Effects of amorphization on the vibrational specific heat of metallic glasses

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The relative change $\Delta C_v(T)/C_v(T)$ in the vibrational component of the heat capacity during amorphization is determined by analyzing experimental data on the temperature dependence of the vibrational heat capacity for several metallic glasses of the metal-metal type and their crystalline analogs. Amorphization is found to produce a maximum in the temperature dependence $\Delta C_v(T)/C_v(T)$; the anomaly in $\Delta C_v(T)/C_v(T)$ is the same for all of the alloys investigated and suggests that the spectral density of the vibrational states is altered at low frequencies.

INTRODUCTION

The vibrational component of the specific heats of amorphous systems has two characteristic low-temperature anomalies. The first anomaly is the contribution which is linear in T to the vibrational heat capacity $C_v(T)$ for materials that are amorphous at temperatures $T \lesssim 1$ K; this anomaly can be described by the two-level model of Anderson *et al.*[1] and Phillips.[2] This model postulates the existence of a novel class of excitations which are characteristic of glasses and involve two-level systems; moreover, it provides a method for calculating how these excitations affect the temperature dependence $C_v(T)$ of the specific heat.

The second low-temperature anomaly for amorphous systems involves the increase in C_v for $2 \leqslant T \leqslant 50$ K, which is generally faster than T^3. The two-level model is unable to account for this behavior.

These anomalies have been studied in detail in investigations of the dielectric and semiconductor properties of amorphous systems and may be regarded as well established and universal.[3–6] The question of whether they are always present in metallic glasses is less clear and more complicated; this is the case not only for the first anomaly for $T \lesssim 1$ K but also for the second anomaly, which would appear to be more amenable to study. The situation is more difficult for metallic glasses because they are conductors, which makes it necessary to correctly identify the electronic and the vibrational components C_v and C_e to the specific heat and allow for the temperature dependence of the electron conductivity; the correct separation of the C_e and C_v is particularly important for temperatures between 2 and 50 K. Among other things, this requires that the temperature dependence $C(T)$ of the specific heat be measured experimentally for a wide range of T extending up to the crystallization temperature of the metallic glass. In addition, in order to compare the temperature dependence $C(T)$ for metallic glasses one must also consider the single-phase crystal analogs which have similar short-range orders. For metallic glasses, these are the metastable crystalline (MC) phases which form during the transition to the equilibrium crystalline state. We note that in the overwhelming majority of cases, amorphous metallic alloys enter a two-phase equilibrium crystalline state upon heating.

An attempt was made in Refs. 7–9 to correctly analyze $C(T)$ for metal glasses. In particular, it was pointed out that the deformation of the low-frequency portion of the vibrational spectrum for the metallic glass $Zr_{75}Rh_{25}$ [assessed in terms of the relative change in the vibrational specific heat C_v for $2 \leqslant T \leqslant 50$ K as compared with the MC analog] resembles the deformation caused by doping a lattice of light atoms with a heavy impurity or by attenuating the force constants, in which case resonant changes in the vibrational state density occur at low frequencies.

The microscopic nature of the spectra for specific vibrational excitations in amorphous systems was recently worked out in Refs. 10 and 11, where an interesting attempt was made to give a unified treatment of their influence on the thermodynamic properties of amorphous materials.

We were thus motivated in our present work to analyze the anomalous vibrational specific heats $C_v(T)$, $2 \leqslant T \leqslant 50$ K, for the metallic glasses $Zr_{75}Rh_{25}$, $Zr_{70}Be_{30}$, $Zr_{60}Be_{40}$, $Mg_{70}Zn_{30}$, and $(Mg_{70}Zn_{30})_{95}Pb_5$ and compare them with the corresponding crystal analogs. We analyzed a wide range of metallic glasses in order to study the universal nature of this anomaly more precisely and examine its relationship to the singularity in the vibrational spectrum of amorphous materials reported in Ref. 7.

DESCRIPTION OF THE SAMPLES AND EXPERIMENTAL METHOD

The amorphous glasses were produced by rapidly quenching the molten material on the outer surface of a rotating copper disk. The quenching rate was $\sim 10^6$ deg/s, and the amorphous samples were ribbon-shaped of width 1.5–2 mm and thickness ~ 0.03 mm. The ribbons were pressed into pellets prior to the specific heat measurements, after which the amorphous samples were annealed to temperatures $T_{\rm ann}$ high enough to form a metastable crystalline state. We then remeasured C_v for the annealed samples. The temperatures T_m and T_s for the transitions to the metastable and stable crystal phases were determined by differential calorimetry[12,13] and from the temperature dependence $\rho(T)$ of the electrical resistance. The values of T_m and T_s are given in Table I.

We used x-ray and electron diffraction to analyze the structure of the samples. The general form of the x-ray dif-

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TABLE I.

System	2θ, deg	$\Delta(2\theta)$, deg	d_{eff}, Å	T_s, °C	T_M, °C	T_{ann}, °C	d_{am} g/cm³	d_{MC} g/cm³
$Zr_{75}Rh_{25}$	37	5	2,97	990	453	530	7,52	7,64
$Zr_{70}Be_{30}$	38,5	6,5	2,86	393	314	355	5,72	5,62
$Zr_{60}Be_{40}$	36,25	6,2	3,03	515	429	490	5,47	5,35
$Mg_{70}Zn_{30}$	38	5,6	2,90	190	103	160	2,98	3,05
$(Mg_{70}Zn_{30})_{95}Pb_5$	37,5	6	2,93	200	99	170	3,56 *	3,24

*Repeated measurements of the density of the system $(Mg_{70}Zn_{30})_{95}Pb_5$ gave d values which were larger for the amorphous than for the crystalline state; further study is needed to determine the reason for this.

fraction curves was typical for amorphous metals and indicated that no long-range order was present. Table I gives the positions (2θ) of the first broad peaks, the width $\Delta(2\theta)$ of the peaks at half-maximum, and the calculated values d_{eff} for the effective distances between the nearest neighbors.[14]

The temperature coefficient α_T^{am} was negative for all of the amorphous systems that we studied; this contrasted with the "normal" behavior $\alpha_T^{cr} > 0$ for the crystal analogs.[15] The MC phases were identified from the x-ray structure results, which confirmed the published data for these systems. The samples in the MC state had the following structures: the $Mg_{51}Zn_{20}$ structure (Ref. 16) for the $Mg_{70}Zn_{30}$ system; an orthorhombic B_f-structure of the type CrB for the $Zr_x Be_{1-x}$ samples for $x = 0.6$ and 0.7 (Ref. 17); and an $E9_3$ structure[18] for the $Zr_{75}Rh_{25}$ system.

We measured the specific heats for T from 2 K to the MC transition point T_m in a zero magnetic field; we also carried out measurements in a magnetic field of ~ 6 T for $2 \leqslant T \leqslant 7$ K. The method used to measure C_v is described in Refs. 19 and 20; the random error was 1–2% for $2 \leqslant T \leqslant 5$ K and 0.4–1% for $5 \leqslant T \leqslant 100$ K. A differential scanning calorimeter was used to measure the specific heats by the method in Ref. 21 for $T > 100$ K; these measurements were accurate to within 2%.

The Curie temperature T_C for the transition to the superconducting state was measured by the induction technique and by analyzing the specific heat and electric resistance curves. The resistance $\rho(T)$ was measured by a 4-wire circuit using a dc current.

MEASUREMENT RESULTS AND DISCUSSION

Table II shows the measured temperature dependences of the specific heats for alloys in the amorphous and MC states. We see that the amorphous transition was accompanied by a marked increase in T_C The coefficients γ for the electron specific heat increased appreciably for all of the Zr-based alloys, both for low temperatures [$\gamma(0)$] and in the high-temperature limit [γ_{HT}]; in addition, the characteristic Debye temperature $\Theta(0)$ dropped abruptly. The Debye temperature Θ_{HT} in the high-temperature limit dropped during amorphization for the alloys $Zr_{70}Be_{30}$ and $Zr_{60}Be_{40}$, in which the two components have widely differing masses (by contrast, Θ_{HT} increased for $Zr_{75}Rh_{25}$, for which the components Zr and Rh have nearly equal masses). Since $\Theta(0)$ and Θ_{HT} decreased during amorphization for alloys with different component masses, the overall vibrational spectrum became smoother. The small difference in the values of Θ_{HT} for the $Mg_{70}Zn_{30}$ alloys in the amorphous and MC states barely exceeded the experimental error in Θ_{HT}.

We have already noted that the specific heat of amorphous materials increases anomalously rapidly (faster than the Debye law $\propto T^3$) at low temperatures $T = 2$–50 K. Figure 1 plots the temperature dependence $C_v(T)$ of the vibrational specific heats in the amorphous and MC states. The curves are plotted in C_v/T^3 vs T coordinates, as is customary for analyzing the departures of $C_v(T)$ from the T^3 Debye law. We took C_v equal to the difference C–C_e, where C is the total specific heat and C_e is the electronic component, and we

TABLE II.

System		T_C, K	$\Theta(0)$, K ±1,5 %	$\gamma(0)$, mJ/g-at·K² ±2%	Θ_{HT} K ±3%	$(A + \gamma_{HT})$, mJ/g-at·K² ±5%	γ_{HT} mJ/g-at·K² ±10%	A, mJ/g-at·K² ±10%
$Zr_{75}Rh_{25}$	am	4,23	190	5,1	289	10,4	3,1	7,3
	MC	2,92	204	4,0	277	9,5	2,5	7,0
$Zr_{70}Be_{30}$	am	3,5	234	4,4	546	5,2	2,7	2,5
	MC	1,8	354	3,26	586	7,2	2,2	5,1
$Zr_{60}Be_{40}$	am	2,7	289	4,25	529	2,9	3,5	0,7
	MC	0,43	420	2,10	610	1,5	4,2	2,7
$Mg_{70}Zn_{30}$	am	0,11 *	305	1,32	313	3,2	1,0	2,2
	MC	–	356	1,52	323	4,1	–	–
$(Mg_{70}Zn_{30})_{95}Pb_5$	am	–	240	1,18	308	3,4	–	–
	MC	–	253	1,78	326	5,7	–	–

*The values of T_C were taken from Ref. 30.

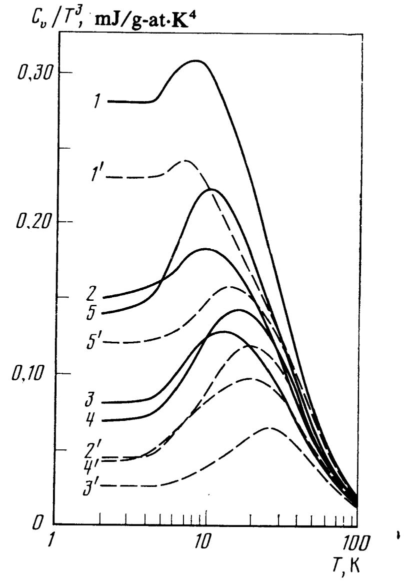

FIG. 1. Temperature dependence of the vibrational specific heat for alloys in the amorphous and MC states: 1) $Zr_{75}Rh_{25}$; 2) $Zr_{70}Be_{30}$; 3) $Zr_{60}Be_{40}$; 4) $Mg_{70}Zn_{30}$; 5) $(Mg_{70}Zn_{30})_{95}Pb_5$. The solid and the dashed curves correspond to the amorphous and MC states, respectively.

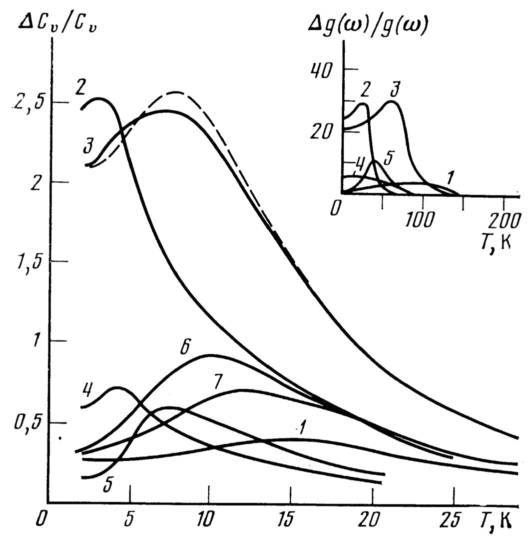

FIG. 2. Temperature dependence of the relative change in the vibrational specific heats during amorphization: 1) $Zr_{75}Rh_{25}$; 2) $Zr_{70}Be_{30}$; 3) $Zr_{60}Be_{40}$; 4) $Mg_{70}Zn_{30}$; 5) $(Mg_{70}Zn_{30})_{95}Pb_5$; 6) $Mg_{97}Pb_3$; 7) $V_{97}U_3$. The dashed curve corresponds to an electron-ion interaction function of the form $\alpha^2(\omega) = \text{const}/\omega$ for amorphous $Zr_{60}Be_{40}$. The insert shows the qualitative changes in the vibrational spectral density at low frequencies during amorphization.

allowed for the effects of the temperature-dependent electron-ion interaction. The technique used to calculate $C_e(T)$ for the superconducting alloys (for which the electron-ion interaction cannot be neglected) is based on the theory in Ref. 22 and is described in detail in Refs. 8 and 9.

Figure 1 shows that as a function of T, C_v/T^3 has peaks for $T = 7$–30 K for all of the systems investigated. These maxima show that $C_v(T)$ deviates from the T^3 law and in fact increases faster than T^3. The same was true for all of the alloys whether in the metallic glass or MC states, the only difference being that in the former case the peaks were higher and occurred at lower temperatures. We note that peaks are present in $C_v(T)/T^3$ not only for the MC phases of the alloys but also in other crystalline materials in thermodynamic equilibrium [e.g., Si, Ge (Ref. 6), Mg (Ref. 23), Sn, and Bi (Ref. 24)].

This implies that in general, the anomalous low-temperature specific heats of amorphous materials for $T = 2$–50 K cannot be characterized simply as an excess in $C_v(T)$ over the Debye value, because a similar excess also occurs in crystalline materials. This anomaly is better characterized in terms of the relative change $\Delta C_v(T)/C_v$ in the vibrational specific heat for the amorphous material as compared with the specific heat of the corresponding crystalline analog with identical chemical and topological order:

$$\Delta C_v(T)/C_v(T) = [C_v^{\mathrm{am}}(T) - C_v^{\mathrm{MC}}(T)]/C_v^{\mathrm{MC}}(T).$$

This characteristic was employed previously to analyze what happens to $C_v(T)$ for crystals containing heavy atomic impurities when the excitation spectrum is altered by doping the crystal with heavy impurities or by attenuating the force constants that describe the interaction between an impurity atom and the atoms in the host lattice.[25]

Figure 2 plots $\Delta C_v(T)/C_v(T)$ for the various alloys during amorphization. In all cases, the curves contain peaks for $T = 3$–16 K which differ considerably in magnitude and occur at different temperatures. For comparison, Fig. 2 also shows $\Delta C_v(T)/C_v(T)$ for two crystals with heavy impurity atoms (curves 6 and 7, corresponding to 2.8 at. % lead in magnesium and 2.8 at. % uranium in vanadium, respectively).[26,27] As was noted previously in Ref. 7, the dependences $\Delta C_v(T)/C_v(T)$ are similar for amorphization of a crystalline alloy and for crystals doped with heavy impurity atoms. In the latter case, however, the behavior of $\Delta C_v(T)/C_v(T)$ is associated with a resonant low-frequency alteration of the vibrational spectrum of the host crystal during doping, as is clearly demonstrated by the results of inelastic neutron scattering experiments.[28]

Judging from the behavior of $\Delta C_v(T)/C_v(T)$ alone, we can only suggest that amorphization is accompanied by a similar alteration of the vibrational spectrum of the initial crystalline system (at least, the effects on C_v are similar). However, the procedure in Refs. 8 and 9 for deducing the vibrational spectrum from $C_v(T)$ can be used to derive a very crude estimate for the nature and magnitude of the spectral changes for the amorphous alloy as compared with the spectrum for the crystalline analog. The insert in Fig. 2 shows the results for the five amorphous alloys that we studied. We conclude that the spectral changes resulting from amorphization are indeed similar to what occurs when crystals are doped with a heavy impurity—i.e., they resemble a resonant restructuring associated with the generation of quasilocal oscillations in the spectrum. However, we must of course recall that the data on $\Delta g(\omega)/g(\omega) = [g_{\mathrm{am}}(\omega) - g_{\mathrm{MC}}(\omega)]/g_{\mathrm{MC}}(\omega)$ were obtained by inverting the temperature dependence $C_v(T)$ and can serve only as a very rough illustration.

We make two more observations regarding the experimental results shown in Fig. 2. First, the specific choice of the electron-ion interaction function $\alpha^2(\omega)$ used to calculate

$C_e(T)$ is unimportant—the results for $\alpha^2(\omega) = \text{const}$ and $\alpha^2(\omega) = \text{const}/\omega$ are similar. Second, there is a correlation between the magnitude of the peak in $\Delta C_v(T)/C_v(T)$ and the change ΔV in the volume of the alloy during amorphization, the former increasing with the latter (i.e., as the density drops).

Most theoretical treatments of the vibrational spectra of amorphous materials (cf., e.g., Refs. 10, 11, 29) claim on qualitative grounds that amorphization is accompanied by an increase in the density of vibrational states at low frequencies; the characteristic spectral peaks and valleys become blurred, and the upper edge of the spectrum shifts toward higher frequencies. These treatments say nothing about the presence of peaks and dips in the vibrational spectral density at low frequencies.

The anomalous behavior of the specific heats of amorphous materials for $T = 2$–50 K has recently been attributed[10,11] to unusually strong anharmonic effects associated with fluctuations in the structural parameters in the amorphous material, some of which correspond to very small or even negative local quasielastic constants. These anharmonic effects give rise to spectral peaks near ~ 30 K. The interest in this approach is enhanced further because it can accommodate the two-level model in amorphous materials and provide a unified method for analyzing their thermal properties.

The above data on $C_v(T)$ for several metallic glasses and their crystalline analogs qualitatively support the method developed in Ref. 10. Unfortunately, they do not permit a quantitative assessment, and it is not possible to reach a definitive conclusion regarding the position, character, and scale of the singularity in the vibrational state density function for amorphous materials.

CONCLUSIONS

The above analysis of the experimental data on $C_v(T)$ for several types of metallic glasses and their crystal analogs yields the following conclusions.

1. Amorphization is associated with a peak in the temperature dependence $\Delta C_v(T)/C_v(T)$ of the relative change in the vibrational specific heat. The magnitude and temperature positions of the peak depend on the metallic glass. Plots of the reduced vibrational heat capacity $C_v(T)/T^3$ of amorphous materials indicate that for metallic glasses, $C_v(T)$ departs from the T^3 Debye law. However, this is also true for all of the metastable crystalline analogs of the glasses, as well as for many other stable crystalline systems. The anomalous behaviour of $C_v(T)/T^3$ is thus not limited to amorphous materials or metallic glasses.

2. The universal nature of the anomaly in $\Delta C_v(T)/C_v(T)$ for the metallic glasses suggests that the vibrational state density is altered at low frequencies. This change influences the specific heat [the magnitude and position of the peak in $\Delta C_v(T)/C_v(T)$] in much the same way as the alterations in the phonon spectrum produced by doping light atomic crystals with a few at. % of a heavy impurity.

3. Studies of inelastic neutron scattering by metallic glasses and their crystal analogs may yield more precise information regarding the nature of the changes in the vibrational state density at low frequencies.

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