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Superconductivity in amorphous *versus* crystalline $\text{Cu}_{0.33}\text{Zr}_{0.66}$ alloys

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Résumé. — On a déterminé les paramètres fondamentaux qui régissent le comportement supraconducteur de l'alliage $\text{Cu}_{0.33}\text{Zr}_{0.66}$ à l'état amorphe et cristallin, à partir de mesures de chaleur spécifique effectuées entre 0,3 K et 10 K. On montre qu'un modèle de liaison forte rend compte des différences importantes qui existent entre les deux phases.

Abstract. — The basic parameters underlying the superconducting behaviour of amorphous and crystalline, $\text{Cu}_{0.33}\text{Zr}_{0.66}$ alloys have been determined from specific heat measurements, performed between 0.3 K and 10 K. A tight-binding model is shown to account for the significant differences existing between the two alloy phases.

Much attention has recently been focused on the electronic structure of amorphous transition metal alloys, including both theoretical attempts to work out the density of electronic states [1, 2] and direct experimental results from ultraviolet and X-ray photoemission spectroscopy [3, 4]. Much progress has yet to be made, however, to understand the relationship between the band structure results and the overall physical properties of these alloys. Reliable information concerning the electronic density of states in close vicinity of the Fermi level is presently lacking. Whereas these data are beyond the investigative reach of photoemission experiments, they can be obtained from low temperature specific heat measurements.

In this paper we shall report low temperature specific heat results on the amorphous and crystalline $\text{Cu}_{0.33}\text{Zr}_{0.66}$ alloy. The main point which emerges from these measurements is the significant difference between the properties of the two alloy phases — specifically between their superconducting behaviour — although there is close similarity between their photoemission spectra. We shall further qualitatively discuss these differences within the tight-binding model for transition metals [5].

The amorphous alloy was prepared from electrolytic copper and Kroll zirconium by levitation melting and melt-spinning in a helium gas atmosphere [6]. The crystalline alloy was obtained by annealing an ini-

tially amorphous sample at 610 K for 30 min. in ultra high vacuum. X-ray diffraction patterns were made using $\text{CoK}\alpha$ radiation in order to check the structure of the samples. No trace of crystallinity was found in the amorphous state and the crystalline alloy exhibited the MoSi_2 type structure in accordance with previous work [7]. By differential thermal analysis [8] the crystallization temperature and the glass transition temperature were determined to be respectively $T_x = 650$ K and $T_g = 595$ K.

The specific heat was measured between 0.3 K and 10 K by the a.c. calorimetry technique as previously described [9]. The sample masses were 13.7 and 10.8 mg for the amorphous and crystalline phases respectively.

The data are displayed on figure 1 as C/T versus T^2 .

Fig. 1. — The molar specific heats of $\text{Cu}_{0.33}\text{Zr}_{0.66}$ alloy in amorphous and crystalline states. Normal state data on the amorphous sample have been obtained below the superconducting transition point by applying a magnetic field of 3.6 T.

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Table I. — *The experimental values of the electronic specific heat coefficients and of the Debye temperature θ_D .*

	Amorphous $\text{Cu}_{0.33}\text{Zr}_{0.66}$	Crystalline $\text{Cu}_{0.33}\text{Zr}_{0.66}$	Pure Zr
γ (mJ/mole.K)	4.51 ± 0.08	2.24 ± 0.04	2.78
θ_D (K)	202 ± 4	315 ± 13	289 ± 24

These plots are fairly linear, indicating that the present measurements can be fitted to the conventional expression $C(T) = \gamma T + \beta T^3$ which includes the usual electronic and lattice terms. The values of the coefficient of the electronic specific heat γ and of the Debye temperature θ_D which have been thus deduced are listed in table I and compared with the corresponding values for pure zirconium [10].

An additional linear contribution from tunnelling states in the lattice has been observed in many glasses. From specific heat measurements of amorphous $\text{Zr}_{0.7}\text{Pd}_{0.3}$ [19] and $\text{Zr}_{0.75}\text{Rh}_{0.25}$ [20] in the superconducting state, this contribution has been estimated to represent about two percent of the normal state electronic term so that it has been neglected in the present analysis.

From a photoemission study [4] of the Valence band in the amorphous $\text{Cu}_x\text{Zr}_{1-x}$ system, two conclusions have been drawn previously concerning the electronic structure in the vicinity of the Fermi level : first that it is mainly determined by the Zr-4d states, and, second, that the density of states at the Fermi level is slightly reduced compared to Zr. The present results and our previous work [11] on $\text{Cu}_{0.60}\text{Zr}_{0.40}$ do support the first conclusion, but they undoubtedly rule out the second one.

It appears also on figure 1 that the amorphous alloy undergoes a sharp superconducting transition at $T_c = 2.27$ K, with a transition width of 50 mK, whereas the crystalline compound remains in the normal state down to the lowest temperature of our measurements, viz. 0.3 K. The specific heat jump at T_c is $\Delta C(T_c)/\gamma T_c = 1.68$. As compared to the B.C.S. prediction of 1.43, this result may be taken as a first indication that amorphous $\text{Cu}_{0.33}\text{Zr}_{0.66}$ is an intermediate coupling superconductor. Moreover the electronic specific heat in the superconducting state may be fitted to an exponential for T_c/T ranging from 1.2 to 3, namely $C_{es}/\gamma T_c = 11.23 \exp(-1.59 T_c/T)$. We thus obtain the following estimate of the energy gap : $2 \Delta(0)/k_B T_c = 3.86$, which is slightly enhanced compared with the B.C.S. value of 3.53. Finally, by using the empirical Mc Millan's [12] formula :

$$T_c = \frac{\theta_D}{1.45} \exp \left[- \frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62 \lambda)} \right]$$

where the effective Coulomb repulsion parameter μ^* is assumed to be 0.13, the electron-phonon mass enhancement factor λ is obtained : $\lambda = 0.57$. All these results point to the conclusion that the coupling is of intermediate strength in amorphous $\text{Cu}_{0.33}\text{Zr}_{0.66}$.

We then find the renormalized value for the electron single spin density of states at the Fermi level $N(0) = 3 \gamma / 2 \pi^2 k_B^2 (1 + \lambda) \simeq 0.6$ state/eV.atom, which is appreciably higher than the corresponding quantity in pure zirconium : 0.42 state/eV.atom.

To analyse this set of data more fully let us look at them in view of additional information. It should be mentioned first that the shape of the valence band, as revealed by photoemission spectra, is fairly similar in amorphous and crystalline alloys which have the same composition [4]. Thus the topological disorder due to lack of long range periodicity in the amorphous phase is of secondary importance as far as the density of electronic states is concerned. This result may be easily understood within the framework of the tight-binding approximation [1-5]. In this scheme the density of electronic states $N(E)$ is primarily dependent upon the local atomic arrangement ; thereby the shape of the band is not drastically sensitive to the lattice structure. $N(E)$ can be evaluated through its moments. Though a knowledge of the atomic distribution functions up to any order is, in principle, needed, $N(E)$ may be described as a first approximation by a Gaussian distribution fitted to the second order moment μ_2 [13]. The bandwidth w is then simply proportional to $\sqrt{\mu_2}$. It should be added that w is a measure of the major contribution to the cohesive energy E_c of the material — that contributed by the tightly bound d-electrons. Now the second order moment can be written : $\mu_2 = X \bar{\beta}^2$, where X is the coordination number and $\bar{\beta}$ the averaged value of the next-nearest neighbour overlap integrals. $\bar{\beta}$ decreases with the interatomic spacing R like $e^{-q_0 R}$, where the Slater coefficient q_0 is roughly given by $q_0 R \simeq 3$ in the lattice equilibrium condition. Thus we can approximate $E_c \sim w \sim \bar{\beta}(R) \sqrt{X}$.

For the system of interest here, alloying effects must be taken into account. Photoemission measurements have shown that the valence band of the alloy exhibits a two-peaked structure. Due to the large distance in energy between the atomic d-levels of Cu and Zr, it may be induced that the lower part of the band is mainly related to the Cu d-states and the upper part to the Zr d-levels. Denoting by $X(\text{Zr-Zr})$ and $X(\text{Zr-Cu})$ the number of Zr and Cu nearest neighbours around a given Zr atom, respectively, and by $\bar{\beta}_{\text{Zr-Zr}}$ and $\bar{\beta}_{\text{Zr-Cu}}$ the corresponding overlap integrals, the Zr d-band width is proportional to $\sqrt{\mu_2(\text{Zr})}$, with :

$$\mu_2(\text{Zr}) = X(\text{Zr-Zr}) \bar{\beta}_{\text{Zr-Zr}}^2 + X(\text{Zr-Cu}) \bar{\beta}_{\text{Zr-Cu}}^2.$$

Considering the difference in the radial extension of the Cu and Zr d-orbitals we can assume

$$\bar{\beta}_{\text{Zr-Zr}} \gg \bar{\beta}_{\text{Zr-Cu}},$$

since the Zr-Zr and Zr-Cu interatomic distances are comparable. Thus we can simply write :

$$\mu^2(\text{Zr}) \simeq X(\text{Zr-Zr}) \bar{\beta}_{\text{Zr-Zr}}^2.$$

We shall further assume that the contribution of the Zr d-electronic states to the cohesive energy of $\text{Cu}_{0.33}\text{Zr}_{0.66}$ prevails over that of the Cu d-states. With this over simplified picture in mind we are going now to estimate the band effects involved when transforming from the amorphous to the crystalline state and the resulting effects on the superconducting behaviour.

Without distinguishing between the Cu and Zr atoms we introduce an average coordination number $\bar{X}$ and an average interatomic distance $\bar{R}$ which are connected to each other through the density ρ of the material : ρ is indeed proportional to $\bar{X}\bar{R}^{-3}$. Density measurements [14] on $\text{Cu}_{0.33}\text{Zr}_{0.66}$ have given the same result in either state, consequently the relative variations in $\bar{X}$ and $\bar{R}$ which arise when crystallization takes place are approximately given by $\delta\bar{X}/\bar{X} \simeq 3 \delta\bar{R}/\bar{R}$. The actual values of Zr-Zr, Cu-Cu and Cu-Zr distances are taken from structural studies of the amorphous [15] and crystalline [7] phases respectively, and, knowing the concentration of the atoms, we can deduce the average interatomic distances $\bar{R}$ in both cases. Hence we estimate for the relative change in $\bar{R}$ upon crystallization : $\delta\bar{R}/\bar{R} \simeq 3\%$. In addition, the afore-mentioned structural studies reveal no apparent traces of chemical ordering in the amorphous state, so that we assume

$$\delta X(\text{Zr-Zr})/X(\text{Zr-Zr}) \simeq \delta\bar{X}/\bar{X} = 3 \delta\bar{R}/\bar{R} \simeq 10\%.$$

Now, from the actual change in the Zr-Zr atomic distances $R(\text{Zr-Zr})$, which is

$$\delta R(\text{Zr-Zr})/R(\text{Zr-Zr}) \simeq -1.7\%,$$

we deduce an estimate of the corresponding change in the averaged overlap integrals :

$$\delta\bar{\beta}/\bar{\beta} = -q_0 R(\text{Zr-Zr}) \delta R(\text{Zr-Zr})/R(\text{Zr-Zr}) \simeq 5\%.$$

Finally we have :

$$\begin{aligned} \delta w/w &\simeq \delta E_c/E_c \simeq \delta X(\text{Zr-Zr})/2 X(\text{Zr-Zr}) + \\ &+ \delta\bar{\beta}_{\text{Zr-Zr}}/\bar{\beta}_{\text{Zr-Zr}} \simeq 10\%. \end{aligned}$$

Let us now consider the electron-phonon coupling constant λ . According to Mc Millan [12] it is given by $\lambda = N(E_F) \langle I^2 \rangle / M \langle \omega^2 \rangle$, where $\langle I^2 \rangle$ is the square of the matrix element for electron-phonon scattering averaged over the Fermi surface, M the ionic mass and $\langle \omega^2 \rangle$ an appropriate averaged squared phonon frequency. In the case of transition metals, λ has also been related to the cohesive energy [16] by using the tight-binding approximation and by assuming the ions to be rigid towards lattice dis-

tortions, with the result that $N(E_F) \langle I^2 \rangle \simeq q_0 E_c$. Combining these two relations and designating by subscripts A and X the quantities relative to the amorphous and crystalline states respectively, we obtain :

$$\lambda_X/\lambda_A = (E_{CX}/E_{CA}) (\theta_{DA}/\theta_{DX})^2 \simeq 0.45$$

and

$$\langle I^2 \rangle_A / \langle I^2 \rangle_X = 0.55.$$

The lower value which is obtained for $\langle I^2 \rangle_A$ is a direct consequence of the narrowing of the d-band and of the lengthening of the Zr-Zr interatomic spacing in the amorphous state compared to the crystalline one. It is related to a reduction of the averaged squared value of the electron velocity at the Fermi level [16].

Thus amorphicity affects the superconducting behaviour of $\text{Cu}_{0.33}\text{Zr}_{0.66}$ alloy in two opposing ways : by increasing the density of states at the Fermi level and softening the phonons, superconductivity is promoted, but, at the same time, it is weakened by the more tightly localized character of the d-electrons. We conjecture that these considerations yield the basis for a deeper understanding of the differences which prevail between the superconducting behaviour of transition metals compared to simple metals in the amorphous state [17]. In a previous theoretical work [21], the above mentioned interplay of the parameters involved in the superconducting behaviour of amorphous transition metals has been identified, and the same general conclusions have been drawn. However, only the change in the atomic volume has been considered explicitly in this theory, although it has been recognized that a change in the coordination number might be significant.

As a final comment it should be added that the difference between the elastic properties of transition metals glasses and those of their crystalline counterparts have been semiquantitatively explained within the tight-binding model [18]. It has been pointed out that, for an individual atom in the glassy state, there exist directions of easiest vibration which are related to the description of the disordered structure. However, due to the lack of a better knowledge of the atomic arrangement, only average value of the vibration frequency has been estimated, implying that all sites are more or less equivalent. Such an assumption is not necessarily true because of the occurrence of density fluctuations and soft regions in the material. This situation, as well as alloying effects, may explain the difference between the predicted value of 10% and the present experimental value of 35% for the lowering of θ_D in the amorphous state.

Anyway, the tight-binding model gives a qualitative account for the observed trends of the change in the properties of the $\text{Cu}_x\text{Zr}_{1-x}$ system when transforming from the crystalline to the amorphous state : similarity in the valence band shape of the two phases, but substantial variations in the Debye temperature, the

electron density of states at the Fermi level and the electron-phonon coupling constant, involving marked differences in the superconducting behaviour of the two phases.

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