PHYSICAL REVIEW B VOLUME 32, NUMBER 3 1 AUGUST 1985

Specific heat of thin-film amorphous molybdenum-based alloys

D. Mael, W. L. Carter,* S. Yoshizumi, and T. H. Geballe†
Department of Applied Physics, Stanford University, Stanford, California 94305

(Received 4 March 1985)

We have studied the effects of transition-metal (TM) and metalloid (*M*) substitution in amorphous molybdenum-based TM-*M* alloys. Absolute-specific-heat measurements of thin-film (~1 μm thick) samples of Mo-Ge, Mo-Si, and Mo-Ti-Si alloys prepared by magnetron sputtering were made using the relaxation-time-constant method. A comparison of the superconducting transition width made both thermally and electrically indicates that the sample homogeneity is better than 0.1% for length scales greater than the coherence length. Both the electronic density of states and T_c with increasing metalloid concentration and [Ti]/[Mo] ratio, in agreement with a rigid-band model. We compare our results to current theories relating the electron-phonon coupling constant $\lambda_{e\text{-ph}}$ to the electronic density of states.

INTRODUCTION

There is a great deal of current interest in the bulk structural and electronic properties of amorphous alloys, especially with regard to superconductivity. Because of the metastable nature of many of these systems, they are mostly prepared as thin films. Specific heat has also been measured on bulk amorphous superconductors;[1] however, because of our concerns about sample homogeneity, we needed thin films, whose material properties could be very well characterized.

One of the most interesting points to address in these alloys is the relationship between the metal concentration and electronic density of states as the system runs from metal to insulator. Using recently developed small-sample techniques,[2] we have measured the specific heat of superconducting Mo-based alloys over a wide range of compositions. The specific-heat measurement allows us to obtain not only the density of states, but other important properties, such as the Debye temperature (Θ_D) as well.

SAMPLE PREPARATION AND CHARACTERIZATION

We prepared the amorphous Mo-based alloy films by magnetron sputtering from targets of the respective elements in $\sim 6\times 10^{-3}$-Torr Ar gas at room temperature. The films averaged 1 μm thick and were deposited on $(6\times 6\times 0.2)$-mm^3 sapphire substrates. The substrates were mounted on a rotating table with the targets aimed so as to impinge on a common area at the center of rotation in order to achieve compositional homogeneity in the films. The rotation speed was typically 300 rpm and the sputtering rate 5 Å/sec. X-ray and transmission-electron-microscope (TEM) analyses show evidence for the amorphous phase only. The structural results were consistent with those reported by Kortright[3] using synchrotron radiation.

EXPERIMENTAL SETUP

The specific heat of the samples was measured by a time-constant-relaxation method, with τ ranging from 10 msec to 1 sec, using silicon-on-sapphire sample platforms (bolometers). The relaxation sweeps were signal averaged for increased signal-to-noise ratio. In addition, the data points were taken repeatedly to keep scatter error to less than 1%. Thus, the major source of error in the measurement was the weight of the sample. For a typical 300-μg sample, we knew the weight reproducibly to ±3 μg for an error of 1%. The absolute accuracy of sample plus addenda, as confirmed by measurements on known standards, is 1% in the temperature region where we take our data.

The contribution of the sapphire, aluminum contact pads, and electrical lead wires to the total heat capacity ranges from 75% of the total (at ~10 K) to 85% of the total (at ~2 K). Thus, we are limited to a sample specific-heat accuracy of 4—7%. The renormalized density of states (γ^*), and Debye temperature (Θ_D), are obtained by using a fit to $C/T=\gamma^* T+\beta T^3$ above T_c, coupled with the constraint that the entropy be the same in the superconducting state and the normal state. Thus, the values of γ^* and Θ_D are measured with an accuracy of ±5%. Our results for the systems studied are listed in Table I, and the plots of C/T versus T^2 are shown in Fig. 1. Values of γ^* are plotted in Fig. 2.

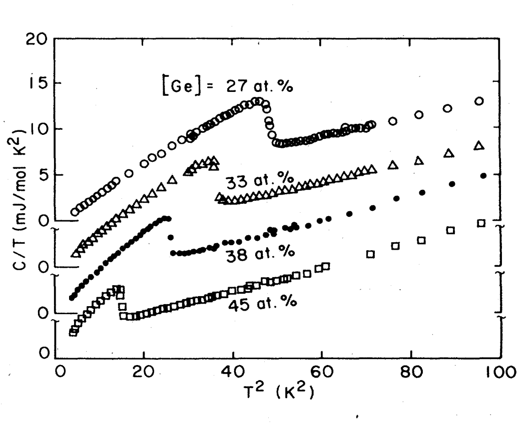

FIG. 1. Specific heat of $\mathrm{Mo}_x\mathrm{Ge}_{1-x}$ alloys for samples measured in this study.

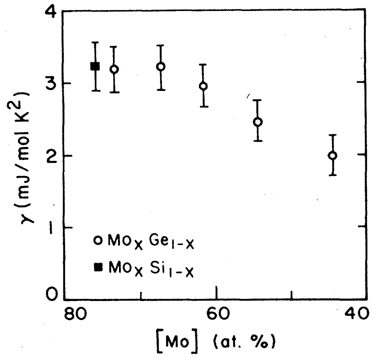

FIG. 2. Values of γ^*, the electronic-specific-heat coefficient, for this study.

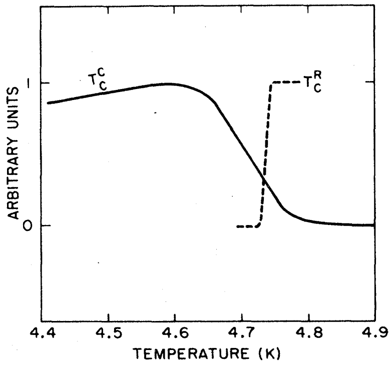

FIG. 3. Superconductivity transition temperature of $Mo_{76}Ge_{33}$ measured by resistivity and by specific heat.

RESULTS AND DISCUSSION

Initially, we were concerned that our samples might not be completely homogeneous.[4] As previously mentioned, x-ray and TEM measurements showed only the amorphous phase; however, our present measurements offer the opportunity to investigate the degree of large-scale inhomogeneity in our samples. Our approach to this problem is to examine the superconducting-temperature transition width ΔT_c as measured by four-terminal resistance (van der Pauw) ΔT_c^R and by specific heat ΔT_c^C on the same sample. The transitions are shown in Fig. 3.

We begin our analysis with the specific-heat transition. According to the Ginzburg criterion for our material, $\xi_0 = 60$ Å, $T_c = 5$ K,

$$t_c = \frac{1}{32\pi^2}\left[\frac{k_B}{\Delta C \xi_0^3}\right] \cong 10^{-3} \tag{1}$$

[where $t = (T - T_c)/T_c$ and ΔC is the specific-heat jump at T_c], fluctuations will not become important until we are within ~ 50 mK of T_c. Thus we can treat the ΔT_c^C with a mean-field approach, in which the superconducting behavior of the sample will be governed by its material properties on a length scale of ξ_0.

It has been suggested[5,6] that intrinsic compositional fluctuations over the size of a coherence length ξ_0 might be responsible for this transition width. This is, for a random solid solution $A_{1-x}B_x$, a mean composition deviation of $\langle \Delta x^2 \rangle^{1/2}$ over volume $V \sim 4\pi/3\xi_0^3$ would lead to a T_c spread of

$$\langle \Delta T_c^2 \rangle^{1/2} = \frac{dT_c}{dx} \langle \Delta x^2 \rangle^{1/2} . \tag{2}$$

For our materials, $\xi_0 = 60$ Å, which means that V contains $N \sim 10^4$ atoms and thus, according to Poisson statistics, would show a composition variation of $1/\sqrt{N}$ or 1%. Also, for Mo_xGe_{1-x}, $d(T_c)/dx = 180$ mK/at. %. Consequently, we might expect to see a transition width $\langle \Delta T_c^2 \rangle^{1/2}$ of about 180 mK, which is in good agreement with our measured specific-heat value of 200 mK. Thus, the width of the specific-heat transition can be well explained without requiring any macroscopic inhomogeneity in the sample.

The above model implies that macroscopic inhomo-

TABLE I. Values of material parameters for the α-Mo_xGe_{1-x} systems.

Alloy	γ $\left[\frac{\text{mJ}}{\text{mol K}^2}\right]$	Θ_D (K)	λ ($\mu^* = 0.1$)	$N_b(0)$ $\left[\frac{\text{states}}{\text{eV atom}}\right]$	T_c^R (K) ΔT_c^R (K)	T_c^C (K) ΔT_c^C (K)
$Mo_{73}Ge_{27}$	3.05	266	0.672	0.775	7.01–7.03 0.02	6.8–7.05 0.15
$Mo_{67}Ge_{33}$	3.07	267	0.637	0.797	5.92–5.94 0.02	5.8–5.95 0.15
$Mo_{62}Ge_{38}$	2.92	254	0.612	0.770	5.05–5.07 0.02	4.9–5.1 0.2
$Mo_{55}Ge_{45}$	2.51	254	0.562	0.683	3.90–3.92 0.02	3.7–3.95 0.25
$Mo_{43}Ge_{57}$	2.06	295	0.455	0.600		
$Mo_{76}Si_{24}$	3.23	300	0.651	0.829		7.2–7.4 0.2
$(Mo_{88}Ti_{12})_{77}Si_{23}$	2.95	309	0.614	0.773		6.0–6.25 0.25

geneities of less than about 1% will be effectively masked by this intrinsic randomness of the two components, and so, while we claim that there is no need to postulate large-scale inhomogeneity to explain ΔT_c^C, we also cannot yet rule out such inhomogeneity of less than 1%. To do so, we turn to the resistive transition ΔT_c^R, where ΔT_c^R is measured by the van der Pauw method and is thus sensitive to any of a large class of inhomogeneities.

Since $\Delta T_c^R < 50$ mK, we now find ourselves in a regime where fluctuations are dominant. In Fig. 4 we have plotted $\Delta\sigma/\sigma_0$ versus t, where $t=(T-T_c)/T_c$, $\Delta\sigma$ is the fluctuation conductivity, and σ_0 is the residual normal-metal conductivity. In three dimensions (3D), we would expect to see fluctuation conductivity in accordance with the predictions of Aslamazov and Larkin,[7]

$$\Delta\sigma/\sigma_0 \propto t^{-1/2} . \tag{3}$$

We do find this approach to work well down to about 20 mK from T_c, at which point $\Delta\sigma/\sigma_0$ deviates from the $t^{-1/2}$ fit, and approaches t^{-1} as would be expected for 2D behavior. However, at this point, $\xi(t) \sim 1000$ Å is still much less than the thickness of the sample (1.5 μm). We can thus rule out a 3D to 2D crossover as the sole explanation for this deviation. Instead, we think it is reasonable to postulate a small-amplitude compositional inhomogeneity that could be due to very slow drifts in deposition rates during the time of a measurement. If this were the case, then by our previous arguments we would require only a 0.1% composition gradient to account for the observed spread in T_c, well within the expected stability of the sputtering equipment.

We can now turn to the question of why the onset of T_c^R occurs after about 20% of the material has become superconducting according to the specific heat. This can be understood by combining our explanations of the transition widths of ΔT_c^C and ΔT_c^R. In effect, as the temperature is lowered, isolated regions of size ξ_0^3 show a contribution to the heat capacity due to the pairing condensation before there are enough of them to link up to form continuous superconducting filaments of length $\xi(t)$. The exact offset of T_c^R with respect to T_c^C caused by this is difficult to calculate. The experimental result that 20–25% of the heat-capacity transition has taken place before T_c^R seems reasonable.

Thus, we can conclude that the samples are homogeneous on a small length scale of 60 Å and such large-scale compositional inhomogeneities as may exist are $\lesssim 0.1\%$ over the size of 1000 Å and can be accounted for by long-term drifts in deposition rates.

Two other samples were measured, $Mo_{76}Si_{24}$ and $(Mo_{88}Ti_{12})_{76}Si_{24}$, to study the effects of substitutions on the metal and the metalloid sites. In the first case, we can compare Si to Ge. The value of γ^* for $Mo_{76}Si_{24}$ shown in Fig. 2 is consistent with the values for the Mo-Ge samples, indicating that the metalloid replacement does not appreciably affect the electronic density of states. However, Θ_D did increase significantly, which shows that the Si substitution stiffens the lattice.

In the other sample, 12 at. % of the Mo is replaced by Ti, in going from $Mo_{76}Si_{24}$ to $(Mo_{88}Ti_{12})_{76}Si_{24}$. Here Θ_D increased only slightly, indicating that the metal substitution did not affect the lattice stiffness. However, γ^* has decreased significantly, showing that the metal is responsible for changes in the density of states, since Ti has fewer electrons per atom than Mo.

TIGHT-BINDING ANALYSIS

The electron-phonon coupling constant λ can be extracted from McMillan's[8] approximate solution to the Eliashberg equations,

$$T_c = \frac{\Theta_D}{1.45} \exp\left[-\frac{1.04(1+\lambda_{e\text{-ph}})}{\lambda_{e\text{-ph}} - \mu^*(1+0.62\lambda_{e\text{-ph}})} \right] . \tag{4}$$

For the range of concentrations used here, it is believed μ^* can be assumed to be 0.1, consistent with the tunneling results for amorphous N-stabilized Mo and Nb.[9]

For transition-metal alloys Varma and Dynes[10] have argued using a nonorthogonal tight-binding analysis that $\lambda_{e\text{-ph}}/N_b(0) = \langle I^2 \rangle / M \langle \omega^2 \rangle$ is approximately constant. Here $N_b(0)$ is the bare density of states, $\langle I^2 \rangle$ is the average electron-phonon interaction matrix element at the Fermi surface, $\langle \omega^2 \rangle$ is the average squared phonon frequency, and M is the ionic mass. For calorimetric data, $\langle \omega \rangle^2$ is assumed to be proportional to Θ_D^2. Thus, in this model, λ depends only on $N_b(0)$, so that T_c depends mainly on $N_b(0)$ through λ, and only weakly on Θ_D.

The results for $\lambda_{e\text{-ph}}$ versus $N_b(0)$ are plotted in Fig. 5.

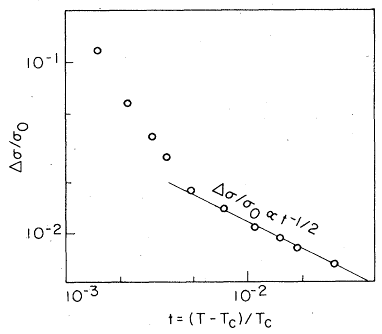

FIG. 4. Fluctuation conductivity $\Delta\sigma/\sigma_0$, vs reduced temperature t.

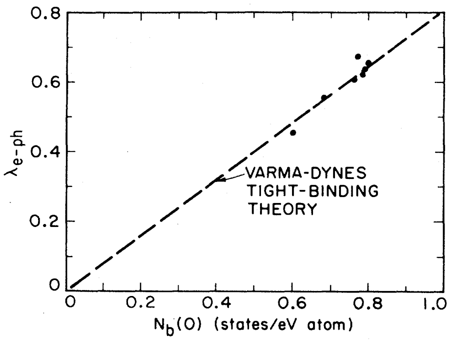

FIG. 5. Electron-phonon coupling constant $\lambda_{e\text{-ph}}$ vs density of states $N_b(0)$.

If the tight-binding analysis is correct, the data should lie on a line through the origin. The trend is roughly linear. The highest point deviates from the line. It is for a sample which is close to the Mo-rich boundary of the amorphous range of composition, and thus is in a sense less stable than the others. The Varma-Dynes analysis might be expected to fail near the limits of metastability. However, we need more data in this region before we can make a definitive statement.

With this in view, we can also examine how the bare density of states changes as the density of conduction electrons of the alloy is changed. In this approach, if we assume that the metal is the sole contributor of the conduction-band electrons, that the Fermi surface in this amorphous system is roughly spherical, and that the d band is rigid for the metals in this region,[11] then we would expect to see $N_b(0) \propto n^{1/3}$, where n is the electron density. Our data are not inconsistent with this analysis (Fig. 6).

In conclusion, we have made the first specific-heat measurements on thin-film metastable amorphous-alloy systems. Comparison of the superconducting transition as measured by heat capacity and resistivity shows that the samples are homogeneous over macroscopic distances. The microscopic material parameters $N_b(0)$ and $\lambda_{e\text{-ph}}$ obey relatively simple relationships when the system is far away from structural or electronic transitions. We are currently continuing the research in the metal-insulator—transition region.

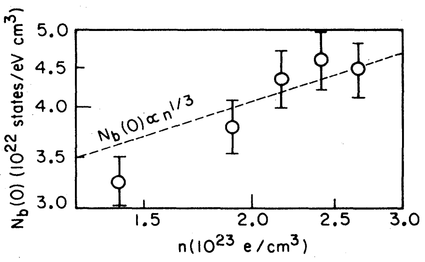

FIG. 6. Bare density of states $N_b(0)$ vs density of electrons.

ACKNOWLEDGMENTS

The work of D. Mael, W. L. Carter, and T. H. Geballe at Stanford was supported by the Air Force Office of Scientific Research under Grant No. F49620-83-C-0014. S. Yoshizumi was supported by the National Science Foundation (NSF) Materials Research Laboratory Grant No. DMR-83-16982, and samples were prepared at the Stanford University Center for Materials Research under NSF Materials Research Laboratories Program support.

---

[*] Present address: Naval Research Laboratory, Washington, D.C. 20375.

[†] Also at Bell Communications Research, Murray Hill, NJ 07974.

[1] W. L. Johnson and S. T. Hopkins, Solid State Commun. **43**, 537 (1982).

[2] S. R. Early *et al.*, Physica **107B**, 327 (1981).

[3] J. Kortright, Ph.D. dissertation, Stanford University, 1984 (unpublished).

[4] W. L. Carter, S. J. Poon, G. W. Hull, Jr., and T. H. Geballe, Solid State Commun. **30**, 41 (1981).

[5] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, Oxford, 1958).

[6] W. L. Johnson and C. C. Tsuei, Phys. Rev. B **13**, 4827 (1976).

[7] L. G. Aslamazov and A. I. Larkin, Phys. Lett. **26A**, 238 (1968).

[8] W. L. McMillan, Phys. Rev. **167**, 331 (1968).

[9] D. Kihmi, Ph.D. dissertation, Stanford University, 1980 (unpublished).

[10] C. M. Varma and R. C. Dynes, *Superconductivity in d- and f-Band Metals,* edited by D. H. Douglass (Plenum, New York, 1976), p. 507.

[11] C. C. Tsuei, in *Superconductor Materials Science,* edited by S. Foner and B. Schwartz (Plenum, New York, 1981), p. 735.