# Influence of the Superconducting State upon the Low-Temperature Properties of Metallic Glasses

J. L. Black and P. Fulde
*Max-Planck-Institut für Festkörperforschung, 7000 Stuttgart, Germany*
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We consider the effects of the superconducting state upon the ultrasonic properties of metallic glasses at low temperatures. A number of measurable effects are predicted. Their observation would confirm the influence of conduction electrons upon two-level systems in these materials.

The evidence for the existence of low-energy two-level system (TLS) in metallic glasses has become increasingly convincing.[1-6] Of the remaining questions, perhaps the most outstanding is how these tunneling states relate to their well-known counterparts in insulating glasses.[7,8] Recent work by Golding *et al.*,[2] suggests that the principal differences can be explained by the interaction between TLS and the conduction electrons. In this Letter, we propose some experimental tests in superconducting metallic glasses, which can conclusively decide the validity of this viewpoint.

Our calculation is based upon a simple idea: By introducing a BCS-type energy gap in the electronic excitation spectrum, the importance of the TLS-electron interaction should be drastically diminished. The TLS in the metal should thus behave essentially as though they were in an insulating glass.

It has been emphasized elsewhere[1,2,5] that metallic glasses at low temperatures differ most strongly from insulators in that the TLS possess a very rapid "spin-lattice" relaxation rate $T_1^{-1}$. As outlined in Ref. 2, this short $T_1$ explains the principal puzzles in the low-temperature ultrasonic properties of metallic glasses: difficulty of saturation, strong deviations from insulating-glass laws for relaxational ultrasonic attenuation and velocity, and the lack of two-pulse or coherent effects. Furthermore, Golding *et al.*[2] developed the idea that a "Korringa-type" process[9] can plausibly explain this short $T_1$. In the following, we wish to discuss the effects of the superconducting state upon this process.

The following Hamiltonian describes the interacting TLS–conduction-electron–phonon system in metallic glasses[2,10,11]:

$$H=\sum_{\vec{k},\sigma}\epsilon_k c_{\vec{k}\sigma}^{\dagger}c_{\vec{k}\sigma}+\sum_l E^l S_z^l+(1/N)\sum_{\vec{k},\sigma,\vec{q},l}(V_{\parallel}S_z^l+V_{\perp}S_x^l)e^{i\vec{q}\cdot\vec{R}_l}c_{\vec{k}\sigma}^{\dagger}c_{\vec{k}+\vec{q},\sigma}+\sum_{l,\nu}(2M_\nu S_x^l+D_\nu S_z^l)e_\nu, \tag{1}$$

where $E^l$ is the energy splitting for the TLS located at $\vec{R}_l$ and described by the $s=\frac{1}{2}$ pseudospin $\vec{S}^l$. The quantities $V_{\parallel}$ and $V_{\perp}$ are (in general $q$-dependent) interaction matrix elements normalized to the average atomic volume $v=V/N$. As discussed elsewhere,[12] these interaction terms arise from electron-ion coupling. The interaction matrix elements $M_\nu$ and $D_\nu$ describe coupling to strain fields $e_\nu$ induced by phonons of polarization $\nu$. Because of the short electronic mean free path in metallic glasses, the direct electron-phonon contribution to the ultrasonic absorption and velocity is negligibly small.

To lowest order in $V_{\perp}$, perturbation theory yields a TLS inverse lifetime for $E^l=E$ which is given by $T_1^{-1}=(\pi/4\hbar)(\rho V_{\perp})^2 E\coth(\beta E/2)$. This Korringa-like result is dependent upon $\rho$, the electronic density of states per atom (including *both* electronic spin directions). In Ref. 2, it was shown that $\rho V_{\perp}\approx 0.2$ leads to a value of $T_1$ in the nanosecond regime for $T\lesssim 1$ K and $E/h\approx 1$ GHz. Since this rate dominates the one-phonon relaxation processes[7] [from the $M_\nu e_\nu$ term in Eq. (1)] by several orders of magnitude, we shall henceforth restrict our attention to the Korringa process. It is now straightforward to generalize this result to the case in which the electronic spectrum is modified by the BCS energy gap. This yields[13]

$$T_1^{-1}=(\pi/4\hbar)(\rho V_{\perp})^2\int_{-\infty}^{\infty}d\epsilon_1\int_{-\infty}^{\infty}d\epsilon_2 n(\epsilon_1)n(\epsilon_2)(1-\Delta^2/\epsilon_1\epsilon_2)f(\epsilon_1)f(-\epsilon_2)\delta(\epsilon_2-\epsilon_1-E)+(E\rightarrow -E), \tag{2}$$

where $n(\epsilon)=|\epsilon|(\epsilon^2-\Delta^2)^{-1/2}$ if $|\epsilon|>\Delta$, and zero otherwise. Here $\Delta$ is the BCS energy gap (or order parameter) and $f(\epsilon)=(e^{\beta\epsilon}+1)^{-1}$. The coherence factor $1-\Delta^2/\epsilon_1\epsilon_2$ corresponds to the time-reversal-invariant interaction of Eq. (1).[14] Accordingly, Eq. (2) differs strongly from the well-known Korringa law for the NMR $T_1^{-1}$ in superconductors, but closely resembles the ultrasonic attenuation due to elec-

 

tron-phonon coupling.[13,15]

Figure 1 shows the result of a numerical evaluation of Eq. (2) for various values of $E/k_B T_{c0}$, where $T_{c0}$ is the superconducting transition temperature. For the simplest case, $E=0$, the relaxation arises only through thermally excited quasiparticles:

$$T_1^{-1} = (\pi/\hbar)(\rho V_\perp)^2 k_B T (e^{\beta\Delta}+1)^{-1}. \tag{3}$$

This result displays exponential activation when $T \ll T_{c0}$ and the ubiquitous square-root dependence[13] when $T \approx T_{c0}$. Whenever $E$ is nonzero, the condition $E \geq 2\Delta$ will eventually be fulfilled as $T$ increases toward $T_{c0}$. This occurrence results in a discontinuous enhancement of $T_1^{-1}$, leading to a rate which is greater than the rate in the normal metal. The physical origin of this additional relaxation is the ability of the TLS to create (or annihilate) a pair of quasiparticles out of the condensed BCS ground state.[15] This pair-excitation channel can actually exist down to $T=0$ for $E>2\Delta(T=0)$.

As examples of experiments which should reflect the pronounced effects of Fig. 1, we now consider the relaxational ultrasonic absorption $\alpha(\omega)$ and velocity change $\delta c$, which have already demonstrated the importance of the Korringa relaxation in normal metallic glasses.[2] These two quantities arise through the phonon-TLS coupling in Eq. (1) and are given by the standard expressions[2,16]

$$\begin{Bmatrix} \alpha/\omega \\ -2\delta c/c \end{Bmatrix} = \frac{\beta}{4\rho_m c^3}\int_0^\infty dE\,\mathrm{sech}^2\left(\frac{\beta E}{2}\right)\int_0^1 dr\,P(r)D^2\frac{1}{(\omega T_1)^2+1}\begin{Bmatrix} \omega T_1 \\ c \end{Bmatrix}, \tag{4}$$

where $c$ is the sound velocity, $\rho_m$ is the mass density, $\omega$ is the ultrasonic frequency, and $P(r) = \frac{1}{2}\bar{P}r^{-1}(1-r)^{-1/2}$. In accordance with the tunneling model,[7] we have borken up the full TLS density of states into an integral over the partial density of states, $P(r)$. The variable $r$ is equal to $\Delta_T^2/E^2$, where $\Delta_T$ is the tunneling energy and $E$ is the full energy splitting of the TLS ($E^2=\Delta_T^2+\Delta_A^2$ with $\Delta_A^2$ being the asymmetry energy). It follows that $D=2\gamma(1-r)^{1/2}$ and $V_\perp = r^{1/2}K_\parallel$, where $\gamma$ and $K_\parallel$ refer to the modulation of the asymmetry by phonons and conduction electrons, respectively.[7,11]

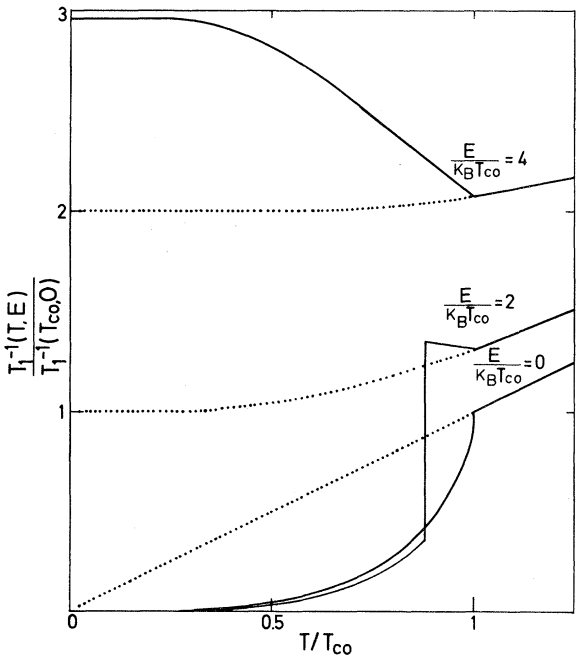


FIG. 1. TLS Korringa rate in BCS superconductor with transition temperature $T_{c0}$ and TLS energy splitting $E$. Rates are normalized by $T_1^{-1}(T_{c0},0) = (\pi/2\hbar) \times (\rho V_\perp)^2 k_B T_{c0}$. Dotted curves show normal-state rates

The results of a combination of Eqs. (1) and (4) are shown in Fig. 2. These curves show how strongly the superconducting state should affect the TLS-induced relaxational ultrasonic attenuation and velocity in metallic glasses at low temperatures. At lower temperatures, both attenuation and velocity shift become exponentially activated, at which point the neglected phonon relaxation processes become important.

The shapes of the curves in Fig. 2 are only moderately affected by the ultrasonic frequency. At lower frequencies the curves tend to reach their high temperature asymptotes more quickly as $T$ increases. For the attenuation this asymptote is a constant, $\alpha(\omega)=\pi K\omega/c$, whereas the velocity approaches $\delta c/c = -\frac{1}{2}K\ln(T/\omega)$ when $T > T_{c0}$. It should be emphasized that this asymptotic behavior follows from the broad distribution of rates inherent in the tunneling model. Our use of the tunneling model is justified by the experimental results in nonsuperconducting metallic glasses which are consistent with the high-temperature behavior of Eq. (4).[1,2,5]

A further consequence of this theory is that the ultrasonic properties should be affected by the application of a magnetic field. For fields exceeding the upper critical field $H_{c2}$, superconductivity is suppressed, and the relaxation rate returns to its normal-state value. Thus the curves

of Fig. 2 represent the two extreme cases $H = 0$ (full curves) and $H > H_{c2}$ (dotted curves).

For fields intermediate between these two extremes, there is in general no simple theory. One exception is the gapless superconductivity regime,[14] defined by temperatures close to $T_c(H)$, which is the transition temperature in the presence of the field. We have worked out the theory for the case when the $\vec{A}\cdot\vec{p}$ effects of the magnetic field dominate the $\vec{\mu}\cdot\vec{H}$ effects. Generalizations to other cases will be discussed elsewhere. It is found that an expansion in the spatially-averaged order parameter $\langle|\Delta(\vec{r})|^2\rangle$ yields

$$T_1^{-1} = \frac{\pi}{4\hbar}(\rho V_\perp)^2 \coth\left(\frac{\beta E}{2}\right)\left(E - \frac{\langle|\Delta|^2\rangle}{2\pi T_c}\,\mathrm{Im}\left\{\psi^1\left(\frac{1}{2}+\frac{\alpha - iE}{2\pi T_c}\right)\right.\right.$$
$$\left.\left. - \frac{4\pi T_c}{iE}\,\frac{E+i\alpha}{E+2i\alpha}\left[\psi\left(\frac{1}{2}+\frac{\alpha-iE}{2\pi T_c}\right)-\psi\left(\frac{1}{2}+\frac{\alpha}{2\pi T_c}\right)\right]\right\}\right), \quad (5)$$

where $\psi$ is the digamma function, $\psi^1$ is the trigamma function, and $\alpha$ is a pair-breaking parameter which relates to the magnetic-field–induced reduction in $T_c$ via $\ln(T_c/T_{c0}) = \psi(\frac{1}{2})\psi(\frac{1}{2}+\alpha/2\pi T_c)$. The dependence of $\langle|\Delta(\vec{r})|^2\rangle$ as a function of $\alpha$, $T_c$, and $T$ is given as in Ref. 14.

In Eq. (5) the term proportional to the square of the order parameter represents a change in the Korringa rate due to the superconducting correlations, just as in the BCS case of Fig. 1.

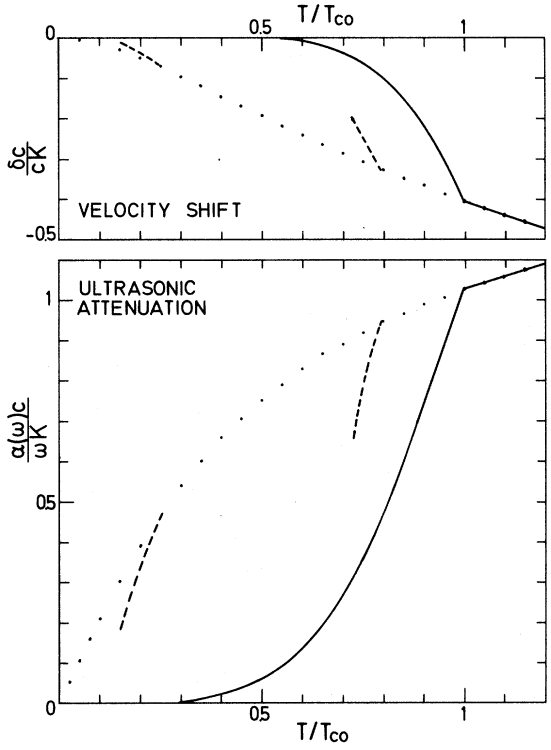


FIG. 2. Relaxational ultrasonic attenuation and sound velocity plotted vs reduced temperature. The frequnecy is $(500T_{c0})$ MHz with $T_{c0}$ measured in degrees and $\rho V_\perp = 0.2$. Dotted curves show normal-state results. The dashed segments show the results of a magnetic field in the gapless regime. The constant $K$ is given by $\bar{P}_\gamma^{\,2}/\rho_m c^2$.

There are, however, significant differences in the $T$ and $E$ dependences. First of all, a linear temperature law arising from the dependence $\Delta^2 \sim (T_c - T)$ replaces the square-root behavior of Fig. 1. Secondly, the discontinuities at $E = 2\Delta$ are not present in the gapless regime since there is no longer a gap in the excitation spectrum.

The experimental consequences of this gapless theory are indicated in Fig. 2 as dashed deviations from the normal-state curves. The predicted changes in slope near $T_c$ as a function of field should be observable.

In conclusion, it should be noted that we have considered in detail only relaxational ultrasonic properties of metallic glasses. On the other hand, the characteristic temperature and magnetic field dependence of the Korringa rate below $T_c$ should also lead to observable effects in the resonant ultrasonic properties.[1,2,8] There is good evidence, for example, that the relatively high saturation threshold $\varphi_c$ in normal metallic glasses is attributable to the short $T_1$ by means of the relation[2,8] $\varphi_c = \hbar^2 \rho_m c^3 \gamma^{-2} T_1^{-2}$. With use of the fact that $\hbar\omega \ll k_B T_{c0}$ for frequencies less than 1 GHz, it is permissible to use the simplified expression given in Eq. (3) to yield $\varphi_c = (\pi^2/4)\rho_m c^3 \gamma^{-2}(\rho V_\perp)^4 \times (k_B T_{c0})^2[1 - 6.1(1 - T/T_{c0})^{1/2}]$ near $T_{c0}$, showing the expected square-root dependence. For frequencies comparable to $k_B T_{c0}/\hbar$, the discontinuities in $T_1^{-1}$ should show up as jumps in the threshold.

Finally, as mentioned earlier, the TLS relaxation for $T \ll T_{c0}$ and $H = 0$ should be controlled by processes similar to those which dominate in insulating glasses. These include the one-phonon direct process[7] and the spectral diffusion process[17] derived from "spin-spin" interactions. Since these two mechanisms are known to yield rather long relaxation times (microseconds), it is to be expected that superconducting metallic glass-

es will support phonon echoes,[18] which require long phase-memory times, and two-pulse saturation effects,[8,19] which require long saturation recovery times. To summarize, we are suggesting tests of the hypothesis that TLS in metals are strongly influenced by coupling to the conduction electrons. Only our ability to take this coupling into account permits a meaningful comparison of TLS in metals with those in insulators.

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## Theory of Structural Phase Transitions in Poly(Vinylidene Fluoride)

N. C. Banik, F. P. Boyle,[a] T. J. Sluckin,[b] and P. L. Taylor
*Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106*

and

S. K. Tripathy and A. J. Hopfinger
*Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106*

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The statistical mechanics of the polymer poly(vinylidene fluoride) are studied by means of a formalism in which interchain and intrachain forces derived from conformational analysis are combined in a transfer-integral approach through a mean-field approximation. The theory is successful in yielding several observed phases of this material and in predicting the effect of uniaxial stress on the most stable phase.

This paper reports the results of a calculation of the statistical mechanics of a crystalline polymer by means of a technique in which interchain interactions are approximated in a mean-field formalism. Good qualitative agreement is found when the several crystalline phases and one melt phase of poly(vinylidene fluoride) that emerge from this calculation are compared with the experimental observations. We believe this to be the first reported work in which such a rich variety of stable and metastable phases of a polymer has resulted from a calculation in which there are no adjustable parameters, and of which the starting point is the calculation of potential energy by means of conformational analysis.

Poly(vinylidene fluoride), also known as $PVF_2$, has the molecular structure shown in Fig. 1. In our model of this polymer all carbon-carbon bond lengths and included angles are assumed to be "hard" variables and remain constant. Only

 