low-frequency measurements in any non-Zr-based superconducting amorphous alloys. Because the normal conducting metallic glass $Pd_{78}Si_{16}Cu_6$ behaves as expected,[1,2,30] we could think that the effects we observe are related to some particular contribution of the Zr atoms. New unpublished results on superconducting $(Mo_xRu_{1-x})_{80}P_{20}$ amorphous alloys indicate that depending on the alloy composition there is a slight increase of Q^{-1} or even a well-defined plateau below T_c in the superconducting state.[57] The measured sound velocity has many of the main features we observe in the Zr-based amorphous alloys in the superconducting state.[57] No normal state results have been obtained yet.

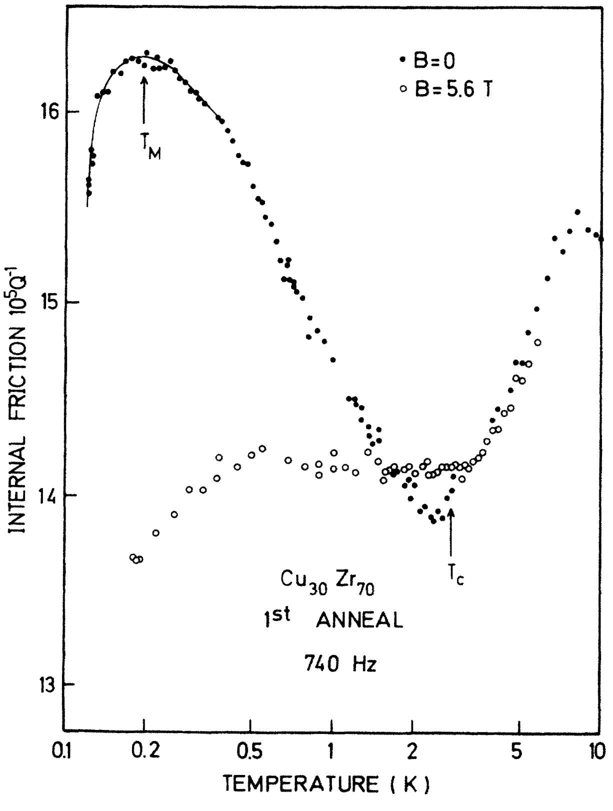

FIG. 10. The same as Fig. 9; $T_M = 0.19$ K and $T_c = 2.715$ K.

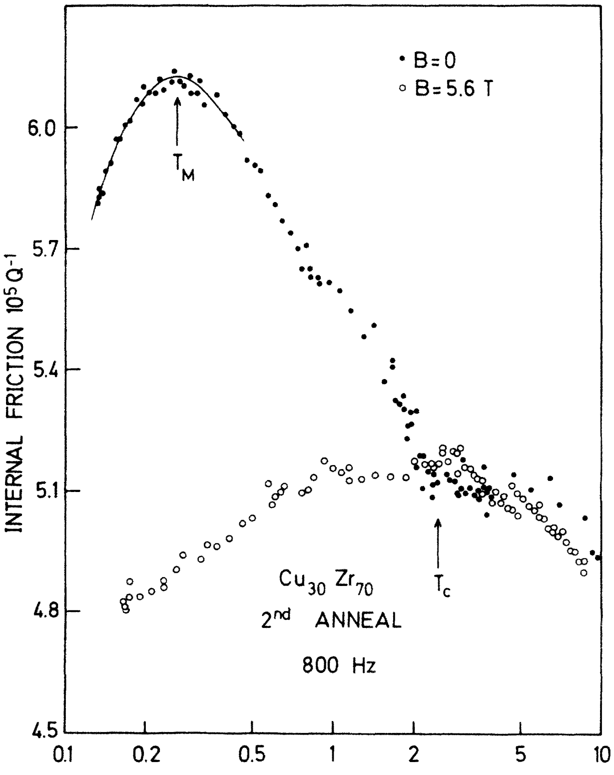

FIG. 11. The same as Figs. 9 and 10; $T_M = 0.26$ K and $T_c = 2.436$ K. Note that, above T_c, the peak obtained in the previous sample states is completely vanished. Note also that in the normal state the internal friction reaches the plateau regime at higher temperatures (~ 0.6 K) than obtained for the first anneal (Fig. 10). The relative increase of this temperature is approximately the same as the change in T_M.

B. Stability of the tunneling systems

Our internal friction results in the superconducting state reveal that the main decrease upon annealing in the absorption or thus sound-velocity temperature dependence comes from a decrease in the coupling constant γ between the TS and phonons. A comparison between the sound velocity for the as-quenched state and an early result[22] of a room-temperature annealed sample supports also that the coupling constant is very sensitive to the relaxed state of the amorphous structure.

Grondey *et al.*,[19] argued that a constant specific heat and the increase of the thermal conductivity upon annealing, could be qualitatively understood by a particular change of the TS distribution function $P(E,u)$. Our results indicate that such an interpretation is not needed to explain the annealing evolution. Moreover, our low-frequency measurements are more sensitive to the low-u region of the relaxation time spectrum than thermal conductivity, therefore, with the picture of Grondey *et al.*, we would expect an increase of Q^{-1} or in the T dependences of the sound dispersion upon annealing.

Certainly, we cannot completely rule out the possibility of a nontrivial transformation in the function $P(E,u)$ upon annealing, in such a way that it produces the observed changes in Q^{-1} and the thermal conductivity, and maintains the specific-heat constant. But we must stress that it is not trivial to find new functions $P(E,u)$ which agrees with the formidable amount of data of measured properties in amorphous materials; even slight changes in $P(E,u)$ can lead to contradictions with the sound velocity and internal friction or ultrasonic attenuation T dependences. The discussion below will be based on the result of the stability of the tunneling entities upon annealing in the measured melt-spun amorphous alloy.

The structural models proposed by Banville and Harris and Harris and Lewis[14] showed strong correlation between the probability of occurrence of tunneling systems and voids in the disordered structure. These voids would disappear upon annealing and, as a consequence, the amount of the TS would decrease. Obviously, our results do not support this interpretation. Nevertheless, we should take into account that in their structural model and upon computer simulated relaxation, a much bigger densification ($\cong 10\%$ increase in ρ_d) than in our case is obtained.

The proposed correlation between voids and the TS is, in spite of our results, an attractive picture. We believe that it cannot be ruled out completely. It is possible to think that "extrinsic" defects (within the interpretation of Egami *et al.*[15]) could be related with voids and also provide a non-negligible number of the TS. The observed difference between melt-spun[19] and sputtered[28] amorphous metals upon annealing may come from a different contribution of "extrinsic" defects.

The structural defects in amorphous structures have been related with high-stress and low-symmetry regions through computer simulation studies.[15] These structural defects, which could be related to the tunneling entities, are "intrinsic" of the disorder and more related to relaxed structures, thus more stable defects. Other computer simulation studies have also shown the possibility of multilevel systems in disordered structures involving many atoms.[16] This states were proved to be rather stable with respect to computer simulated relaxation. It is not clear which kind of relation exists between the liquidlike clusters proposed by the free-volume model[9] and the defects obtained in the computer-simulation studies. Because the free-volume model is based on thermodynamic and kinetic arguments, there are no evident contradictions. However, some detailed theoretical predictions from the free-volume model in relation to the density of states of the TS have not found experimental support.[69]

The stability of the tunneling systems could arise from topological considerations. Rivier[11] has proposed that the TS are related to disclinations, a class of defects not present in crystals because their elastic energy is too high, but which could be essential constituents of glasses. The disclination lines thread odd numbered faces in a Voronoi partition of the solid, therefore they were called odd lines by Rivier. The odd lines form loops or end at the sample surface, therefore, to eliminate an odd line, one needs to shrink its diameter to zero or move it out of the sample through the surface. In that sense, disclinations are relatively stable entities. Results of critical currents in several amorphous superconductors[32] suggest that disclinations in glasses could explain, in a semiquantitative fashion, the pinning forces observed when the conditions for two-dimensional Larkin-Ovchinikov theory[79] are fulfilled. The effect of annealing on disclinations, seen by the pinning forces, is very similar to that on the density of states of the TS. In amorphous superconductors usually a decrease in the pinning force upon annealing is observed.[32] The pinning force is proportional to $n_d D^4$, where n_d is the density and D the mean diameter of the disclination loop. In Ref. 32 a decrease of about 40% was observed in $n_d D^4$ between the as-quenched sample and the point at which microcrystallites start to appear. Thus a slight decrease in D could produce the change in pinning force. If the density of states of TS is related to the number of disclinations n_d, a more severe heat treatment would be needed to shrink some of the loops to zero and thus decrease P (or n_d). Unfortunately, no microscopic theory of the interaction of the odd lines with phonons has been developed, so that we cannot use this model to fit the observed decrease of the coupling constant at constant density of states.

It was usually observed that the coupling constant between phonons and the TS is rather large, from our data in the as-quenched state, we estimate $\gamma \cong 0.83$ eV. A large value for the coupling constant would support the theory of the critical behavior of the double-well potential model. Karpov, Klinger, and Ignat'ev[12] proposed a general approach (which basically does not contradict the above-mentioned models) to describe microscopically double-well potentials, i.e., TS in amorphous materials. They proposed critical potentials with two minima separated by a barrier dependent on the relative contributions of harmonic and anharmonic terms. The critical property of these potentials is related with an unusually small spring constant, resembling the behavior observed in the case of local defects with a low force-constant impurity in solids.[71] It was experimentally shown that anharmonicity plays an important role in the elastic behavior of the localized defect when the spring constant is low.[72] Galperin, Gurevich, and Parshin,[13] based on the critical potential picture, obtained an expression for the coupling constant which depends on the anharmonic contribution. Considering the TS of second type (nonzero anharmonic term) which are stronger coupled to phonons, they arrived to

$$\gamma^2 \propto W^2 \tilde{t}^4 / \eta_L^2 \ ,$$

where W is the characteristic energy of the potential ($\sim$30K), η_L is a constant related to the atomic mass and energy ($\sim$30 eV), and $\tilde{t}$ is the reduced coefficient of the anharmonic contribution to the two-well potential. Because W and η_L would be rather constant upon annealing, we obtain that a small decrease ($\sim$30%) in $\tilde{t}$ reduces γ^2 by a factor of 3. Taking into account the experimentally proved huge sensitivity of the anharmonicity with hydrostatic pressure, found in special local defects in crystalline solids,[72] we could expect a decrease in $\tilde{t}$ through a slight densification or even a local atomic regrouping upon annealing.

Because the critical potential model arrives at the concept of two different critical two-well potentials (types 1 and 2), a question arises about the concentration of each type in real amorphous systems. Furthermore, we could ask which kind of the TS we are testing with low-frequency phonons. From the available experimental data in metallic glasses, which show that the C values obtained at low frequencies are much larger than for high-frequency experiments, we conclude that the vibrating reed tests the second kind of the TS (more strongly coupled to phonons).

VI. SUMMARY

We have measured the evolution of the internal friction and sound velocity in the amorphous superconductor $Cu_{30}Zr_{70}$ upon annealing with the vibrating reed technique. From the internal friction results we conclude that the tunneling systems are rather stable entities which could be related with topological defects characteristic of disordered structures. The TS-phonon coupling constant decreases upon annealing while the TS density remains fairly constant, thus leading to a decrease in the internal friction and the temperature dependences of the sound velocity.

With thermal treatments we show that if TS are responsible for the temperature dependence of the sound velocity at low temperatures and in the superconducting state, they also should be the main cause of the phonon relaxation interaction up to 10 K in the normal state.

Our results support the conclusions obtained in an earlier experiment:[22] the superconducting and normal-state behavior of the internal friction and sound velocity cannot be understood within the standard tunneling model and the proposed interaction between tunneling systems and electrons (the new observed features in our work were summarized at the beginning of the discussions).

We have shown that below T_c the difference in the sound velocity between the normal and superconducting states, depends on the relaxed structure, and, consequently, on the coupling constants. The idea of a reduction of the effective density of states of TS with conduction electrons is partially supported by the large internal friction increase in the superconducting state below T_c. But to explain the normal as well as the superconducting state data in the internal friction and sound velocity, a more complex electron-dependent mechanism than a simple decrease in P is needed.

We want to stress that the tunneling model and in particular the mechanism of the interaction between tunneling systems and conduction electrons is not a problem related only with amorphous materials. The same situation can be found in hydrogenated niobium,[73] special two-dimensional materials,[67] and also in the new high-T_c ceramics. Recent measurements indicate the existence of tunneling excitations in the $YBa_2Cu_3O_{7-x}$ and $EuBa_2Cu_3O_{7-x}$[74,75] ceramic superconductors and probably also in $La_{1.8}Sr_{0.2}CuO_4$.[76,77] Understanding of the TS-electron interaction could give important clues as to novel mechanisms which could give rise to superconductivity at high temperatures.

ACKNOWLEDGMENTS

The technical assistance of M. E. de la Cruz and H. Tutzauer is gratefully acknowledged. We are grateful to G. Weiss and H. Raad for providing us with their unpublished data on Mo-Ru-P amorphous alloys. We wish to thank Professor S. Hunklinger and Dr. M. Núñez Regueiro for stimulating discussions on various aspects of this work. This work was partially supported by Third World Academy of Science through Research Grant No. 87-30. P.E. received additional support from the Consejo Nacional de Investigaciones Científicas y Técnicas of Argentina.

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