Effect of structural relaxation of the amorphous alloy $Ni_{34}Zr_{66}$ on the temperature dependence of a superconducting gap

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The temperature dependence of the superconducting gap in the amorphous alloy $NiZr_2$ was determined from the tunnel characteristics of point junctions with aluminum tips before and after the structural relaxation. In both cases the gap turned out to be somewhat smaller than that predicted by the Bardeen–Cooper–Schrieffer theory. Annealing decreases the discrepancy from 10 to 5%.

The superconducting transition in amorphous alloys of transition metals[1–3] exhibits certain peculiarities. First, the transition can be extremely narrow, of width $\delta T_c \approx 4$–5 mK (Ref. 4). So small a width, $\delta T_c/T_c \approx 10^{-3}$ was previously reached only in painstakingly prepared ultrapure single crystals. This property of amorphous materials is due to the absence of macroscopic structure defects. In addition, its realization requires a high degree of composition homogeneity over scales exceeding the coherence length.

Another peculiarity of the superconducting transition is less clear. A non-crystallizing anneal by structural relaxation only, which is practically undetectable by x-ray methods, can shift the transition, usually towards lower T_c, by an amount $\Delta T_c \approx (0.1\text{–}0.15)T_c$ and leave the transition narrow, $\delta T_c \approx \Delta T_c/100$ (Refs. 4–6). The accompanying changes of the elastic constants[7] and phonon-spectrum parameters[8] are very small, as well as the changes of the resistivity.[9]

Attempts have been made[10] to attribute the decrease of T_c to annealing of two-level states. Since, however, the number of degrees of freedom of the aggregate of the atoms is conserved, such an anneal should be accompanied by an increase of the phonon-state density in the Debye-frequency region, but it is very difficult to assess this factor. It has furthermore been experimentally established in fact, for the materials dealt with in the present paper, that structural relaxation is not accompanied by a substantial decrease of the linear contribution to the heat capacity.[8] It follows hence that in this material annealing does not eliminate the two-level states.

It appears that the main result of structural relaxation is an increase of the "chemical ordering" (Ref. 11), i.e., an increase of the short-range order. If this premise is assumed, there remains the question of how the short-range order influences the superconducting properties. Hoping to gain information on this subject, we have undertaken a study of the tunneling characteristics. We report here the first result of this study, measurements of the temperature dependence of the gap width $\Delta(T)$ before and after structural relaxation, based on an analysis of the current–voltage characteristics of tunnel junctions.

EXPERIMENT

The investigated object was an amorphous tape of composition close to the very thoroughly investigated $NiZr_2$. The results reported in practically the papers cited above are for this very alloy, although they all apply also to other amorphous superconducting alloys of transition metals.[1–4] In particular, the coherence length ξ of $NiZr_2$ was measured a number of times, and amounts to approximately 60 Å (Refs. 2–4).

We studied the current-voltage characteristics of an Al–Al_2O_3–$NiZr_2$ point-contact tunnel junction. The aluminum tip was made from chemically pure wire 0.25 mm in diameter by chemical annealing followed by oxidation. The radius of the tip obtained in this manner was approximately 0.5 μm. The motion of the mechanical system for bringing the tip to the sample could be controlled accurate to 0.01 μm. The normal resistance R of the tunnel junctions ranged from 10 to 100 kΩ. The junction leakage current during the $I(V)$ curve plotting did not exceed $0.1\,V/R$. The superconducting temperature was measured independently by a four-point system with clamped contacts. Since the transition is narrow, the accuracy of the relative temperature $t = T/T_c$ at which the $I(V)$ characteristic was plotted was not worse than 1%.

The initial tape from which the samples were cut had the following parameters: Ni content 34 at.%, resistivity at room temperature $\rho = 170\ \mu\Omega\cdot$cm, $\rho_{4.2\ K}/\rho = 1.057$, density 7.06 g/cm^3, $T_c = 2.46$ K, and $\delta T_c \lesssim 4$–5 mK. The annealing procedure, based on an earlier investigation of the initial stages of crystallization of the same material,[6] consisted of slow (about 1 hour) heating to 380°, soaking for one hour at this temperature, and cooling at the same rate as the heating. The annealing was carried out in an oil-free vacuum of $5\cdot 10^{-8}$ Torr. Absence of crystallization in the sample was monitored by continuously measuring the resistivity in the course of the annealing. The value of T_c after the annealing was 2.17 K, i.e., $\Delta T_c/T_c \approx 12\%$. The transition width δT_c not only failed to increase but, on the contrary, decreased to as low as 2 mK for one of the samples.

RESULTS

A typical family of $I(V)$ curves for one of the junctions is shown in Fig. 1. The most distinctive feature of these curves is the presence of a sharp turn even at high values of the relative temperature t. According to theory and numerous experiments, the $I(V)$ characteristics of a tunnel junction between a metal and a superconductor should have no such turns.[12] The difference is evident from Fig. 2, which shows a comparison of one of the experimental curves with one calculated from the equation

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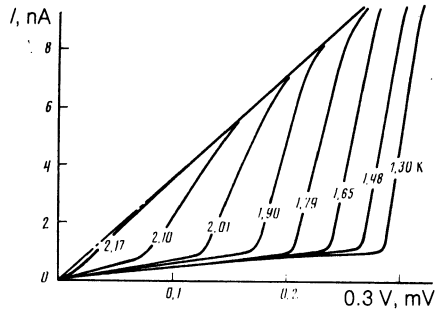

FIG. 1. Current–voltage characteristics at various temperatures (marked on the curve) of a junction with a heat-treated amorphous alloy: $R = 29$ kΩ, $T_c = 2.18$ K.

$$I(V)=\frac{1}{eR}\int_{\Delta}^{\infty}\frac{\varepsilon\, d\varepsilon}{(\varepsilon^2-\Delta^2)^{1/2}}\left[f\left(\frac{\varepsilon-eV}{T}\right)-f\left(\frac{\varepsilon}{T}\right)\right]. \qquad (1)$$

where ε is the energy measured from the Fermi level, $f(x) = (1+e^x)^{-1}$, and R is the junction resistance at $T > T_c$. We have therefore previously undertaken a special investigation of these characteristics. On the basis of this investigation, described in detail in Ref. 13, we propose a model whose main premises are the following.

The anomalous shape of the $I(V)$ characteristics of a tunnel junction between an aluminum tip and a superconducting amorphous alloy is due to a combination of the smallness of the junction ($d \approx 10$ Å according to Ref. 13) and the smallness of the carrier mean free path in the amorphous alloy. It is assumed that the realized combination of parameters induces a superconducting state in the junctions' aluminum contact layer, despite the presence of an insulating layer. This blocks the tunnel current at low voltages $eV < \Delta$. The current growth, which begins at $eV = \Delta$, is due to opening of a new channel—two-particle tunneling of electrons through an intermediate state, in the form of a Cooper pair in the thin induced superconducting layer. When the current increases to the normal value $I \approx \Delta/eR$, it destroys the superconductivity in the vicinity of the junction.

Of importance to us in the present paper is that this interpretation of the experimental data permits the turn voltage V_t to be identified with the value of the gap $\Delta(T)$: $\Delta(T) = eV_t(T)$. The method of determining the voltage V_t is clear from Fig. 2.

All the measurement results are gathered in Fig. 3 and plotted in the normalized coordinates $t = T/T_c$ and $\zeta = 2\Delta/\bar{\alpha}T_c$ ($\bar{\alpha} = 3.52$ is a constant from the Bardeen–Cooper–Schrieffer (BCS) theory, and the temperature is in energy units). They are compared with the corresponding dependence in the BCS model, taken from Ref. 14 (solid line). There is evidently a systematic difference between $\zeta(t)$ of the non-annealed and annealed materials. Unfortunately, the relatively low values of T_c prevent measurements at low t, where Δ no longer depends on t. Assuming, however, that in first-order approximation the form of the $\zeta(t)$ curve does not differ from the theoretical, so that the recorded difference is due to the difference between the normalization factors α and $\zeta(t)$, we obtain in place of the theoretical value $\bar{\alpha} = 3.52$ the values $\alpha_1 = 3.17$ for the non-annealed material and $\alpha_2 = 3.32$ for the annealed.

The values of α_1 and α_2 were obtained from the experimental data in the vicinity of the point $t = 0.75$, near the center of the interval shown in the inset. A more detailed analysis creates the impression that the differences cannot be reduced to a single coefficient, since they increase for large t and decrease together with t. This, however is in fact already at the measurement-accuracy limit. At any rate, the differences in the cited values of α (11 and 6% compared with $\bar{\alpha}$) is indicative of the magnitude of the effect.

DISCUSSION

Tunnel experiments with amorphous semiconductors have been carried out so far only on cold-deposited films,[15–17] with $\alpha \gtrsim \bar{\alpha}$ as the result. A large value of α is usually evidence of strong electron–phonon interaction, and $\alpha \to \bar{\alpha}$ in weak interactions. Some special cause is necessary for $\alpha < \bar{\alpha}$ to set in. The best known cause is the influence of spin fluctuations.

We know that scattering by paramagnetic impurities leads to finite lifetimes τ_s of superconducting pairs, and also

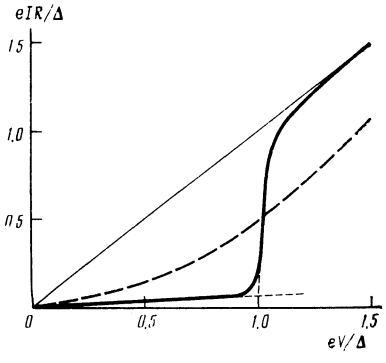

FIG. 2. Comparison of the experimental curve obtained with a non-annealed amorphous alloy at $T = 1.3$ K, $t = T/T_c = 0.53$, and $R = 58$ kΩ (solid curve) with calculation by Eq. (1) for the same Δ and t (dashed line).

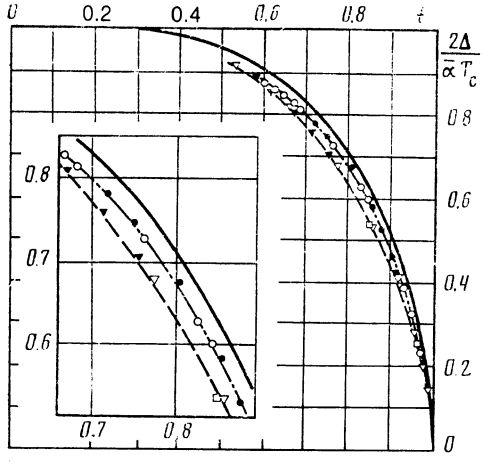

FIG. 3. Superconducting gap as a function of temperature for an amorphous alloy of composition $NiZr_2$ alloy quenched (triangles and squares) or heat-treated (circles) alloy. The dark and light symbols pertain to different samples.

to a lowering of T_c and to an increase of the gap Δ (Ref. 18). The decrease of Δ is faster than that of T_c, so that such a scattering lowers α. According to the plots in Ref. 19, a 10% decrease of α occurs if the collision frequency is

$$\hbar/\tau_s = \Gamma \approx 0.02\Delta_0, \tag{2}$$

where Δ_0 is the value of the gap in an impurity-free superconductor at $T = 0$. In this case the decrease of T_c is small:

$$\Delta T_c \approx 0.03 T_c. \tag{3}$$

In an Ni–Zr alloy it is the matrix atoms that are paramagnetic, not the impurities. Therefore, strictly speaking, the results of Refs. 18 and 19 do not hold for this alloy. We shall use them, however, for qualitative estimates. Assuming that the initial value of α with spin scattering turned off would be $\bar{\alpha}$, we get for an non-annealed tape $\Delta\alpha/\bar{\alpha} \approx 0.1$ and hence the estimates (2) and (3). If, however, we assume an initial value $\alpha_0 = 4.5$, we get $\Delta\alpha/\alpha_0 \approx 0.3$ and in place of the estimates (2) and (3) we have $\Gamma/\Delta_0 \approx 0.12$, $\Delta T_c/T_c \approx 0.17$.

The influence of the magnetic moments is taken into account in a consistent description of superconductivity in a paramagnetic matrix, by using the parameter λ_s of the interaction with the spin fluctuation and by replacing the usual MacMillan equation

$$T_c = \frac{\Theta}{1.45} \exp\left(-\frac{1+\lambda}{\lambda-\mu^*}\right) \tag{4}$$

(Θ is the Debye temperature, λ and μ^* are the electron–phonon and Coulomb-interaction constants) by[3,20]

$$T_c = \frac{\Theta}{1.45} \exp\left(-\frac{1+\lambda+\lambda_s}{\lambda-\lambda_s-\mu^*}\right). \tag{5}$$

It appears, however, that correlated decreases of T_c and α should occur in this case.

Let us examine from this standpoint the results of annealing our tape. A lower T_c is accompanied by a larger α. This means that the influence of the annealing on T_c is not due to a change of the interaction with the magnetic subsystem.

The influence of non-crystallizing annealing on the superconducting gap was measured directly for cold-deposited amorphous Nb stabilized by a nitrogen impurity.[17] The value of T_c itself responded to annealing just as in transition-metal alloys. Upon annealing, however, α decreased, i.e., ΔT_c and $\Delta\alpha$ had the same sign. Note that the initial value of α in Nb was larger than $\bar{\alpha}$, so that α approached $\bar{\alpha}$ after annealing, just as in the case of $NiZr_2$.

The deviations of α from $\bar{\alpha}$ are usually correlated with the deviations of the relative value of the specific-heat jump $\beta = (c_s - c_n)/c_n$ from the theoretical value of $\bar{\beta}$ in the transition. This is not so in our case. According to data of Refs. 8 and 11, $\beta > \bar{\beta}$ for alloys close to $NiZr_2$ in composition, and annealing increases the difference $\beta - \bar{\beta}$.

CONCLUSION

One of the most interesting questions in superconductivity physics is that of zero-phonon mechanisms of superconductivity. Measurement of α is one of the sources of information, albeit indirect, on the nature of the interaction that leads to superconductivity in a given substance. Proximity of α to $\bar{\alpha}$ indicates only that the interaction is weak. The analysis should focus on the variation of α. We have attempted above to show that in $NiZr_2$ these changes cannot be attributed to the magnetic part of the interaction, i.e., to electron–electron interaction via magnons. There are, however, also other possibilities.

In the two-phonon *s–d* model an effective attraction between the electrons can result from *s–d* exchange.[21] There are grounds for assuming that the electron spectrum in amorphous zirconium alloys can be described in the two-band model and that, moreover, in one of the bands the electron states are close to localized.[22] If it is assumed that *s–d* exchange contributes to the effective attraction between the electrons, the strong influence of chemical ordering becomes more understandable. The *s–d* interaction is decreased because of the decrease of the overlap region of the wave functions of electrons from different bands (*d* electrons located mainly on interatomic orbitals), on the one hand, and delocalized *s* electrons, on the other. This lowers T_c and α approaches $\bar{\alpha}$, since the remaining part of the interaction is purely phonon.

Additional experiments are needed, of course, to verify the described hypothesis that *s–d* interaction makes a substantial contribution to the effective interelectron attraction in amorphous alloys.

[1] S. J. Poon, in *Amorphous Metallic Alloys*, F. E. Luborsky, ed., Butterworth, 1983, p. 432.
[2] M. Tenhover and W. L. Johnson, Phys. Rev. B **27**, 1610 (1983).
[3] Z. Altounian and J. O. Strom-Olsen, *ibid.*, p. 4149.
[4] S. J. Poon, *ibid.*, B **27**, 5519 (1983).
[5] A. Inoue, K. Matsuzaki, N. Toyota *et al.*, J. Mat. Sci. **20**, 2323 (1985).
[6] G. E. Abrosimova, A. S. Aronin, V. F. Gantmakher *et al.*, Fiz. Tverd. Tela (Leningrad) **30**, 1424 (1987) [Sov. Phys. Solid State **30**, 822 (1987)].
[7] M. Thomas, M. G. Scott, and R. W. Cahn, in *Rapidly Quenched Metals*, S. Steeb and H. Warlimont, eds., Elsevier, 1985, p. 739.
[8] H. W. Gronert, D. M. Herlach, A. Schroder, R. van der Berg, and H. von Lohneysen, Z. Physik B **63**, 173 (1986).
[9] J. Hillaret, E. Balanzat, N. Derradji, and A. Chamberod, J. Non-Cryst. Sol. **61–61**, 781 (1984).
[10] R. Harris, L. J. Lewis, and M. J. Zuckermann, J. Phys. F **13**, 2323 (1983).
[11] D. M. Kroeger, C. C. Koch, J. O. Scarbrough, and C. G. McKamey, Phys. Rev. B **29**, 1199 (1984).
[12] L. Solymar, *Superconductive Tunneling and Applications*, Chapman and Hall, 1972.
[13] V. F. Gantmakher, A. A. Golubov, and M. V. Osherov, Zh. Eksp. Teor. Fiz. **96**, 1435 (1989) [Sov. Phys. JETP **69**, 813 (1989)].
[14] B. Mühlschlegel, Z. Physik B **155**, 313 (1959).
[15] G. Bergmann, Phys. Rep. **27**, 159 (1976).
[16] W. L. Johnson, C. C. Tsuei, S. I. Raider, and R. L. Laibowitz, J. Appl. Phys. **50**, 4240 (1979).
[17] D. B. Kimhi and T. H. Geballe, Phys. Rev. Lett. **45**, 1039 (1980).
[18] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **39**, 178 (1960) [Sov. Phys. JETP **12**, 1243 (1961)].
[19] S. Skalski, O. Betbeder-Malibet, and P. R. Weiss, Phys. Rev. A **136**, 1500 (1964).
[20] J. M. Daams, B. Mitrovic, and J. P. Carbotte, Phys. Rev. Lett. **46**, 65 (1981).
[21] B. T. Geĭlikman, Usp. Fiz. Nauk **88**, 327 (1966) [Sov. Phys. Usp. **9**, 142 (1967)].
[22] V. F. Gantmakher, G. I. Kulesko, and V. M. Teplinsky, J. Phys. **28**, 509 (1987).

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