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Comparison between the Amorphous and Crystalline (A-15) Phases on Nb_3Ge

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A comparative study on the superconducting and the normal-state properties of the amorphous, low-T_c (3.9 K) and the crystalline, high-T_c (2.18 K) phases of Nb_3Ge suggests that changes in the strength of electron-phonon interaction account, in large part, for the drastic reduction in T_c. This result is consistent with a dehybridization between Nb $4d$ and Ge $4p$ orbitals at E_F in amorphous Nb_3Ge as shown by recent x-ray photoemission spectroscopy measurements and a microscopic theory of dielectric screening and lattice dynamics.

In the crystalline state (with the A-15 structure), the intermetallic compound Nb_3Ge exhibits superconductivity with the highest onset transition temperature ($T_c \sim 23$ K) attained to date.[1] On the other hand, the amorphous phase of Nb_3Ge becomes superconducting at a much lower temperature ($T_c \sim 4$ K).[2] To obtain a better understanding of superconductivity in the high-T_c crystalline (c) and the low-T_c amorphous (a) phases of Nb_3Ge, it may be fruitful to compare the superconducting and the normal-state properties of these phases. Efforts along these lines have already resulted in a variety of studies, e.g., x-ray photoemission,[3] x-ray absorption fine structure,[4] and superconductive tunneling.[5] In this note, we present the results of low-temperature specific-heat measurements on an amorphous Nb_3Ge film (~ 8 μm thick). With this new piece of information, together with the existing data, we will then show, by a comparison between the amorphous and crystalline phases of Nb_3Ge, that changes in the strength of the electron-phonon interaction account in large part for the drastic reduction in transition temperature.

The amorphous state of Nb_3Ge was achieved by rf sputtering from a Nb_3Ge target onto a substrate (sapphire or fused quartz) held at liquid-nitrogen temperature. The noncrystallinity of the sput-

tered films was checked by x-ray and electron diffraction. An analysis of the radial distribution function for the amorphous Nb_3Ge samples reveals that the short-range order can be approximately described, as for many other amorphous transition-metal–metalloid alloys, in terms of a Bernal model of dense random packing of hard spheres.[6]

In a recent study of superconducting materials for high-magnetic-field applications,[7] it was found that films of amorphous alloys such as a-Nb_3Ge, a-Nb_3Si, and a-V_3Si are highly flexible and ductile unlike their crystalline counterparts which are all extremely brittle. In fact, it is found that the amorphous film can be peeled off from the substrate if the film thickness is about 2 μm or more. This fact allows us to obtain a small, but self-supporting sample (~ 7 mg). This proved to be necessary in order to measure the specific heat. A sapphire substrate (even if it is very thin, say, $\frac{1}{32}$ in. thick) constitutes an addendum of comparable heat capacity to that of the Nb_3Ge film over the experimental temperature range and thus decreases accuracy considerably. All measurements were performed, point by point, using the thermal relaxation technique first described by Bachmann *et al.*[8] The apparatus was calibrated against a 99.999% pure Cu standard and all numbers quoted in this Letter are with reference to this calibration. The estimated maximum absolute error in the measurement of the heat capacity is ± 10%. It was necessary to evaporate a thin (~ 1000 Å) Au film onto the Nb_3Ge film (thickness ~ 8 μm) in order to increase the thermal conductance of the sample sufficiently so that the internal relaxation time of the sample did not have to be taken into account. The results of such experiments are presented in Fig. 1 where the total specific heat C divided by temperature T is plotted against T^2. The inset in this figure shows the resistive superconducting phase transition of the same specimen used in the calorimetric measurement. Both the electrical-resistance and specific-heat measurements indicate a sharp and well-defined phase transition with $T_c = 3.9$ K. A least-squares fit of the normal-state heat capacity to the standard equation $C = \gamma T + \beta T^3$ yields $\gamma = 12 \pm 2$ mJ/mole K^2 and $\beta = 0.71 \pm 0.02$ mJ/mole K^4, which corresponds to a Debye temperature $\Theta_D = 222 \pm 3$ K.[9] (All errors are expressed in terms of standard deviations for a least-squares fit to the data.) Equating the experimental electronic entropy of the superconducting state to that estimated for

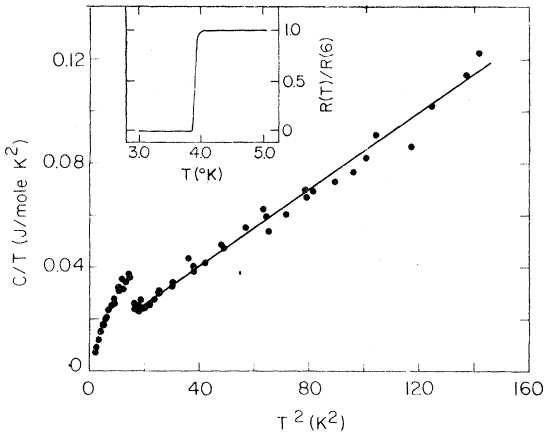

FIG. 1. Total specific heat of a-Nb_3Ge as a function of temperature (1.5°K < T < 16°K). The data for the normal state are least-squares fitted by the equation $C = \gamma T + \beta T^3$. The inset shows the resistance $R(T)$, normalized at $T = 6$°K, of the same specimen used in the calorimetric measurement.

the normal state from the β value for $T > T_c$ also yields $\gamma = 12$ mJ/mole K^2. This lends further credence to our determination of γ. The Debye temperature for crystalline Nb_3Ge ($T_c \sim 21.8$ K) was found to be 302 K.[10] This ~ 27% decrease for Θ_D in going from the crystalline to the amorphous state is larger than that observed for many other metallic conductors.[11] Approximately a factor of 2.5 drop in γ was found for a-Nb_3Ge ($\gamma = 30.3 \pm 1$ mJ/mole K^2 for A-15 Nb_3Ge).[10] The data for the superconducting state ($T < 4$ K) can be described very well by the following expression (as shown in Fig. 2):

$$C = A \exp(-B/T) + \beta T^3, \quad (1)$$

where A and B are found to be 0.46 J/mole K and 5.9 K, respectively. In the weak-coupling limit, the BCS theory predicts $A = 8.5\gamma T_c = 0.4$ J/mole K and $B = 1.44 T_c = 5.62$ K, and γ is expressed in joules/mole K^2. The fact that the experimental values for A and B agree well with those predicted by BCS theory is consistent with a recent report that the values of the ratio of energy gap to transition temperature $[2\Delta(0)/kT_c]$ in amorphous-transition-metal–based superconductors such as a-Nb_3Ge and a-Nb_3Si are found to be 3.5 ± 0.1 in agreement with the BCS theory in the weak-coupling limit. The value of $2\Delta(0)/kT_c$ for the high-T_c A-15 Nb_3Ge was reported[12] to be 4.2, suggesting a strong electron-phonon coupling. The value of the specific-heat jump at T_c can be measured from Fig. 1:

$\Delta C = 70.2$ mJ/mole K;

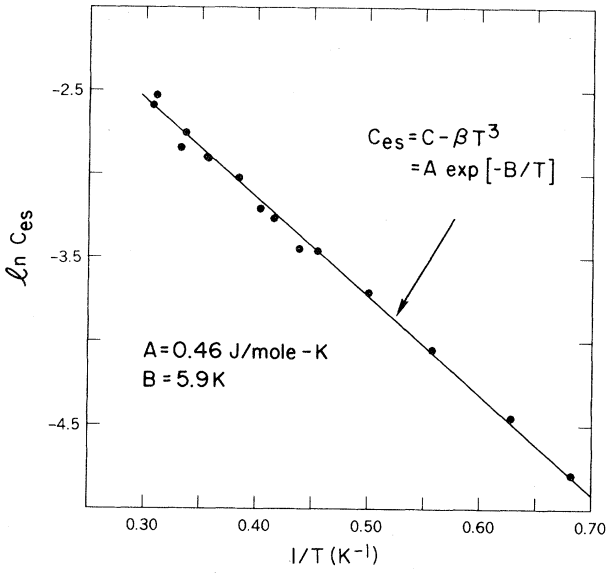

FIG. 2. The electronic specific heat of a-Nb_3Ge in the superconducting state ($C_{es}=C-\beta T^3$).

and the value of $\Delta C/\gamma T_c$ is found to be 1.5 in good agreement with the BCS prediction (i.e., 1.43). In short, our experiment results indicate that a-Nb_3Ge is a typical BCS weak-coupled superconductor while in its crystalline counterpart c-Nb_3Ge, the electron-phonon interaction is strong.

In order to explore more quantitatively the origin of the difference in superconducting transition temperature for a- and c-Nb_3Ge, the dimensionless electron-phonon coupling parameter λ is calculated for the two phases of Nb_3Ge by using the well-known McMillan formula[13] for T_c:

$$T_c=\left(\frac{\Theta_D}{1.45}\right)\exp\left[\frac{-1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right], \qquad (2)$$

where μ^* is the effective electron-electron Coulomb pseudopotential (we assume $\mu^*=0$, 11 for both c- and a-Nb_3Ge). For the case of a-Nb_3Ge, $\lambda=\lambda_a$ is found to be approximately 0.6 from Eq. (2) with $\Theta_D=222$ K and $T_c=3.9$ K. For the single-phase c-Nb_3Ge sample used in the heat-capacity measurement by Stewart, Newkirk, and Valencia[10] ($T_c=21.8$ K, $\Theta_D=302$ K), we obtain $\lambda=\lambda_c=1.2$. It should be pointed out that, as suggested by Allen and Dynes,[14] the McMillan equation introduces a significant error in determining λ for very strong-coupled superconductors. If the Allen and Dynes correction is taken into account, the value of λ for c-Nb_3Ge ($T_c=23$ K) is estimated to be 1.7–1.9.[15] In the following analysis, we will take $\lambda_c=1.7$.

It is noted the ratio of λ_c to λ_a is unusually large (i.e., $\lambda_c/\lambda_a=2.8$). The significance of this large reduction in λ associated with the crystalline- to amorphous-phase transition can be discussed in terms of the three factors of which λ is composed: i.e., $\lambda=N(E_F)\langle I^2\rangle/M\langle\omega^2\rangle$. Here $N(E_F)$ is the bare electronic density of states at the Fermi energy, $\langle\omega^2\rangle$ an average square phonon frequency, and $\langle I^2\rangle$ the Fermi-surface average of the electron-phonon interaction. With the renormalization effect arising from the electron-phonon interaction taken into account, one can relate $N(E_F)$ to γ determined from the specific-heat measurements by $\gamma=(1+\lambda)\frac{2}{3}\pi k^2N(E_F)$ which leads to the conclusion that $[N(E_F)]_c/[N(E_F)]_a=(1+\lambda_a)\gamma_c/(1+\lambda_c)\gamma_a=1.7$. Using the results reported in this Letter and the findings of a recent tunneling study,[5] we have reanalyzed the data by Wiesmann *et al.*[16] on the temperature coefficient of the upper critical field, $dH_{c2}(T_c)/dT$, and the normal-state resistivity, ρ_0, near T_c to estimate the variation of $N(E_F)$ as a function of T_c. The drop in $N(E_F)$ for Nb_3Ge is ~50% as T_c changes from ~21 to ~4 K, in good agreement with the results of the specific-heat measurements. The second factor, $\langle\omega^2\rangle$, cannot be evaluated without the knowledge of the Eliashberg function, $\alpha^2(\omega)F(\omega)$, which requires accurate neutron-scattering measurement and tunneling spectroscopy. In the absence of such data, several authors have assumed that $\langle\omega^2\rangle$ is proportional to $\Theta_D{}^2$.[17,18] In a recent report of superconductivity in the high-pressure phase of Ba,[19] it was assumed that $\langle\omega^2\rangle\propto T_M$, the melting temperature which is, in turn, proportional to $\Theta_D{}^2$ according to Lindemann's formula for melting point. In the following discussion, we will assume $\langle\omega^2\rangle=b\,\Theta_D{}^2$, b being a proportionality constant. It is to be remembered that this assumption could result in an error as much as ~±30%.[20] Based on the above discussion and the Θ_D data for a- and c-Nb_3Ge, we obtain $\langle\omega^2\rangle_c/\langle\omega^2\rangle_a=1.85$. With the aid of the expression for λ and the values of $[N(E_F)]_c/[N(E_F)]_a$ and $\langle\omega^2\rangle_c/\langle\omega^2\rangle_a$, we are in a position to evaluate $\langle I^2\rangle_c/\langle I^2\rangle_a$:

$$\frac{\langle I^2\rangle_c}{\langle I^2\rangle_a}=\frac{[N(E_F)]_a}{[N(E_F)]_c}\frac{\langle\omega^2\rangle_c}{\langle\omega^2\rangle_a}\frac{\lambda_c}{\lambda_a}=3.$$

The uncertainty in estimating $\langle\omega^2\rangle_c/\langle\omega^2\rangle_a$ can be translated into the conclusion that $\langle I^2\rangle_c/\langle I^2\rangle_a$ for Nb_3Ge is at least 2 and could be as large as 4. Even without Allen and Dynes' correction, these numbers vary between ~1.5 and 2.5. This result is very surprising in view of the fact $\langle I^2\rangle$ is generally considered as an "atomic property"[21] and

is not significantly affected by the change in the atomic arrangement.

Although the importance of $\langle I^2 \rangle$ in determining the T_c of a superconductor is well recognized, the empirical values of $\langle I^2 \rangle$ for only a handful of superconductors have been reported. Microscopic and systematic calculation of $\langle I^2 \rangle$ for a number of transition-metal elements, compounds, and alloys were published only very recently.[20,22] Of these theoretical calculations, the one proposed by Hanke, Hafner, and Bliz is probably most relevant to the experimental finds of the present investigation. Based on a microscopic theory of dielectric screening and lattice dynamics, they conclude that, for transition-metal intermetallic compounds such as NbC, hybridization of the relatively localized electronic states (i.e., the 4*d* states of Nb atoms) and the conduction-band states (i.e., the *s*, *p* states from a nonmetal element such as C, Ge, etc.) at the Fermi level can lead to the reasonancelike increase of the nonlocal dielectric function ϵ^{-1} (as defined in Ref. 22). This in turn, enhances $\langle I^2 \rangle$ and produces some phonon softening. Recent x-ray photoemission-spectroscopy measurements[3] of crystalline ($T_c = 16$ K) and the low-T_c (~ 3.7 K) amorphous phases of Nb_3Ge indicates that changes in the valence bands and core levels suggesting a dehybridization between Nb 4*d* and Ge 4*p* orbitals at E_F. This observation is consistent with the experimental finding of this study that $\langle I^2 \rangle$ is greatly reduced in the amorphous state of Nb_3Ge

It should be pointed out that the value of $N(E_F)$, ~ 0.57 (eV spin atom)$^{-1}$, for the *A*-15 *c*-Nb_3Ge as determined from γ is *not* anomalously high for an *A*-15 compound. In fact, it is significantly lower than that of some of the *A*-15 compounds with $T_c \lesssim 18$ K (e.g., Nb_3Al, Nb_3Sn, V_3Si, etc.).[23] Furthermore, the Debye temperature of *c*-Nb_3Ge does not distinguish itself among those of other relatively low-T_c, *A*-15 superconductors.[23] Therefore, it is tempting to suggest that, in the search for high-T_c superconductors, emphasis should be placed on achieving a strong electron-phonon interaction via, for instance, a hybridization of appropriate electronic states at the Fermi level, provided that this is not accomplished at the expense of decreasing $N(E_F)$ considerably. In this sense, *A*-15 Nb_3Ge probably represents nature's best known example of a compromise between $N(E_F)$, $\langle I^2 \rangle$, and $\langle \omega^2 \rangle$.

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