

# PHYSICAL REVIEW B

## CONDENSED MATTER

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**THIRD SERIES, VOLUME 24, NUMBER 2****15 JULY 1981**

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### Crystallization of amorphous $\text{CuZr}_2$

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(Received 3 March 1981)

X-ray and electrical-resistance studies on amorphous  $\text{CuZr}_2$  show this system to crystallize by a polymorphous transformation directly to the body-centered-tetragonal crystal with no intervening stages. The transformation is excellently described by a Johnson-Mehl-type equation with the kinetics controlled by diffusion with a constant rate of nucleation. The amorphous phase is metastable with an activation energy of  $3.26 \pm 0.10$  eV.

#### I. INTRODUCTION

The recent interest in metallic glasses has been stimulated to some extent by their potential for technical application. However, the metallic glass state is known to be inherently unstable since heating to a sufficiently high temperature invariably transforms it irreversibly into the crystalline state. For any application to be useful this instability must take the form of metastability with a sufficiently high energy barrier against crystallization to ensure a room-temperature lifetime of at least several years. One of the easiest ways to test for this is to examine in detail the crystallization process and from its kinetics try to deduce not only the activation energy but also the mechanisms of crystal growth. As a result there have been many such studies,<sup>1</sup> principally in the transition-metal-based alloys (e.g.,  $\text{FeB}$ ). A difficulty frequently encountered in quantifying the results of these studies is that generally the crystallization process is complex,<sup>1</sup> consisting typically of two or more stages. The reason for this is readily understood: Metallic glasses are most easily formed at alloy compositions where the melting temperature is most suppressed—i.e., at or near eutectic points.<sup>2</sup> But to find an amorphous metal which crystallizes

in a single stage by a simple polymorphous reaction one must start with a composition where a stable compound exists—i.e., at a *maximum* in the constitutional phase diagram, which is exactly where the glass-forming ability is the worst.<sup>3</sup> As a consequence there appear to be few candidates for a simple transformation from the glassy to the stable crystalline state and to our knowledge no experimental evidence for any such system has yet been reported.

Nonetheless there do exist alloy systems which may be made amorphous over a wide enough range of composition to include several stable compounds. An example is Cu-Zr, one of the best known purely metallic glasses. Rapid quenching from the melt allows a glass to be formed from  $\text{Cu}_{25}\text{Zr}_{75}$  to  $\text{Cu}_{70}\text{Zr}_{30}$  in which range three stable compounds have been reported<sup>4</sup>:  $\text{Cu}_{10}\text{Zr}_7$ ,  $\text{CuZr}$ , and  $\text{CuZr}_2$ . Crystallization studies using differential scanning calorimetry (DSC) have been published on both  $\text{Cu}_{10}\text{Zr}_7$  (Refs. 5 and 6) and  $\text{CuZr}$  (Refs. 7 and 8). There remains some discrepancy among the published reports but neither system apparently shows a simple transformation. There is also some uncertainty about the existence of these crystalline phases; no structures have yet been reported (see Note ad-

ded in proof).  $\text{CuZr}_2$ , on the other hand, is a well established stable phase with a relatively simple, body-centered-tetragonal crystal structure having six atoms per unit cell.<sup>9</sup> This composition, then, is a logical place to look for polymorphous crystallization and this has been the motivation for the present work. The transformation was effected through isothermal annealing and monitored through changes in the electrical resistance. The electrical resistance is one of the more structurally sensitive properties of a solid and one in which changes may be measured extremely accurately. Also meaningful measurements may be taken well below the nominal crystallization temperature where the transformation rate is extremely slow.<sup>10</sup> In this sense it is complementary to DSC which is an isochronal heating technique with relatively rapid heating rates. On the other hand, the resistance is not by itself capable of saying how many stages there are in the transformation, unless the transformation is extremely simple. For this reason x-ray-diffraction techniques were also used to monitor the crystallization.

## II. EXPERIMENTAL METHODS

Amorphous samples were prepared by melt-spinning<sup>11</sup> buttons of approximately 1.5 g of crystal-line material. The buttons were prepared by arc-melting appropriate amounts of Cu (99.999% purity) and Zr (99.9% purity) under titanium-gettered argon and were melted several times to ensure homogeneity. The melt-spinning was carried out under helium at 50-kPa pressure on a Cu wheel with a tangential velocity of 50 m/sec. The resulting ribbons (typically 1.3 mm wide by 20  $\mu\text{m}$  thick) were examined by Debye-Scherrer x-ray photography using Ni-filtered  $\text{CuK}\alpha$  radiation. In all the samples examined the diffraction pattern after 24 h showed a strong broad line at  $2\theta = 36.5^\circ$  and a secondary, weak line at  $2\theta = 65^\circ$ .<sup>12</sup> No sharp lines could be detected. After manufacture the samples were stored in liquid nitrogen.

The resistance was measured using a highly sensitive ac difference method<sup>13</sup> under a 15-kPa atmosphere of helium obtained from the boiloff of liquid helium. This precaution was necessary to avoid any oxygen contamination during the annealing experiments. The influence of oxygen on the physical properties of amorphous Cu-Zr is well documented<sup>6,8</sup> and our own initial studies confirmed many of these findings.

The isothermal annealing was carried out in a ser-vocontrolled oven manufactured in the laboratory.

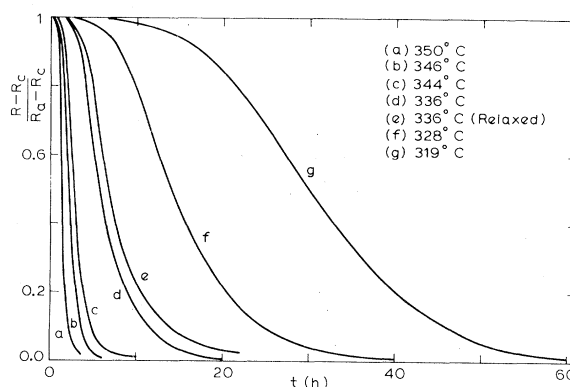


FIG. 1. Fractional resistance change of  $\text{CuZr}_2$  vs isothermal annealing time for different annealing temperatures.

The temperature was stable to  $\pm 0.5$  K. All data were recorded continuously on a strip-chart recorder.

## III. RESULTS

Isothermal annealing was carried out at a series of temperatures between 319 and 350°C. The resistance was measured as a function of time until crystallization was complete, as judged from there being no further changes in resistance. Results are shown in Fig. 1, presented as the fractional change  $(R - R_c)/(R_a - R_c)$ .  $R_a$  and  $R_c$  are the resistances of the amorphous and crystalline phases, respectively. Two features should be noted. First is the existence of an incubation time  $t_{\text{inc}}$  before which no change in resistance could be detected.<sup>14</sup> This incubation period must be allowed for in analyzing the kinetics of the crystallization. The second point is that for all samples the ratio of initial to final resistance,  $R_a/R_c$ , was the same  $1.704 \pm 0.006$ . This remarkable reproducibility at different temperatures suggests a simple transformation, the absence of any adverse oxidation effects, and a high degree of homogeneity in the ribbons. Figure 1 also shows the results for one sample which was treated to a stress-relaxing preanneal at 200°C for 2 h. It will be seen that the characteristics of this sample are very slightly different. Pertinent parameters are summarized in Table I.

After crystallization all samples were x rayed to determine the final crystal structure. For all the ribbons the first 30 diffraction lines ( $2\theta < 150^\circ$  for  $\text{CuK}\alpha$ ) were indexed and identified as belonging to

TABLE I. Resistance ratio  $R_a/R_c$ , incubation time  $t_{inc}$ , characteristic time  $\tau$ , and time exponent  $n$  for various annealing temperatures  $T$ .

$T$ (°C)	$R_a/R_c$	$t_{inc}$ (h)	$\tau$ (h)	$n$
350	1.698	0.42	0.70	2.41
346	1.704	0.50	1.42	2.57
344	1.704	0.68	1.62	2.50
336	1.704	1.64	3.26	2.50
336 <sup>a</sup>	1.701	1.5	4.25	2.50
328	1.711	3.2	9.02	2.48
319	1.703	6.64	19.96	2.59

<sup>a</sup>Relaxed (2 h at 200°C).

the CuZr<sub>2</sub> body-centered-tetragonal structure. No extra lines could be detected, in particular none of those belonging to Cu, Zr, ZrO<sub>2</sub>, or the other Cu-Zr phases were present. In addition a series of x-ray diffraction photographs were taken at different annealing times for  $T = 328^\circ\text{C}$ . The pattern for short annealing times ( $t < 40$  h) shows the coexistence of the diffuse amorphous ring with the crystalline CuZr<sub>2</sub> lines, with the latter becoming progressively stronger as the annealing time is increased. Again no extra lines could be detected.

Finally, to determine the crystallization temperature  $T_c$  one isochronal heating experiment was carried out at a heating rate of  $6^\circ\text{C}/\text{min}$ . The midpoint of the change in resistance gave a  $T_c$  of  $394^\circ\text{C}$ .

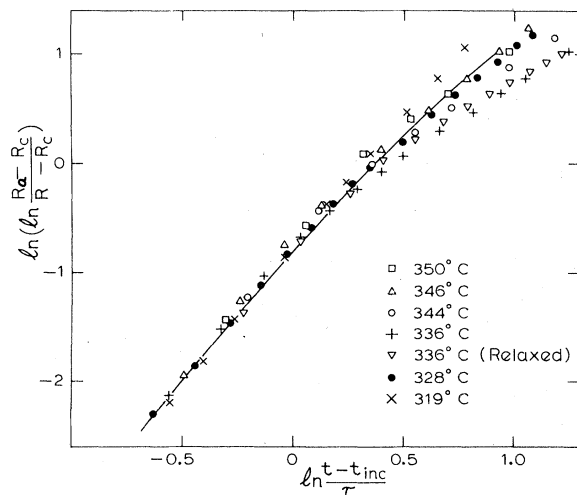


FIG. 2. Fit of the experimental data to the exact solution of transformation rate equation (solid line) corresponding to the Johnson-Mehl equation with  $n = \frac{5}{2}$ .

#### IV. DISCUSSION

The crystallization of CuZr<sub>2</sub> is simple and continuous and should be well represented by the theory of phase transformations.<sup>15</sup> Under isothermal conditions the transformed fraction  $X_c$  is related to the time  $t$ , since the start of the transformation for  $X_c < 0.4$ , by an equation of the Johnson-Mehl type,

$$X_c = 1 - \exp(-t/\tau)^n \quad (1)$$

$\tau$  is a temperature-dependent characteristic time and the time exponent  $n$  is determined by the controlling processes in the transformation.

The resistance of a composite material does not vary linearly with composition but depends on the resistivity of the components, their distribution, and shape. However, in CuZr<sub>2</sub> the difference  $R_a - R_c$  is small and corrections<sup>16,17</sup> to nonlinearity were found to be negligible. Hence we may take the

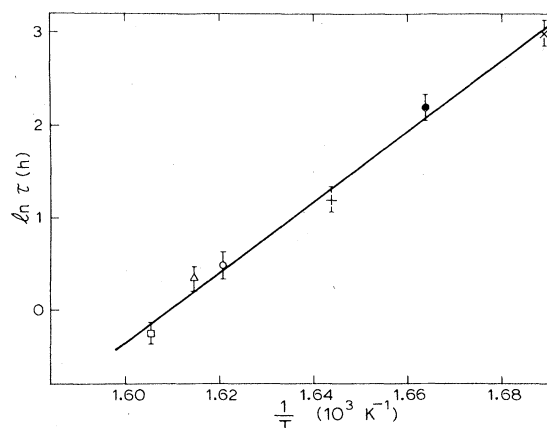


FIG. 3. Arrhenius-type temperature dependence of the characteristic time  $\tau$ . The different symbols refer to the temperatures of Figs. 1 and 2.

fractional change in resistance as representing the transformed fraction. Equation (1) can be rewritten as

$$\ln \ln \left( \frac{R_a - R_c}{R - R_c} \right) = n \ln \frac{(t - t_{inc})}{\tau}, \quad (2)$$

where we have allowed for the incubation period as outlined in Sec. III. That this equation (2) describes the data well is illustrated in Fig. 2. For each annealing temperature a single characteristic time  $\tau$  could be found to map the resistance changes on to a universal curve which at low  $X_c$  is linear with a slope  $n = 2.5 \pm 0.1$ .

The solid line in Fig. 2 is the exact solution of the transformation-rate equation corresponding to the Johnson-Mehl equation with  $n = \frac{5}{2}$  and is in good agreement over most of the range. For  $X_c \geq 0.8$  there appears to be significant deviation from this ideal model behavior. This may be a real effect; once the crystallites cover the full thickness of the sample, growth becomes characteristic of two rather than three dimensions. On the other hand, as  $R$  approaches  $R_c$ , errors in determining  $(R_a - R_c)/(R - R_c)$  become intrinsically large. At present we cannot say which of these effects is more significant.

Activation energies  $\Delta$  for the crystallization may be found from the characteristic time through the usual Arrhenius relation

$$\tau = \tau_0 \exp \left( \frac{\Delta}{kT} \right). \quad (3)$$

A plot of  $\ln \tau$  against  $1/T$  gives a straight line, as shown in Fig. 3, so that the effective activation energy is independent of temperature as one would expect if the same processes are occurring at all temperatures. The slope yields  $\Delta = 3.26 \pm 0.10$  eV (equivalent to 314 kJ/mole).

An activation energy may also be obtained from the incubation time, which may be interpreted as a measure of the time required for stochastic processes to produce nuclei of sufficient size to start growth. The activation energy obtained in this way is  $3.1 \pm 0.2$  eV which, within error, is the same as that for crystallization. This suggests that crystallization also proceeds by the same stochastic (i.e., diffusional) processes. This suspicion is confirmed by the exponent  $n = \frac{5}{2}$ , which is characteristic of diffusion-controlled growth with a constant rate of nuclei formation. Further confirmation may be obtained from an analysis of crystallization temperatures. The diffusion constant is proportional to the inverse

of the viscosity. Using an entropy theory of viscous flow<sup>18,19</sup> one finds

$$\eta = \eta_0 \exp(\Delta/ST), \quad (4)$$

where  $\Delta$  is the activation energy and  $S$  the configurational entropy. In an amorphous solid,  $S$  has only a weak temperature dependence since the configuration is more or less frozen in. Crystallization occurs rapidly when  $\eta$  reaches a critical value of  $\approx 10^{13}$  P. Thus  $T_c$  should scale with  $\Delta$ , if diffusion is the controlling mechanism. In CuZr,  $T_c = 453^\circ\text{C}$  and  $\Delta \approx 4.2$  eV (Ref. 8), and in CuZr<sub>2</sub> the corresponding values are  $394^\circ\text{C}$  and 3.26 eV giving ratios of 173 and 205 K/eV, in reasonable agreement with the model.

Finally, we may also account for the behavior of the relaxed sample. By heating at temperatures far below  $T_c$  the system will diffuse to a local minimum of free energy<sup>20</sup> but at the same time some development towards significant nucleation will occur. This explains both the shorter incubation time<sup>13</sup> and the slightly longer characteristic time which implies a very slightly higher activation energy for the relaxed sample.

## V. CONCLUSION

Amorphous CuZr<sub>2</sub> is a metastable glass with a very clearly defined activation energy of  $3.26 \pm 0.10$  eV. Crystallization proceeds by a simple single-stage transformation directly to the stable CuZr<sub>2</sub> tetragonal structure. The transformation is controlled by diffusional motion of the atoms with a constant rate of nucleation. The nucleation is controlled by the same stochastic processes.

To our knowledge CuZr<sub>2</sub> is the first amorphous alloy reported which transforms by such a simple polymorphous reaction. This makes it a very valuable system for studying the effects of crystallization on various physical properties such as the low-temperature resistivity, thermopower, and superconductivity. Such studies are presently underway on CuZr<sub>2</sub>.

*Note added in proof.* A structure has in fact been reported for Cu<sub>10</sub>Zr<sub>2</sub> by L. Bsenko, J. Less-Common Met. **40**, 365 (1975).

## ACKNOWLEDGMENTS

Useful technical discussions with B. C. Giessen and F. E. Luborsky are gratefully acknowledged. This research was supported by the National Scientific and Engineering Research Council of Canada and the Graduate Faculty of McGill University.

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