Superconductivity and the Very Strong Electron-Phonon Interaction in Amorphous Bi and Bi-Pb Alloys

Superconductivity and the Very Strong Electron-Phonon Interaction in Amorphous Bi and Bi-Pb Alloys*

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Synopsis

The temperature dependence of the electrical resistance $R(T)$ and the upper critical field $H_{c2}(T)$ have been measured in quench-condensed amorphous Bi and Bi-Pb alloys.

The value of the electron-phonon interaction parameter λ was estimated based on the nearly free electron model and the strong coupling theory of superconductivity and turned out to be very large ($\lambda \cong 1$–3) in the amorphous state.

The fact that the estimated λ-value is in good agreement with that estimated from tunnel effect measurements by Chen *et al.* and Knorr and Barth, verified that the nearly free electron model is fairly applicable to the amorphous phase.

After an analysis based on the nearly free electron model and the BCS theory, some other physically important parameters, such as the mean free path l, the Fermi velocity v_F, the coherence length ξ_0, the London penetration depth $\lambda_L(0)$, and the GL parameter κ, were also estimated.

I. Introduction

Currently, many properties of the amorphous state are being intensively studied in a variety of research areas such as, for example, microscopic structure, metallurgy, electronic and magnetic properties, semiconducting and mechanical properties etc.[1]. The amorphous state is also very interesting in the field of superconductivity since very strong phonon softening[2] and extremely short mean free paths[3] of electrons are realized in this state; especially since the discovery of amorphous superconductors[4], which remain amorphous even at room temperature.

It is, therefore, very important to study the typical amorphous superconductors in detail and to clarify the fundamental properties in the amorphous and superconducting states. There are few studies of fundamental properties of superconductor such as, magenetization, three kinds of critical fields; H_{c1}, H_c, and H_{c2}, critical current I_c, specific heat C_v, etc. in the amorphous state. Especially,

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(1) See for instance, Amorphous Material Issue I, Sci. Rep. RITU, **A26** (1976), No. 1 and Amorphous Material Issue II, Sci. Rep. RITU, **A26** (1977) No. 4/5.

(2) T.T. Chen, J.D. Leslie and H.J.T. Smith, Physica, **55** (1971), 439.

(3) S. Fujime, Japan. J. Appl. Phys., **5** (1966), 768 and 778.

(4) W.L. Johnson and S.J. Poon, J. Appl. Phys., **46** (1975), 1787.

there are almost no studies of H_{c2} in an amorphous and superconducting alloy system to date.

From this point of view, we prepared amorphous samples of pure Bi which shows superconductivity only in the amorphous state, and three Bi-Pb alloys, by a quench-condensation method, and studied the temperature dependence of the electrical resistance $R(T)$ between 2 and $\sim$120 K as well as the upper critical field $H_{c2}(T)$ between 1.5 and 4.2 K. The experimental procedure is described in Chapter II, the results are presented in Chapter III, and discussions are given in Chapter IV.

II. Experimental procedure

1. Cryostat and evaporation procedure

The cryostat employed in this work is schematically shown in Fig. 1. This cryostat consists of two spaces for liquid He. The inner Dewar serves also as a holder of the superconducting magnet, which hangs in the liquid He in the outer Dewar. The superconducting magnet formed of 10 mil Nb-Ti single cored wire was made by Vacuum Metallurgical Company and has a maximum field of 60 kG with a homogeneity of 10^{-4}/25 mmDSV. The magnet was energized by a constant current power supply with an electronic sweep generator with a stability of 10^{-4}/30 min.

The sample material was set in a heater, shaped like a conical basket, wound of a 0.1 ϕ tungsten wire. This material was evaporated onto a sapphire substrate ($0.5\times12\times12$ mm^3). By filling both inner and outer Dewars with liquid He, the substrate was cooled via the good thermal conduction of Apiezon N grease and a copper block. By this quench-condensation, all our samples became amorphous. The liquid He in the inner Dewar was pumped out and the copper block was cooled down to about 2.5 K during the sample evaporation. After the quench-condensation of a sample, the temperature dependence of H_{c2} was first measured between 4.2 and 1.5 K, and then the liquid He in the inner Dewar was evaporated out by a 0.1 ϕ–60 Ω manganin heater wound in the copper block. The temperature dependence of the resistance up to $\sim$120 K was then measured by use of the same heater. The resistance was measured always with increasing temperature.

The temperature of the substrate surface during the evaporation was checked, as explained below, by monitoring the resistance of a Pb film which had been evaporated on another part of the substrate at room temperature. When the temperature of the liquid He in the inner Dewar and hence the Cu-block was maintained at 4.2 K, the Pb film showed a superconducting to normal transition during the Bi evaporation. But the Bi film thus evaporated did show superconductivity below 6 K, indicating that it was in the amorphous state. This means the temperature of the substrate surface was between 7.2 and $\sim$10 K since

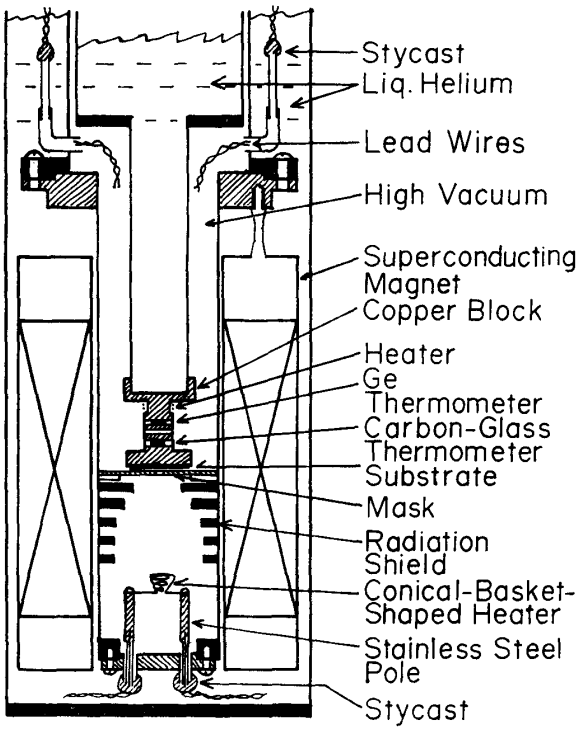

Fig. 1. Schematic illustration of the cryostat.

the crystallizing temperature of the amorphous Bi is about 10–15 K[5]. When the liquid He of the inner Dewar was pumped out and the temperature of the Cu-block was maintained at about 2.5 K, the Pb film showed a very small resistance transition from the superconducting to the normal state. This means that the surface temperature was just around 7.2 K, that is, the transition temperature of pure Pb during the evaporation. The vacuum space of the evaporation was pumped out during evaporation to better than 1.2×10^{-6} Torr, which was measured at a room temperature portion of the pumping line system. The vacuum of the evaporation space which was surrounded by liquid He was, therefore, believed to be better than 10^{-8} Torr.

2. Sample preparation

The purity of used metals were 99.9999% for both Bi and Pb. The alloy materials were made by melting the weighed Bi and Pb in high vacuum. Bi metal or Bi-Pb alloy metal thus prepared was set in the conical-basket-shaped tungsten heater. The metal was first tinned onto the heater by flowing the heater current only a short time in high vacuum. The heater with the metal tinned on it was then installed in the cryostat. According to the results by Kopf[6], there is no concentration shift with evaporation in this alloy system. This is to be

(5) W. Buckel, Z. Phys., **138** (1954), 136.
(6) L. Kopf, Rev. Sci. Instrum., **38** (1967), 734.

expected since the vapor pressures of both metals are almost the same.

The thickness of the sample was measured by an optical interferometer using Hg–2730 Å light. It was also estimated from the weight of the evaporated material. The estimated thickness from the weight agreed with the measured thickness within ±15%. Due to a problem at the time of terminal contact, we could not measure the thickness of pure Bi film by the interferometer. The estimated thickness was, therefore, used for the pure Bi film.

The thickness and some other important parameters of the prepared samples are given in Table 1.

Table 1. Important parameters of the studied samples.

	Pure Bi	$Bi_{75}Pb_{25}$	$Bi_{50}Pb_{50}$	$Bi_{30}Pb_{70}$
d (Å)	410±60	970±80	570±20	810±40
ρ_{res} ($\mu\Omega$cm)	86.6±13.0	67.7±5.6	66.5±2.3	62.8±3.1
T_c (K)	6.12	6.81	6.91	6.95
T_{cryst} (K)	12	32	~120	35
T_{anneal} (K)	16	41	~120	43
T_c' (K)	5.93	6.30	7.72	6.58
$\left.\frac{dH_{c2}}{dT}\right\|_{T_c}$ (kG/K)	~6.45	9.41±0.04	9.19±0.02	8.13±0.07

3. Thermometer and measuring technique

Electrical resistance was measured by a standard dc 4-terminal method. H_{c2} was determined as the magnetic field value where the electrical resistance first appears. The magnetic field was applied perpendicular to the sample film. T_c was determined from the middle point of the resistive transition with temperature.

The temperature of the sample was measured by use of Ge and carbon-glass thermometers from Lake Shore Company, which were set in the Cu-block with Apiezon N grease. Calibrations of the thermometers[7,8] against liquid He vapor pressure and a Pt resistance thermometer calibrated at NBS between 10 and 92 K were made by us.

III. Experimental results

1. Temperature dependence of the electrical resistance

Figs. 2–5 show the results of electrical resistance measurements in amorphous pure Bi and Bi-Pb alloys, respectively. In Fig. 2, pure Bi shows superconductivity up to 6.12 K, where it becomes normal with resistance of 47.5 Ω. The resistance jumps very sharply to about 600 Ω at about $T_{cryst}\cong 12$ K. This

(7) K. Noto, RIISOM Technical Reports, No. **5** (1974), 1 (in Japanese).

(8) Y. Muto, N. Toyota, K. Noto, K. Akutsu, M. Isino and T. Fukase, J. Low Temp. Phys., **34** (1979), 617.

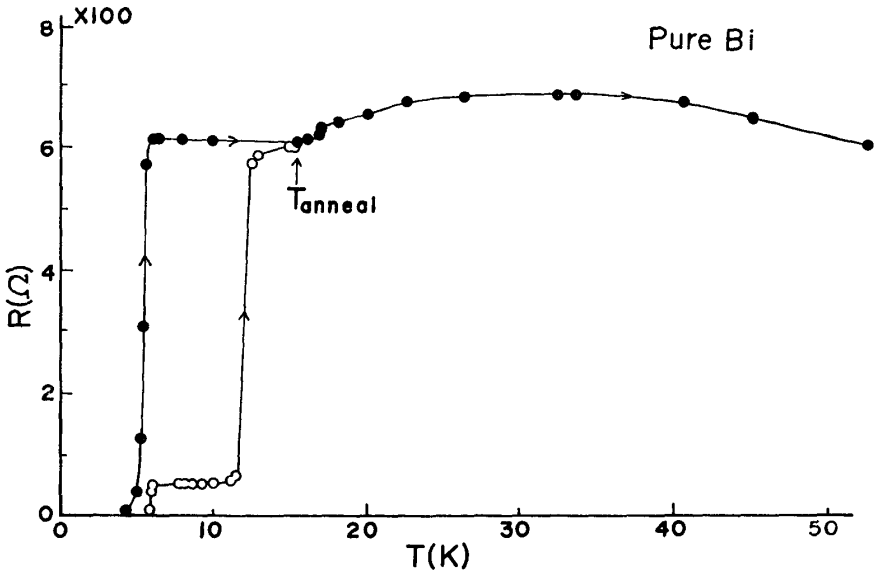

Fig. 2. Temperature dependence of the electrical resistance with increasing temperature in the amorphous pure Bi film. ○: first run, ●: second run after an anneal at $T=T_{anneal}$

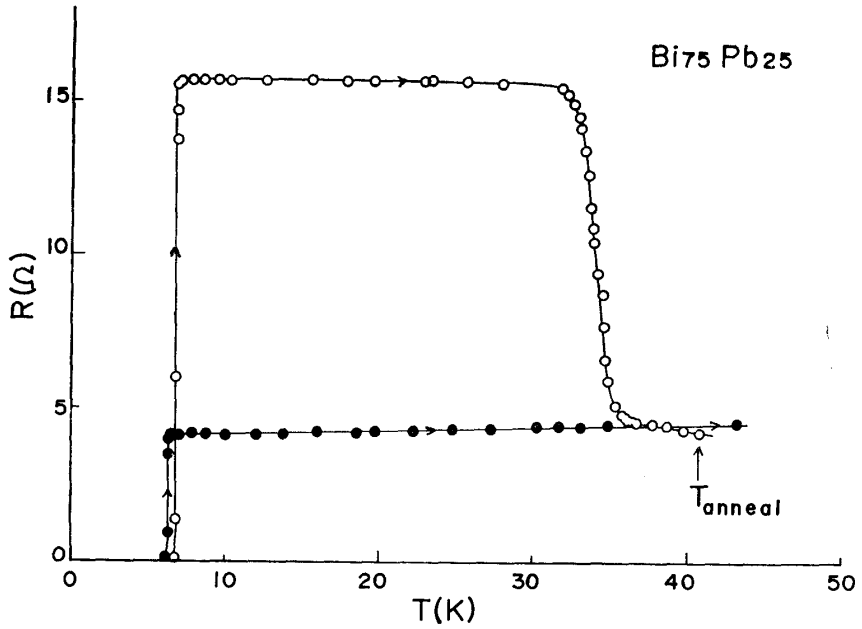

Fig. 3. Temperature dependence of the electrical resistance with increasing temperature in the amorphous $Bi_{75}Pb_{25}$ alloy film. ○; first run, ●; second run after an anneal at $T=T_{anneal}$.

behavior is irreversible and is thought to be a result of crystallization from the amorphous to the disordered state[5]. The crystallization in the disordered state goes slowly, thereafter showing a gradual increase in electrical resistance. This disordered state was verified by the fact that it did still show superconductivity with a little lower T_c' of 5.93 K, and much broader superconducting to normal

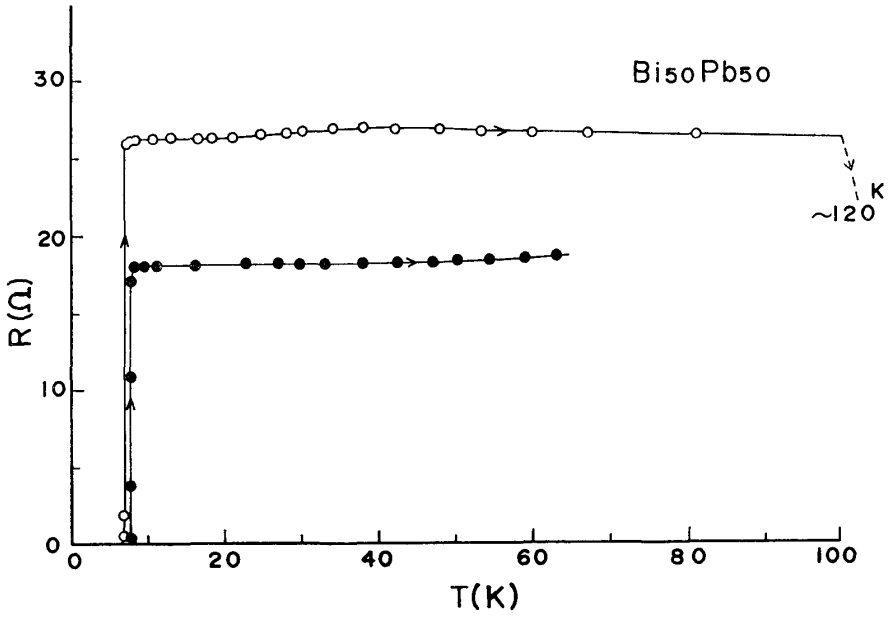

Fig. 4. Temperature dependence of the electrical resistance with increasing temperature in the amorphous $Bi_{50}Pb_{50}$ alloy film. ○; first run, ●; second run after an anneal at $T=T_{anneal}$.

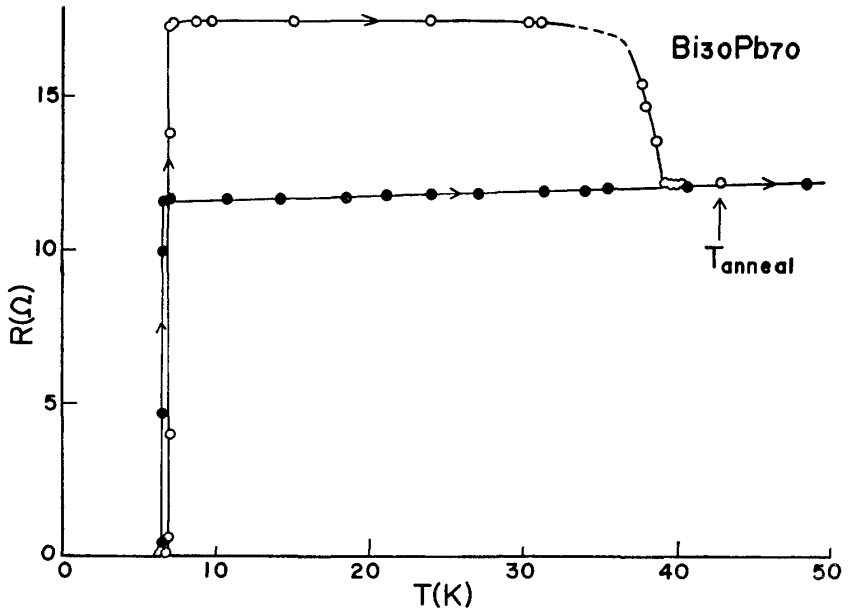

Fig. 5. Temperature dependence of the electrical resistance with increasing temperature in the amorphous $Bi_{30}Pb_{70}$ alloy film. ○; first run, ●; second run after an anneal at $T=T_{anneal}$.

transition when the sample was cooled down again from about 16 K to the liquid He temperature. We denote this temperature as T_{anneal}. The behavior of the electrical resistance after the sample was cooled down from T_{anneal} was also studied with increasing temperature. In the figure, open circles show the first run and

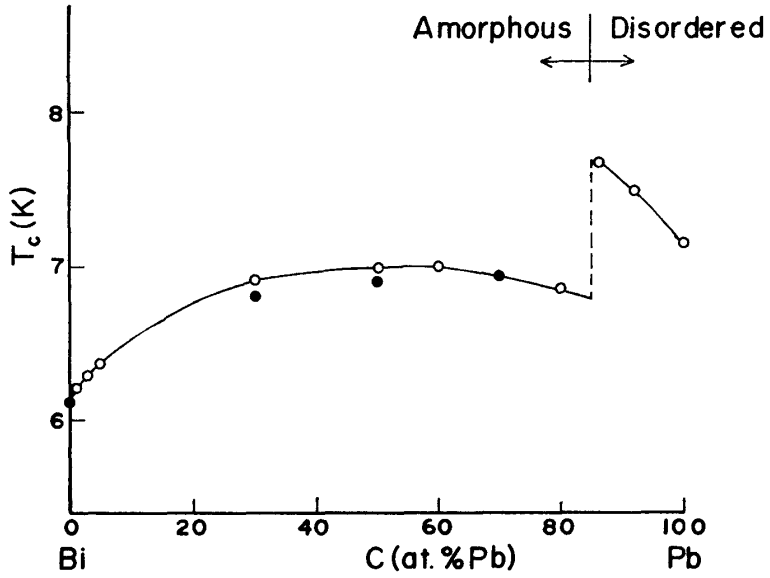

Fig. 6. Concentration dependence of T_c in amorphous Bi-Pb alloy system. ●; ours, ○; Hasse and Seiberth[10].

solid ones the second run of the resistance measurements. This behavior of the electrical resistance is very similar to the results of Buckel and Hilsch[9].

In the amorphous alloy samples in Figs. 3–5, T_c and the crystallization temperature T_{cryst} are higher than those in pure Bi and the resistance jumps to the smaller value at T_{cryst} and decreases further with the gradual crystallization in the disordered state. The reason for this is that the crystalline Bi is semimetallic or semiconducting, while alloys are always metallic in the crystalline phase. The resistance jumps to the smaller value because the mean free path of electrons becomes very large with the crystallization of the alloy samples. The results of measurements of T_c, T_{cryst}, residual resistivity in the amorphous state ρ_{res}, T_{anneal} and the transition temperature in the disordered state T_c' are given in Table 1.

2. Concentration dependence of T_c

In Fig. 6, the measured T_c is plotted against the Pb concentration. The results by Hasse and Seiberth[10] are also shown for comparison. These authors showed that the alloy containing more than 85 at.% Pb becomes not amorphous but only disordered after a quench-condensation. We limited ourselves to the concentration region where the film becomes amorphous after a quench-condensation. As can be seen in the figure, our data agree fairly well with theirs. Therefore, in conjunction with the fact that the resistance shows a very sharp transition at T_{cryst}, we believe that our samples are in a good amorphous state.

(9) W. Buckel and R. Hilsch, Z. Phys., **138** (1954), 109.
(10) J. Hasse and J. Seiberth, Z. Phys., **213** (1968), 79.

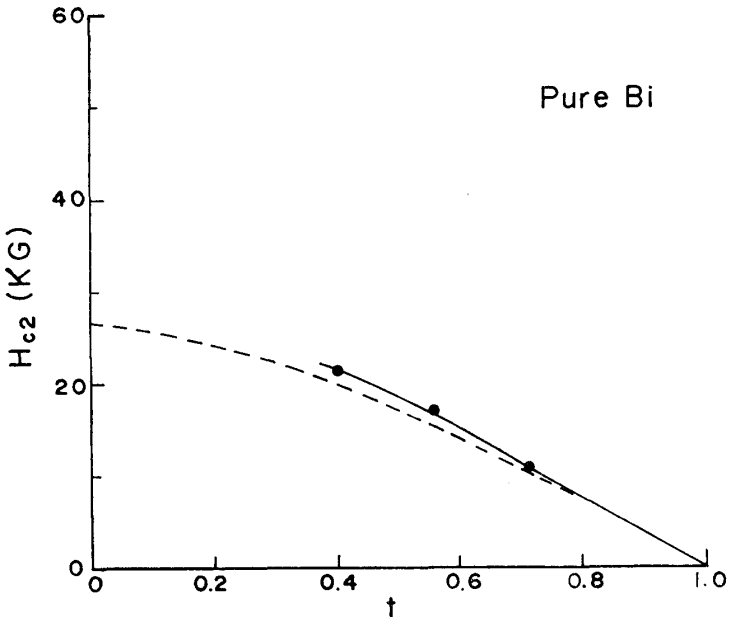

Fig. 7. Dependence of H_{c2} on the reduced temperature in the amorphous pure Bi film.

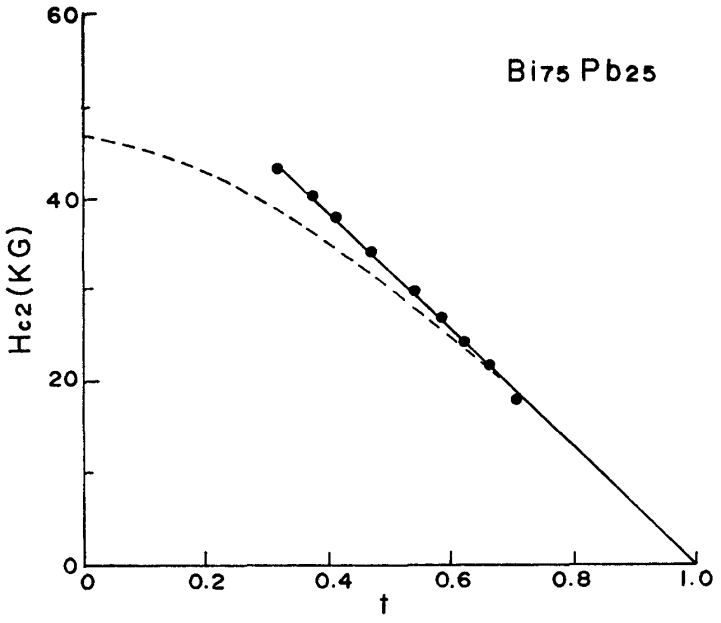

Fig. 8. Dependence of H_{c2} on the reduced temperature in the amorphous $Bi_{75}Pb_{25}$ alloy film.

3. Temperature dependence of H_{c2}

Figs. 7–10 show the results of our measurements of the upper critical field H_{c2} in amorphous pure Bi and Bi-Pb alloys, respectively. H_{c2} of all samples are plotted against the reduced temperature $t=T/T_c$ in Fig. 11. It is noted that in the alloy samples, H_{c2} changes almost linearly with temperature except in the case of pure Bi. In the alloy samples, the slope $dH_{c2}/dT|_{T_c}$ was obtained by a least squares method

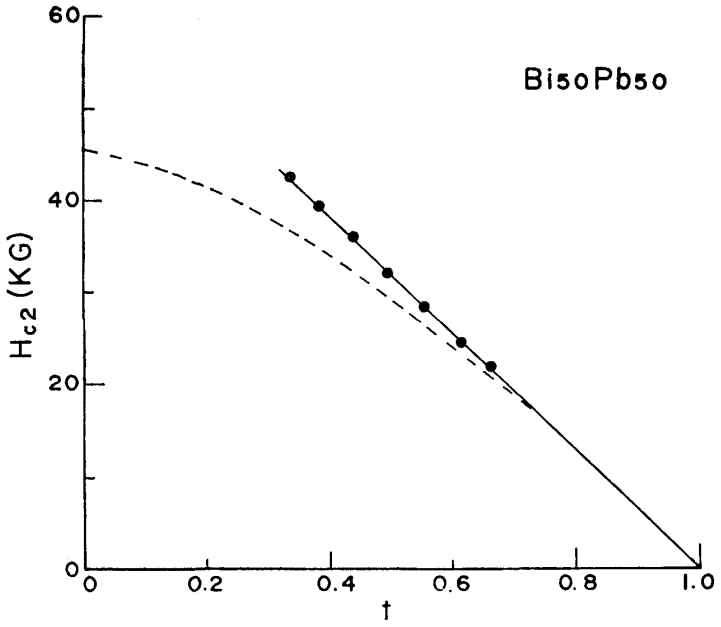

Fig. 9. Dependence of H_{c2} on the reduced temperature in the amorphous $Bi_{50}Pb_{50}$ alloy film.

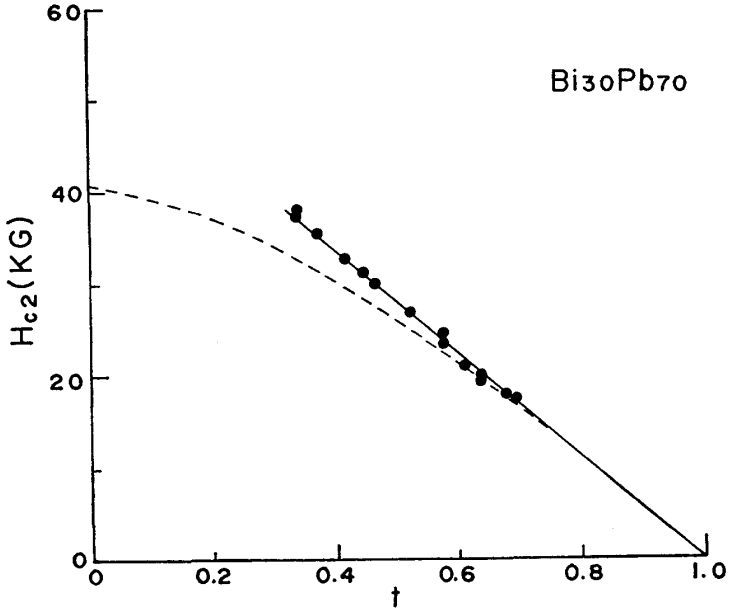

Fig. 10. Dependence of H_{c2} on the reduced temperature in the amorphous $Bi_{30}Pb_{70}$ alloy film.

using the measured values of $H_{c2}(T)$ and T_c which had been obtained by the resistance measurements. In the case of pure Bi, $dH_{c2}/dT|_{T_c}$ was estimated from a reasonable curve through the $H_{c2}(T)$ values and T_c obtained from resistance measurements. The slopes thus obtained are also listed in Table 1.

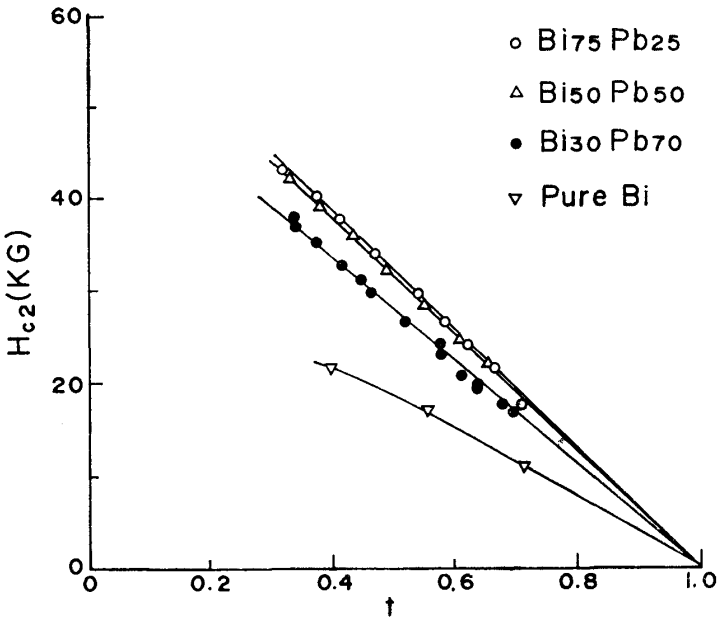

Fig. 11. Dependence of H_{c2} on the reduced temperature in the amorphous Bi-Pb alloy system.

IV. Discussions

We applied the magnetic field perpendicular to the film. For the geometry of a thin film, the flux density B is equal to the external applied field H_e because of the high demagnetization effect ($n=\sim 1$ in CGS-Gauss units). We denote the upper critical field by H_{c2} in Gauss.

Tinkham[11] and de Gennes[12] discussed the angle and thickness dependence of the upper critical field for a film much thinner than the coherence length ($\xi(T) \gg d$). In the case of our amorphous superconductors, where the mean free path ($l \cong 5$–8 Å and, therefore, $\xi(0) \cong 70$–90 Å) is much smaller than the film thickness ($d \cong 500$–900 Å), the upper critical field is certainly a bulk property.

1. Phonon dressing and very strong electron-phonon coupling

Maki[13] and de Gennes[14] derived an expression for $H_{c2}{}^{BCS}$ in the dirty limit which is valid for all temperature regions;

$$ln\left(\frac{1}{t}\right) = \psi\left(\frac{1}{2} + \frac{eDH_{c2}{}^{BCS}}{2\pi c k_B T_c t}\right) - \psi\left(\frac{1}{2}\right), \tag{1}$$

where $\psi(x)$, D and k_B are the digamma function, the diffusion constant and the

(11) M. Tinkham, *Superconductivity*, New York, Gordon and Breach (1965), 75.
(12) P.G. de Gennes, *Superconductivity of Metals and Alloys*, New York, Benjamin (1966), 189.
(13) K. Maki, Physica, **1** (1964), 21.
(14) P.G. de Gennes, Phys. kond. Mat., **3** (1964), 79.

Boltzmann constant, respectively. Equation (1) is expressed asymptotically near T_c and absolute zero as follows,

$$H_{c2}^{BCS}(t) = \frac{4k_BT_c}{\pi e}\left(\frac{c}{D}\right)(1-t)\left[1-\left(\frac{1}{2}-\frac{28}{\pi^4}\zeta(3)\right)(1-t)\right] \quad \text{for } t\to 1 \quad (2)$$

$$H_{c2}^{BCS}(t) = 0.87\left(\frac{c}{D}\right)\frac{k_BT_c}{e}\left[1-\frac{2}{3}\left(\frac{\pi t}{1.75}\right)^2\right] \quad \text{for } t\to 0. \quad (3)$$

One obtains, therefore, at both limits,

$$-\frac{H_{c2}^{BCS}(0)}{T_c\left.\frac{dH_{c2}^{BCS}}{dT}\right|_{T_c}} = 0.69 \quad \text{for } t=0 \quad (4)$$

$$-\left.\frac{dH_{c2}^{BCS}}{dT}\right|_{T_c}\frac{eD}{k_B} = 1.27 \quad \text{for } t=1\,. \quad (5)$$

Following the strong-coupling theory[15], one must make a correction for phonon dressing due to the existence of relatively strong electron-phonon interaction, such as,

$$D^* = \frac{D}{1+\lambda}\,, \quad v_F^* = \frac{v_F}{1+\lambda}\,, \quad N^*(0) = (1+\lambda)\,N_b(0)\,, \quad (6)$$

$$\lambda = \int_0^\infty \frac{2\alpha^2(\omega)\,F(\omega)}{\omega}\,d\omega\,, \quad (7)$$

where v_F, $N_b(0)$, λ and $\alpha^2(\omega)F(\omega)$ are the Fermi velocity, the electronic density of states, the electron-phonon coupling parameter and the phonons spectral function, respectively.

Rainer *et al.*[16,17,18] introduced a temperature dependent enhancement parameter, $\eta_{H_{c2}}(T)$, in connection with the temperature dependence of $(1+\lambda)$, that is,

$$H_{c2}(T) = \eta_{H_{c2}}(T)\,H_{c2}^{el-ph}(T) = \eta_{H_{c2}}(T)(1+\lambda)\,H_{c2}^{BCS}(T)\,. \quad (8)$$

Equations (4) and (5) must be, therefore, rewritten as follows,

$$-\frac{H_{c2}(0)}{T_c\left.\frac{dH_{c2}}{dT}\right|_{T_c}} = 0.69\,\frac{\eta_{H_{c2}}(0)}{\eta_{H_{c2}}(T_c)}\,, \quad \text{for } t=0\,, \quad (9)$$

(15) W.L. McMillan, Phys. Rev., **167** (1968), 331 and D.J. Scalapino *et al.*, Phys. Rev. Lett., **14** (1965) 102 and 106.
(16) D. Rainer and G. Bergmann, J. Low Temp. Phys., **14** (1974), 501.
(17) D. Rainer, G. Bergmann and U. Eckhardt, Phys. Rev. B, **8** (1973), 5324.
(18) G. Bergmann, Phys. Rep., **27** (1976), 159.

and

$$-\frac{dH_{c2}}{dT}\Big|_{T_c}\frac{eD^*}{k_B}=1.27\eta_{H_{c2}}(T_c)\,,\qquad \text{for}\quad t=1\,. \tag{10}$$

As already shown by Bergmann,[18] the slope $dH_{c2}/dT|_{T_c}$ is given as a function of ρ_{res} and λ in terms of $\eta_{H_{c2}}(T_c)$;

$$-\frac{dH_{c2}}{dT}\Big|_{T_c}=\eta_{H_{c2}}(T_c)N^*(0)\,\frac{4k_Be}{\pi}\,\rho_{res}\,, \tag{11}$$

since ρ_{res} is expected to be as follows from consideration of the nearly free electron model:

$$\rho_{res}^{-1}=e^2N^*(0)\,D^*\,. \tag{12}$$

Rainer and Bergmann[16] showed that $\eta_{H_{c2}}(T_c)$ is almost equal to 1 in amorphous superconductors. Taking $\eta_{H_{c2}}(T_c)=1$, we can calculate $N^*(0)$ from Eq. (11) in terms of measured $dH_{c2}/dT|_{T_c}$ and ρ_{res}. On the other hand, the bare density of states $N_b(0)$ is given as follows,

$$N_b(0)=\frac{m}{(\pi^2\hbar^2)}\,(3\pi^2n)^{1/3}\,, \tag{13}$$

based on the nearly free electron model, which is most likely appropriate in the case of amorphous materials, where there is no crystal structure. m and n are the electron mass and the density of electrons per unit volume, respectively. One can now estimate the enhancement parameter $(1+\lambda)N^*(0)/N_b(0)$ and hence λ. The estimated values of $N_b(0)$, $N^*(0)$ and $(1+\lambda)$ are listed in Table 2. The enhancement factor $(1+\lambda)$ estimated from tunneling experiments by Chen *et al*[2]. and Knorr and Barth[19] are also shown in the table for comparison.

There are errors due to inaccuracy in $dH_{c2}/dT|_{T_c}$ and ρ_{res} in our estimate of $(1+\lambda)$ above. Error in the slope $dH_{c2}/dT|_{T_c}$ is at most 0.85%, and that in ρ_{res} is estimated to be at most 8.2%, arising mainly from inaccuracy in the film thickness.

Table 2. Density of states and enhancement parameters in amorphous Bi, Bi-Pb alloy system.

	Pure Bi	$Bi_{75}Pb_{25}$	$Bi_{50}Pb_{50}$	$Bi_{30}Pb_{70}$
$N_b(0)$ (10^{34}erg^{-1}cm^{-3})	1.335	1.395	1.324	1.317
$N^*(0)$ (10^{34}erg^{-1}cm^{-3})	2.64	5.18	4.91	4.60
$1+\lambda(0)$	1.98±0.30	3.71±0.32	3.71±0.14	3.49±0.20
$1+\lambda(0)$ (tunneling)	3.46[a] 2.85[c]	3.78[a]	4.00[a]	3.76[b]

(a) obtained by Chen *et al.*[2] (b) obtained by Chen *et al.*[2] for $Bi_{25}Pb_{75}$
(c) obtained by Knorr and Barth[19]

(19) K. Knorr and N. Barth, J. Low Temp. Phys., **4** (1971), 469.

In the case of pure Bi, the maximum error of ρ_{res} is $\pm 15\%$ as the thickness was estimated only from the weight of evaporated material. The total errors thus estimated are shown in the table.

Additionally, the numerical integration of the electron-phonon interaction parameter: Eq. (7) introduces error since it is necessary to require a low and high frequency cut off. The error due to this cut off is thought to be fairly large for amorphous metals since there is a very large enhancement of low frequency phonons in them. Other workers[2,19] have estimated λ and its associated errors to be in the range ± 0.2 to ± 0.5.

As can be seen in Table 2, the estimated values of $(1+\lambda)$ are in good agreement with those obtained from tunneling experiments except for pure Bi.

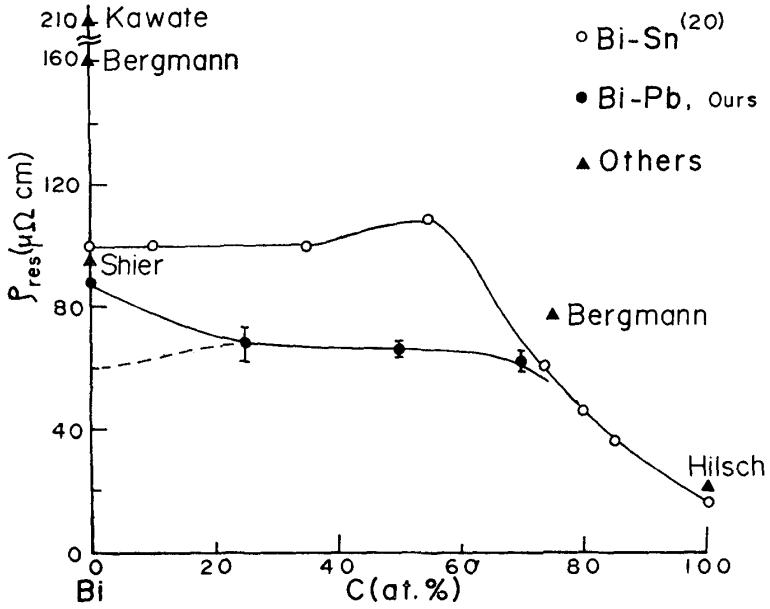

Fig. 12. Concentration dependence of the residual resistivity ρ_{res} in amorphous Bi-Pb and Bi-Sn alloy systems.

The concentration dependence of ρ_{res} is shown in Fig. 12. The results on Bi-Sn alloys by Buckel and Hilsch[20] are also shown together with some other results[21,22,23] for comparison. One notices large divergence in the resistivity value of pure Bi. This is because amorphous Bi is very unstable and its resistivity depends delicately on the evaporation conditions. Some researchers have added low concentrations of impurity to stabilize the amorphous phase in order to study that state of pure Bi. Though our resistivity data for pure Bi is smaller in value than that of Bergmann and Hilsch[20], Shier and Ginsberg[22] and Kawate[23],

(20) W. Buckel and R. Hilsch, Z. Phys., **146** (1956), 27.
(21) G. Bergmann. Phys. Rev. B, **7** (1973), 4850.
(22) J.S. Shier and D.M. Ginsberg, Phys. Rev., **147** (1966), 384.
(23) Y. Kawate, Dr. Thesis (private communication)

there is the possibility that our value is still larger than the proper resistivity of amorphous Bi.

Comparing our data with that of Bergmann[21], we note that he obtained rather larger values of $\rho_{res}=78$, 160 $\mu\Omega$cm for $Bi_{25}Pb_{75}$,$Bi_{85}Tl_{15}$, respectively, than we obtained for our samples. He estimated $(1+\lambda)=3.3$ for $Bi_{25}Pb_{75}$ and found fairly good agreement with that calculated from tunneling data in terms of Eq. (7). He found, however, a much smaller value of $(1+\lambda)=1.85$ for $Bi_{85}Tl_{15}$ than the $(1+\lambda)=3.3$ which is calculated in terms of tunneling data[2] for pure Bi. He attributed this discrepancy either to the experimental problems associated with the tunneling data of amorphous Bi or to the possibility that Bi does not obey the nearly free electron model.

We made, therefore, an extra experiment on $Bi_{90}Tl_{10}$, and obtained a much smaller value of resistivity, that is, $\rho_{res}=98\,\mu\Omega$cm. From the rough estimate made by use of the slope $-dH_{c2}/dT|_{T_c}$ obtained by him, $(1+\lambda)$ turned out to be 3.02 in fairly good agreement with that for pure Bi from the tunneling experiments. We consider, therefore, that the discrepancy reported by Bergmann for $Bi_{85}Tl_{15}$ to be the result of a large resistivity value due to some experimental problem.

Considering again pure Bi, Kawate[23] obtained a very high value of $\rho_{res}=$ 210 $\mu\Omega$cm, but not so large a value of $-dH_{c2}/dT|_{T_c}=7.6$ kG/K as our slope (6.45 kG/K). This fact means perhaps that the slope is not affected so much as the resistivity by the sample preparation procedures. Therefore, we can now estimate in another way the proper resistivity of pure Bi in terms of our slope, $-dH_{c2}/dT|_{T_c}=$ 6.45 kG/K and $(1+\lambda)=3.3$ from the tunneling experiments. The estimated value is $\rho_{res}=60\,\mu\Omega$cm. The total curve extrapolated to this value for the Bi-Pb alloy system in Fig. 12 is qualitatively very much like that for the Bi-Sn alloy system of Buckel and Hilsch[20].

From the discussions given above, the enhancement factor $(1+\lambda)$ obtained from the ratio $N^*(0)/N_b(0)$, where $N^*(0)$ was estimated from our experimental slope $dH_{c2}/dT|_{T_c}$ and $N_b(0)$ expected from the nearly free electron model, is very large, ranging 3.5–3.7, and agrees well with that calculated from the results of tunneling experiments in the case of amorphous Bi-Pb alloys. For pure Bi, there was a large divergence in the resistivity value, which was considered to originate from the instability of amorphous pure Bi. We estimated a most plausible value of ρ_{res} by use of the experimental slope $dH_{c2}/dT|_{T_c}$ for pure Bi. We conclude, therefore, that the bare density of states in the amorphous Bi-Pb alloy system obeys the nearly free electron model and there is a very large phonon dressing of electrons.

2. Temperature dependence of H_{c2} and its deviation from the theoretical curve

As already mentioned in Section IV.1., Maki[13], Helfand and Werthamer,[24]

(24) E. Helfand and N.R. Werthamer, Phys. Rev., **147** (1966), 288.

and Caroli, Cyrot and de Gennes[25] derived the expression for the upper critical field in weak-coupling superconductors with short mean free path as Eq. (1). The broken lines in Figs. 7–10 are calculated according to Eq. (1). The initial slopes at T_c are fitted to the experimental ones. Eq. (1) neglects the spin of the electrons and the spin-orbit coupling. These contributions were examined by Maki[26] and Werthamer, Helfand and Hohenberg[27]. They showed that the initial slope at T_c is not changed with the introduction of the electron spin and spin-orbit coupling. However, the values of H_{c2} at low temperatures are reduced. Eilenberger[28] calculated the upper critical field for the existence of anisotropic impurity scattering and showed that for superconductors with $\kappa>10$ the H_{c2} values for s-scattering and forward scattering differ only by a few percent. The H_{c2} values for forward scattering lie always below those for s-scattering. Rainer *et al.*[16,17,18] have shown that the ratio $\eta_{H_{c2}}(0)/\eta_{H_{c2}}(T_c)$ in Eq. (9) becomes smaller than unity in the usual strong-coupling superconductors, such as, Pb and Hg. They explained that this is because the phonon peak (TA and LA phonon) in these metals lies at relatively high frequency. The borken lines in the figures give, therefore, an upper limit for the theoretical H_{c2} values.

On the other hand, Rainer *et al.*[16,17,18] also showed that one can expect an appreciable enhancement of H_{c2} at low temperature and very large λ value in amorphous materials due to the enhancement of the low energy phonons, which is characteristic of amorphous superconductors.

As can be seen in Figs. 7–10, all experimental values exceed the theoretical limit of H_{c2} at low temperatures. Especially, the measured H_{c2} is almost linear against the temperature in all alloy samples showing a very large enhancement with decreasing temperature. It is considered that the strong electron-phonon coupling due to a very high enhancement of low frequency phonons in amorphous superconductors causes these large H_{c2} values at low temperatures.

3. Estimation of physically important parameters

Using the following equations based on the nearly free electron model,

$$l=\frac{m\cdot v_F}{ne^2\rho_{res}}, \tag{14}$$

$$v_F=\frac{\hbar}{m}(3\pi^2 n)^{1/3}, \tag{15}$$

the mean free path l and Fermi velocity v_F were estimated. One must notice that these values are those for bare electrons.

(25) C. Caroli, M. Cyrot and P.G. de Gennes, Solid State Commun., **4** (1966), 17.
(26) K. Maki, Phys. Rev., **148** (1966), 362.
(27) N.R. Werthamer, E. Helfand and P.C. Hohenberg, Phys. Rev., **147** (1966), 295.
(28) G. Eilenberger, Phys. Rev., **153** (1967), 584.

The BCS coherence length ξ_0, London penetration depth $\lambda_L(0)$, mean free path l_{GL}, coherence length $\xi(0)$ and penetration depth $\lambda(0)$ based on the GL theory and the GL parameter κ were then estimated by use of the following equations based on the BCS theory and the GL theory for the dirty limit,

$$\xi_0 = \frac{\hbar v_F}{\pi \Delta(0)} \tag{16}$$

$$\lambda_L(0) = \left(\frac{mc^2}{4\pi ne^2}\right)^{1/2} \tag{17}$$

$$l_{GL} = \frac{1}{\xi_0}\left(\frac{\xi(0)}{0.85}\right)^2 \tag{18}$$

$$\xi(0) = \sqrt{\frac{\phi_0}{2\pi T_c}\left(-\frac{dH_{c2}}{dT}\right)^{-1}} \tag{19}$$

$$\lambda(0) = 0.615\,\lambda_L(0)\left(\frac{\xi_0}{l}\right)^{1/2} \tag{20}$$

and

$$\kappa = \frac{\lambda(0)}{\xi(0)} \quad . \tag{21}$$

The estimated values are given in Table 3. A value obtained from tunneling experiments by Chen *et al.*[2] was used for $\Delta(0)$ in Eq. (16). One notices that ξ_0 and $\lambda_L(0)$ are the values for a long mean free path. As the mean free path l is clearly much smaller than ξ_0 in our amorphous samples, $\xi(0)$ becomes also very short and the condition $d \gg \xi(0)$ is fulfilled. As already mentioned above, we can, therefore, say there is no thickness dependence of H_{c2} in our samples. Due to this very short mean free path, the GL parameter κ becomes very large ranging from 28 to 39 as can be seen in Table 3, and our samples are clearly in the dirty limit.

Table 3. Physically important parameters in amorphous Bi, Bi-Pb alloy system.

	Pure Bi	$Bi_{75}Pb_{25}$	$Bi_{50}Pb_{50}$	$Bi_{30}Pb_{70}$
l (Å)	5.41	6.99	7.18	7.68
v_F $\left(10^8 \frac{\text{cm}}{\text{sec}}\right)$	1.86	1.86	1.85	1.84
ξ_0 (Å)	3220	2670	2570	2590
λ_L (0) (Å)	142	142	143	144
l_{GL} (Å)	3.68	2.66	2.79	3.13
ξ (0) (Å)	92.5	71.7	72.0	76.4
λ (0) (Å)	2580	2770	2670	2550
κ	27.9	38.6	37.1	33.4

Summary

1. The temperature dependence of the electrical resistance $R(T)$ and the upper critical field $H_{c2}(T)$ have been measured in quench-condensed amorphous Bi and Bi-Pb alloys. From the behavior of $R(T)$, we observed that the sample showed a very sharp transition from amorphous to disordered state, irreversively at T_{cryst}, and the crystallization progressed gradually above T_{cryst}.

2. After an analysis based on the superconductivity theory with the existence of a strong-coupling effect and the nearly free electron model, phonon-dressed density of states $N^*(0)$ and the electron-phonon interaction parameter λ were determined by use of the experimental slope $dH_{c2}/dT|_{T_c}$ and the residual resistivity ρ_{res}. $N^*(0)$ is clearly much larger than the bare density of states $N_b(0)$. Accordingly, λ is also very large ranging from 1 to 3 which, we believe, originates from a very strong enhancement of the low energy phonon spectrum.

3. From the fact that the λ-value obtained agrees very well with that calculated from the results of tunneling experiments, we can conclude that the bare density of states in the amorphous alloy system obeys the nearly free electron model with the phonons dressed by a factor of $(1+\lambda)$.

4. The upper critical field $H_{c2}(T)$ varies almost linearly with T over the whole measured temperature range for all alloy samples. We could also observe an appreciable deviation from the theory of Maki,[13] de Gennes[14] and Werthamer-Helfand-Hohenberg[27] at low temperatures, even in the case of pure Bi. An appreciable enhancement of low energy TA (transverse acoustic) phonons and the strong-coupling behavior of the amorphous metals must be responsible for these discrepancies.

5. Some other physically important parameters, such as the BCS-coherence length ξ_0, GL-coherence length $\xi(0)$, London penetration depth $\lambda_L(0)$, mean free path l, GL-penetration depth $\lambda(0)$ and GL parameter $\kappa=\lambda(0)/\xi(0)$ were estimated for these amorphous Bi and Bi-Pb alloy systems.

6. The samples studied are reasonably in the dirty limit with the κ-value of 28–39 which is a consequence of the extremely short mean free path in the amorphous state.

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