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‡Present address: Naval Research Laboratory, Washington, D. C. 20390.

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Upper Critical Field and the Density of States in Amorphous Strong-Coupling Superconductors

G. Bergmann

Institut für Festkörperforschung der Kernforschungsanlage Jülich, Jülich, Germany

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The upper critical field of the amorphous superconductors $Bi_{0.85}Tl_{0.15}$, Ga, $Sn_{0.86}Cu_{0.14}$, and $Pb_{0.75}Bi_{0.25}$ is measured in the temperature range from 1.5 °K to the zero-field transition temperature. Films of the amorphous metals about 1500 Å thick are obtained by quenched condensation onto a substrate at He temperature. The initial slopes of the $B_{c2}(T)$ curves are used to determine the electronic density of states at the Fermi surface. For all the investigated materials these values were enhanced compared with the density of states which one obtains from the free electron model. For Ga, $Sn_{0.86}Cu_{0.14}$, and $Pb_{0.75}Bi_{0.25}$ the experimental enhancement factor agrees well with the electron-phonon enhancement factor $1+\lambda$, where λ is taken from superconducting-tunneling experiments. The temperature dependence of B_{c2} deviates from that predicted by Werthamer, Helfand, and Hohenberg, showing B_{c2} values too large in the low-temperature region. It is suggested that the strong-coupling behavior of the amorphous superconductors is responsible for the deviation at low temperature.

I. INTRODUCTION

A number of metals can be obtained in the amorphous state by quenched condensation onto a substrate at He temperature. This was first done by Buckel and Hilsch.[1] The residual resistivity of these amorphous metals is very similar to the resistivity of the corresponding liquid metals. Buckel[2] and Fujime[3,4] examined the amorphous metals by electron diffraction. They found that there is no ordering range longer than a few atomic spacings. Such a short-range ordering is also

TABLE I. Composition, thickness, and residual resistivity of the amorphous films are given in the first three columns. Columns four and five give the initial slope of the $B_{c2}(T)$ curve and the transition temperature of the films before coating with Fe. The last column gives the depression of the transition temperature by the coating with Fe.

Alloy	Thickness (Å)	ρ_N (10^{-6} Ωm)	$\frac{dB_{c2}}{dT}\left(\frac{\text{kG}}{°\text{K}}\right)$	T_{c0} (°K)	ΔT_c (°K)
$Bi_{0.85}Tl_{0.15}$	1260	1.6	11.2	6.23	0.1
Ga	1650	0.285	3.05	8.27	0.12
$Sn_{0.86}Cu_{0.14}$	1620	0.47	4.3	6.62	0.04
$Pb_{0.75}Bi_{0.25}$	2000	0.78	9.6	6.90	0.02

present in the liquid metals.

The amorphous metals show many interesting properties. Particularly the amorphous superconductors such as Bi, Ga, Sn, and Pb have a rather high transition temperature and show a strong-coupling behavior, as measurements of the energy gap by Rothenberg and Minnigerode[5] suggested. A systematic investigation of their properties has been started in recent years.[6-15]

In this paper we study the upper critical field of the amorphous superconductors $Bi_{0.85}Tl_{0.15}$, Ga, $Sn_{0.86}Cu_{0.14}$, and $Pb_{0.75}Bi_{0.25}$. Their electron-phonon–coupling term λ, which describes the strength of the electron-phonon coupling, has been measured in superconducting tunneling experiments[8-11] and is of order 2–3. It is a well-known fact that the phonons increase the bare density of states via electron-phonon interaction. The enhancement factor is $1+\lambda$ and has particularly large values for amorphous superconductors. The amorphous superconductors are an interesting example for studying the influence of the electron-phonon interaction on the density of states. First it is very reasonable to calculate the bare density of states N_b by means of the free-electron model. (The structure of the amorphous metals is similar to the structure of the liquid metals and it is an experimental fact that many properties of the liquid metals obey the free-electron model.) Second, the upper critical field yields a dressed density of states $N_{B_{c2}}$. Therefore we are able to determine the ratio of the dressed and the bare density of states and we want to compare it with the value $1+\lambda$ which has been determined in tunneling experiments and describes the phonon enhancement of the density of states.

Furthermore, we are interested in the temperature dependence of the upper critical field. It is a well-known fact that the strong electron-phonon interaction in crystalline Pb and Hg causes deviations in the temperature dependence of the "thermodynamical critical field" from the BCS theory (weak-coupling theory). We wish to see whether the temperature dependence of the "upper critical field" of amorphous strong-coupling superconductors also shows deviations from the weak-coupling theory.

The amorphous superconductors which we want to investigate are unstable and generally transform into the crystalline phase above 20 °K. They can be prepared by quenched condensation onto a substrate at He temperature. Since the amorphous metals have a mean free path which is of the order of atomic distances[1] [the residual resistivity is of the order of 10^{-6} Ωm (see Table I)] we expect critical fields up to 50 kG. We apply the magnetic field perpendicular to the film. For the geometry of a thin film (about 1500-Å thick) the flux density B is continuous at the surface of the film, because of the high demagnetization factor, and equal to the applied flux density B. Therefore we denote the upper critical field by B_{c2}. In a previous paper[16] we showed that the perpendicular critical field of a film is equal to the upper critical field B_{c2} of the bulk superconductor with the same *effective* mean free path. (In a thin film one distinguishes between the effective mean free path which includes collision with the boundaries and the internal mean free path.) In an amorphous superconductor, where the mean free path is much smaller than the film thickness, the upper critical field is certainly a bulk property.

We determine B_{c2} by measuring the resistivity as a function of the temperature in the applied magnetic field and we make every effort to obtain sharp transition curves. From the transition curves we obtain the transition temperature in the magnetic field and therefore $B_{c2}(T)$.

II. EXPERIMENT

A. Cryostat

We need a cryostat which enables us to condense amorphous superconductors by quenched condensation and to apply magnetic fields up to 50 kG. We use a superconducting magnet, which is located in a "magnet cryostat" (Fig. 1). This cryostat consists essentially of a large He container He1, in which the superconducting solenoid M is kept at He temperature. The He bath is surrounded by superinsulation and liquid N_2 to shield the He from heat radiation. The superconducting solenoid has an inner diameter of 70 mm. Therefore we are able to insert another independent cryostat into the interior of the magnet cryostate. We call the second cryostat the "condensation cryostat." Its construction is very simple. It consists of a He chamber He 2 and a vacuum jacket (VJ). At the lower part of the He chamber a quartz plate (Q) is screwed on, with a definite thermal resistance. The quartz plate has gold electrodes which are connected with electrical leads. The quartz plate is

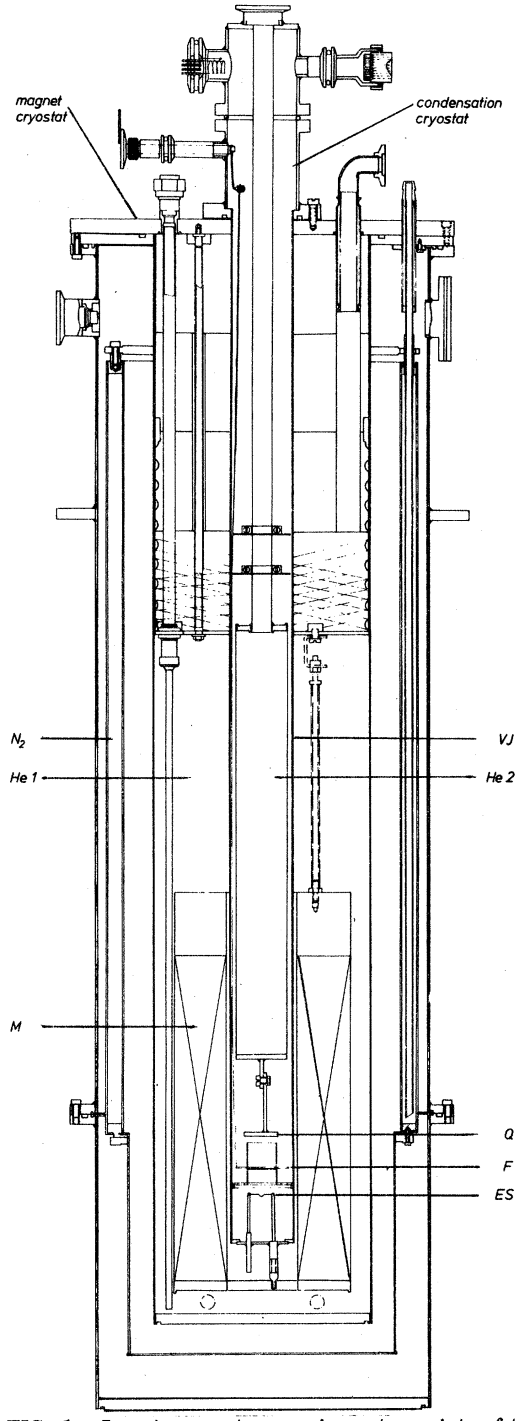

FIG. 1. Low-temperature equipment consists of two independent cryostats, the magnet cryostat and the condensation cryostat. The parts of the magnet cryostat are denoted on the left-hand part. It consists of a He 1 which contains the superconducting magnet M and is surrounded by liquid nitrogen N_2. The condensation cryostat is independent of the magnet and consists of a He container He 2 and a vacuum jacket VJ. At the bottom of the He container a quartz plate Q is screwed on. It faces an evaporation source ES. During the evaporation the flap F is opened.

covered with a mask and serves as the substrate for the amorphous films. It faces the bottom of the cryostat, where the evaporation sources (ES) are located. Since the evaporation sources must be filled with the required metals before each experiment, they are soldered with In into the bottom of the condensation cryostat. We have chosen In as solder for two reasons. First, it has a low melting point, so that the metals in the evaporation sources do not oxidize during the soldering. Second, the transition temperature of the solder must be below He temperature to avoid superconducting inductive currents in the magnetic field. For the same reason we cannot use any solder at the inner He chamber which becomes superconducting above 1.2 °K. Between the evaporation source and the quartz plate a flap (F) is located which can be opened for the evaporation.

B. Measurement

1. Condensation of Amorphous Films

The He chamber of the condensation cryostat is not protected from heat radiation. Therefore the condensation cryostat is inserted into a Dewar with liquid N_2, after reaching high vacuum. The He chamber is filled with liquid He and the substrate is cooled down to He temperature. The evaporation source is heated with alternating current. Here we have the great advantage that all parts of the cryostat which surround the evaporation source are at the temperature of liquid N_2. Therefore the vacuum during the condensation is of the order of 10^{-7} Torr. At first we condense the metal under investigation to a thickness of about 1500 Å. Afterwards we condense on top of the amorphous film a thin layer of Fe (less than monoatomic[17]). The Fe suppresses edge effects[18] of the film.[16] The Fe lowers the transition temperature of the amorphous superconductor by less than 0.1 °K. After the evaporation the condensation cryostat is removed from the N_2 Dewar and placed into the magnet cryostat. During the transfer it is surrounded by superinsulation to protect the cryostat from water condensation and heat radiation. The independence of the magnet cryostat and the condensation cryostat has the advantage that the magnet cryostat can be kept for weeks at low temperature. Between two experiments the condensation cryostat only need be warmed up. This can be done within $\frac{1}{2}$ h, whereas the magnet cryostat requires several days to reach room temperature.

2. Materials Investigated

The pure elements Bi and Ga can be obtained in the amorphous state by quenched condensation. Most of the other nontransition metals have a fine-crystalline structure after quenched condensation.

They can only be stabilized in the amorphous state by the addition of other materials. Therefore we use an alloy of $Sn_{0.86}Cu_{0.14}$, to obtain amorphous Sn. Pb can be brought into an amorphous state by the addition of Cu or Bi. We use an alloy of $Pb_{0.75}Bi_{0.25}$. Since pure amorphous Bi is very unstable we use an alloy of $Bi_{0.85}Tl_{0.15}$. Ga has been investigated in the pure state. The concentrations are given in atomic percent. In all cases the alloys are evaporated from a single source. Kopf[19] has shown that for the system $Pb_{1-x}Bi_x$ the concentration in the film is identical with the concentration in the source. This is not very surprising because Bi and Pb have almost the same vapor pressure. The same is true for the system $Bi_{1-x}Tl_x$. Both metals have a similar vapor pressure as in the system $Pb_{1-x}Bi_x$. For the evaporation of $Sn_{0.86}Bu_{0.14}$ we started with an alloy of $Sn_{0.84}Cu_{0.16}$ and used the transition temperature of the film for a comparison with the results by Fortmann and Buckel.[14] These authors obtained the same T_{c0} for an alloy composition of $Sn_{0.86}Cu_{0.14}$. Therefore we assume that our films have this composition. We estimate that the accuracy of the concentrations is better than 3%.

3. Measurement of Transition Curves

For the measurement of the transition curves we take a film of 10-mm length and 2-mm width. The resistance is measured with four electrodes. The current is of the order of 0.3–1.0 mA. We check that the transition curves do not depend on the current. The perpendicular magnetic field is varied between 0 and 55 kG. The transition curves are plotted on a X-Y recorder. The voltage is applied to the ordinate and the temperature to the abscissa. The temperature is measured by an Allen–Bradley resistor which has a room-temperature resistance of 47 Ω. It is used in a bridge circuit which yields a voltage that is almost proportional to the temperature. In Fig. 2 the transition curves are plotted for the different alloys.

4. Temperature Calibration of Allen-Bradley Resistor

The Allen–Bradley resistor of 47 Ω has been calibrated in zero magnetic field with a Ge resistor. In the temperature range between 1.5 and 4.0 °K, the vapor pressure of liquid He has been used in addition. Both calibrations agree within 0.03 °K. Above the temperature of the liquid He, we used, in addition, the transition temperature of Pb. With these calibration points the resistance of the carbon resistor has been calculated with the help of the three-constant formula. Afterwards we determined the influence of the magnetic field on the resistance of the carbon resistor. For this purpose we kept several temperatures constant by means of the vapor pressure. Then we increased the magnetic field from 0 to 55 kG and measured the reversible resistance as a function of the applied field. It turned out that the magnetic field caused only a small increase of the resistance which corresponds to a shift of the temperature scale. This shift is almost independent of the temperature and is of the order of 0.05 °K at 35 kG and 0.1 °K at 55 kG. It was always taken into account in analyzing the data. The influence of the magnetic field on the resistance of carbon resistors has been investigated by Belanger[20] and Neuringer and Shapira.[21] By calculating the shift of the temperature scale from the change of resistance, which these authors measured, one obtains values of the same magnitude.

5. Determination of Film Thickness

The exact thickness of the films is needed for the determination of the resistivity. For its measurement the film is superimposed with Ag at the end of the experiment. Then its thickness is measured by optical interference according to Tolansky.[22] The evaluation of the interference can be done with an accuracy of about 5%. This procedure caused difficulties only for Ga, because Ga melts at 28 °C. This raises unevenness of the surface of the film and yields broad interferences. Therefore we used for comparison also Ga films with 5 and 10-at.% Ag and extrapolated their resistivity towards 0-at.% Ag. The resistivity of pure Ga and the extrapolated value agreed within 5%.

6. Calibration of Magnetic Field

The magnetic field per current has been calculated from the geometry of the solenoid and measured by NMR. Both values agree within 0.5%. The magnetic field is $2.7I$ kG, where the current I is measured in ampere.

III. EXPERIMENTAL RESULTS

In Fig. 2 the transition curves of the amorphous superconductors $Bi_{0.85}Tl_{0.15}$, Ga, $Sn_{0.86}Bu_{0.14}$, and $Pb_{0.75}Bi_{0.25}$ are plotted. The parameter is the magnetic field perpendicular to the films. The numbers in the middle of the curves yield the applied magnetic field on multiplication by 2.7 kG.

Most of the transition curves are very sharp. This is caused by pinning forces as we shall see later. Only in the region of low magnetic field do we find flux flow. (See Fig. 3.) For the determination of the upper critical field B_{c2}, the sharp transition curves are very favorable. We define the transition temperature as the point of intersection of the linear part of the transition curve with the straight line of the residual resistance. In the discussion we will justify this procedure. In Fig. 4, B_{c2} is plotted as a function of temperature for amorphous $Bi_{0.85}Tl_{0.15}$. Correspondingly, we obtain in

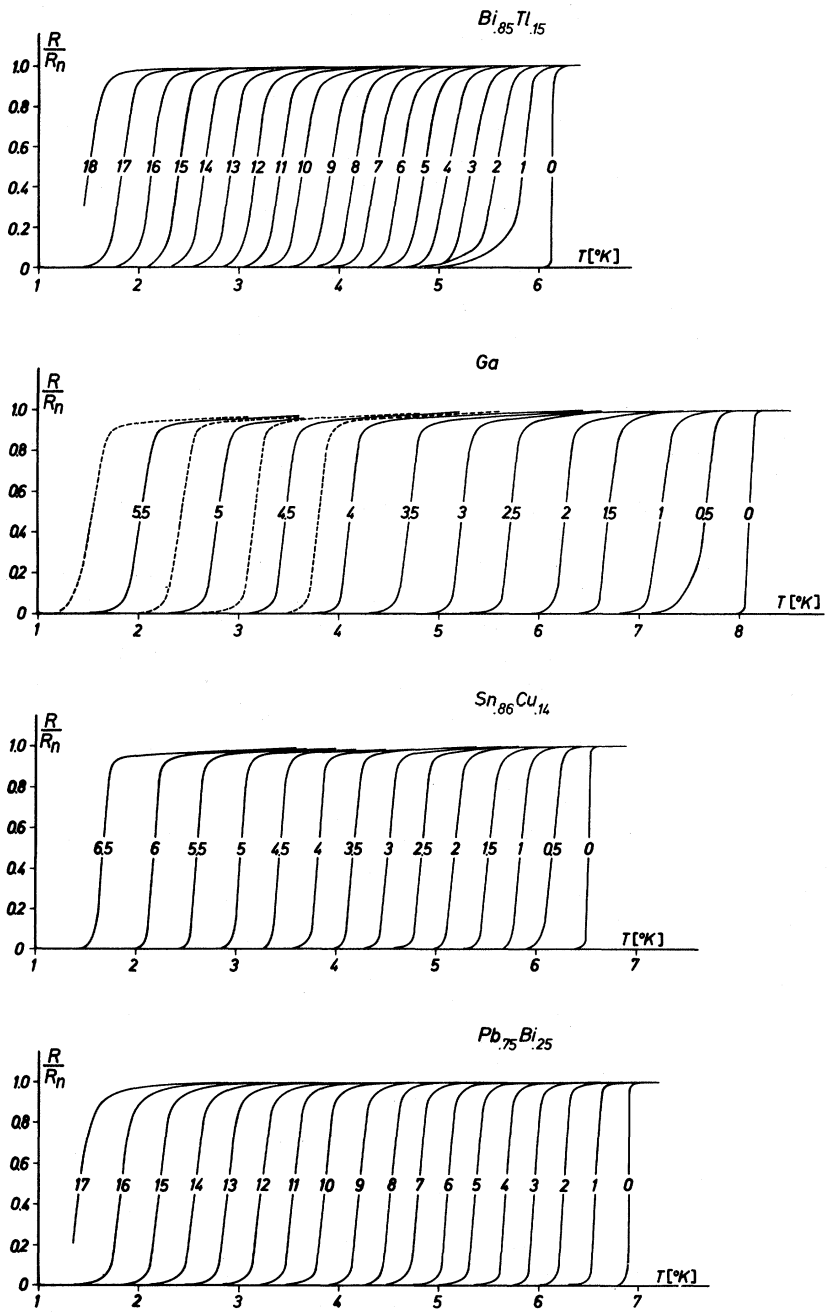

FIG. 2. Transition curves of amorphous $Bi_{0.85}Tl_{0.15}$, Ga, $Sn_{0.86}Cu_{0.14}$, and $Pb_{0.75}Bi_{0.25}$ films in a perpendicular magnetic field. The applied magnetic field is obtained on multiplying the numbers by 2.7 kG. The dotted lines correspond to steps of 0.25 A in magnet current.

Fig. 5 the upper critical field of Ga as a function of the temperature. B_{c2} of Ga is smaller by a factor of 3.5 than that of Bi. As we shall see later, this difference is essentially due to the residual resistivity which is much smaller for Ga. The upper critical field of amorphous $Sn_{0.86}Cu_{0.14}$ is plotted in Fig. 6 as a function of temperature. Figure 7 shows the corresponding result for amorphous $Pb_{0.75}Bi_{0.25}$.

We estimate the inaccuracy of $T_c(B)$ from the extrapolation at 0.1 °K. Even if the extrapolation is not absolutely correct, this would only cause a very small shift of the whole B_{c2} curve because the transition curves are parallel to each other. The Fe which has been superimposed in an extremely thin layer causes roughly a shift of less than 0.1 °K of the whole B_{c2} curve as we pointed out in a former paper.[16] Such a shift can be neglected on a scale of 6–8 °K. The data of the films under investigation are compiled in Table I. The columns contain the composition of the alloys, the thickness of the films, the residual resistivity,

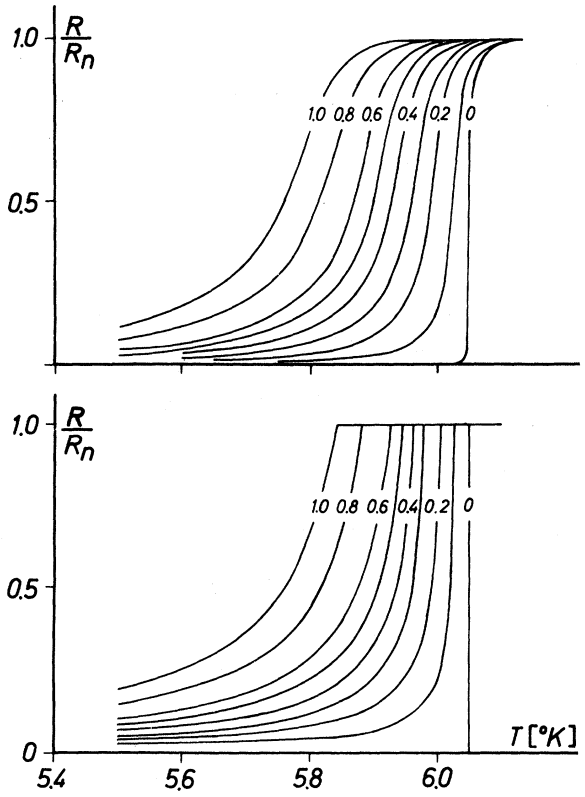

FIG. 3. Transition curves in the flux-flow region for amorphous $Bi_{0.85}Tl_{0.15}$. The upper part shows experimental curves, whereas the lower part is calculated according the theory of Schmid. The applied magnetic field is obtained on multiplying the numbers by 2.7 kG.

the initial slope of the upper critical field at the zero-field transition temperature, the transition temperature without Fe, and the shift of the transition temperature after the coating with Fe.

The values in Table I and the transition curves in Fig. 2 represent only one experiment for each alloy. We did, however, five experiments for $Bi_{0.85}Tl_{0.15}$ which yielded the following initial slopes for B_{c2}: 11.2, 10.0, 10.4, 12.0, and 10.5 kG/°K. There was some effort required to obtain sharp transition curves, as in Fig. 2. Only the underscored values represent experiments with transition curves of the same quality as in Fig. 2 in the whole temperature region. However, the transition curves in the upper quarter of the temperature scale were always as steep as in Fig. 2 and allowed an exact determination of the initial slope. The corresponding results for Ga are, in four experiments, 3.05, 2.9, 3.4 and 3.08 kG/°K. For $Sn_{0.86}Cu_{0.14}$ we obtained 4.4 and 4.3 kG/°K, and for $Pb_{0.75}Bi_{0.25}$ we obtained 9.6 and 9.4 kG/°K. The same reproducibility was obtained for the temperature dependence of B_{c2}. If we adjust the initial slope of different $B_{c2}(T)$ curves to a common value, the resulting curves show for each alloy at most a 2% dispersion. For the two Pb alloys, for example, where the initial slope of 9.6 and 9.4 kG/°K agrees within 2%, the dispersion of the two adjusted B_{c2} curves is less than 1%.

IV. DISCUSSION

A. Transition Curves

Since we will use the transition curves in the perpendicular magnetic field to determine B_{c2} as a function of the temperature we want to discuss the shape of the transition curves in detail. At first we notice that, for example, the transition curve 1 of $Bi_{0.85}Tl_{0.15}$ in the external magnetic field of 2.7 kG (Fig. 2) is much more rounded in the lower part than the transition curve for high magnetic field. A detailed plot of the transition curves for magnetic fields between 0 and 2.7 kG is given in the upper part of Fig. 3. We suggest that flux-flow takes place in this range of the magnetic field. Therefore we plot the corresponding transition curves according to Schmid's[23] theory of flux flow in the lower part of Fig. 3. Schmid calculated the flux-flow conductivity from a time-dependent

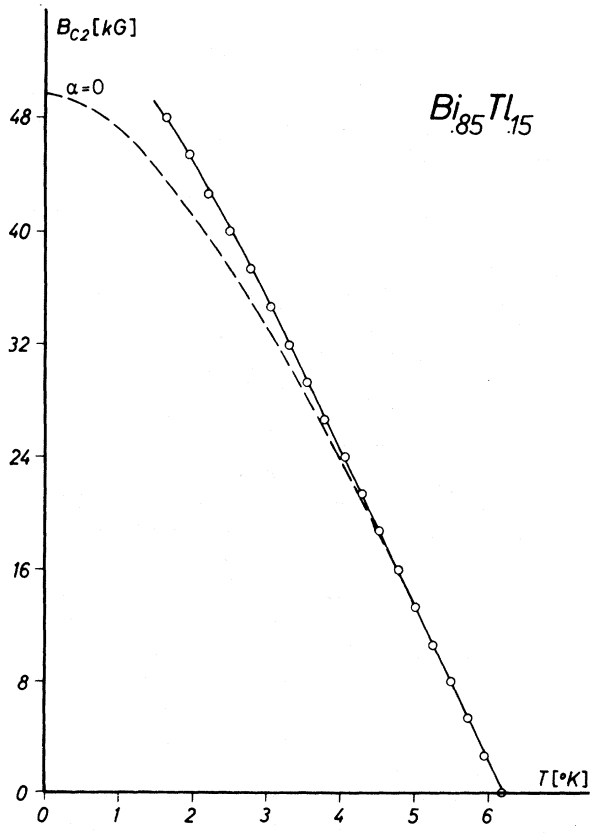

FIG. 4. Upper critical field of amorphous $Bi_{0.25}Tl_{0.15}$ as a function of temperature: solid line, experimental values; dashed line, upper theoretical curve [Eq. (4.6)].

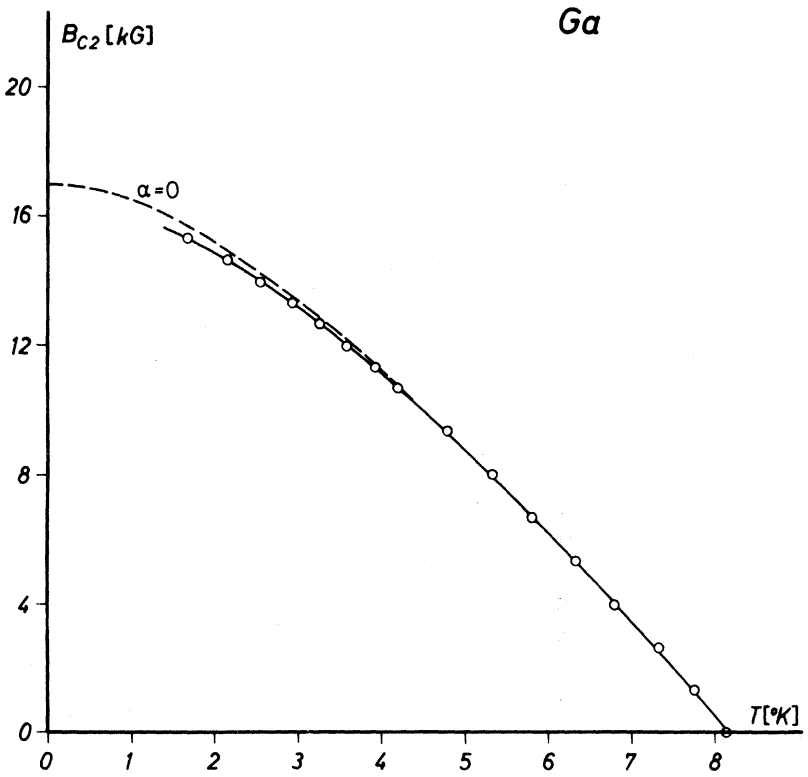

FIG. 5. Upper critical field of amorphous Ga as a function of temperature: solid line, experimental values; dashed line, upper theoretical curve [Eq. (4.6)].

Ginzburg–Landau equation. In the vicinity of B_{c2} he obtained

$$\frac{\sigma}{\sigma_n} = \frac{2.5(dB_{c2}/dT)}{B}(T_{c0} - T) - 1.5 \quad \text{for } T \leqq T_{c0} - \frac{B}{dB_{c2}/dT} . \qquad (4.1)$$

The qualitative agreement shows, indeed, that we have flux flow in this region. The rounding in the upper part of the experimental curves is caused by superconducting fluctuations. Their contribution cannot be calculated adequately in the direct vicinity of the transition temperature. The experimental curves have, in the lower part, a smaller resistance than the theoretical curves. A possible reason for this difference may be a partial pinning.

It is important for the determination of the transition temperature that, according to the theory, T_c in the magnetic field can be found by extrapolation of the linear part of the transition curve towards the residual resistance. We use this procedure for all transition curves.

Even if the theory of Schmid is only valid in the Ginzburg–Landau region, its qualitative predictions can be extended to the low-temperature region. In particular the transition curves should become broader with increasing magnetic field. Obviously this is not found in the experiment. On the contrary, the transition curves are also very sharp for high magnetic fields. The reason for this behavior must be a pinning of the flux lattice. Such a pinning has also been observed by Danner and Baumann[24] in amorphous Ga films. Fortunately the transition curves for the pinned flux lattice

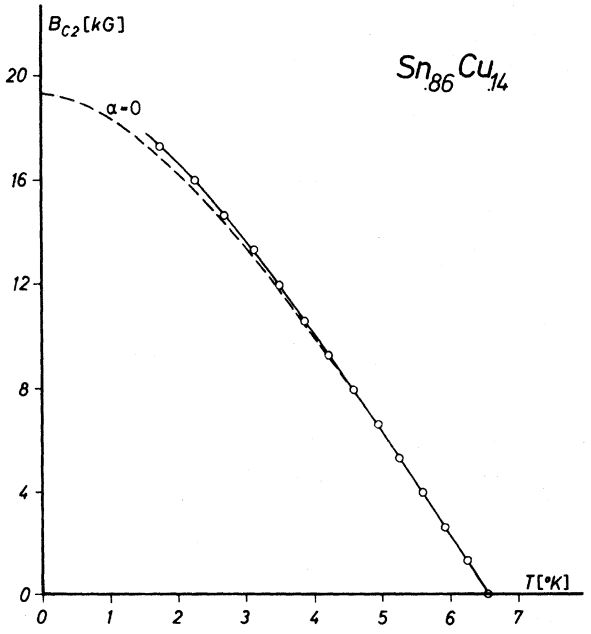

FIG. 6. Upper critical field of amorphous $Sn_{0.86}Cu_{0.14}$ as a function of temperature: solid line, experimental values: dashed line, upper theoretical curve [Eq. (4.6)].

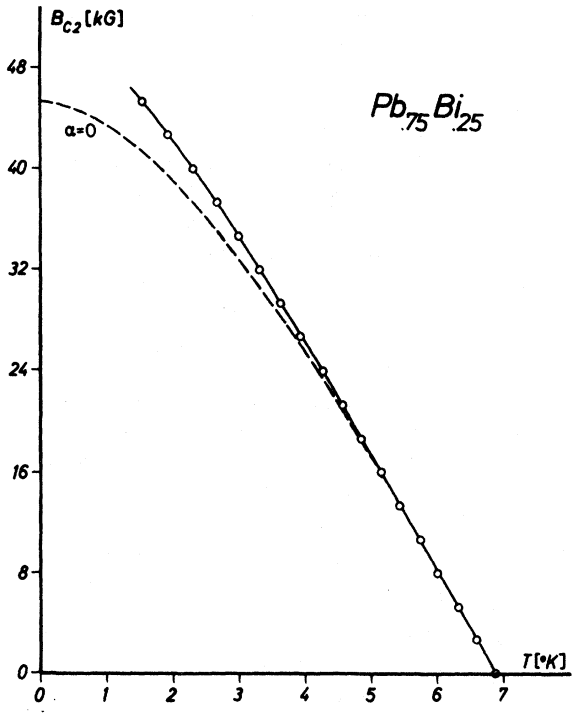

FIG. 7. Upper critical field of amorphous $Pb_{0.75}Bi_{0.25}$ as a function of temperature: solid line, experimental values; dashed line, upper theoretical curve [Eq. (4.6)].

can be much better evaluated than would be the case for the smeared transition curves.

B. Density of States from Initial Slope of B_{c2}

Many of the complications of the theory of B_{c2} can be neglected in the vicinity of the transition temperature T_{c0}, in particular, the spin polarization, the spin-orbit coupling, and the details of the scattering mechanism. According to the Ginzburg–Landau–Abrikosov–Gor'kov (GLAG) theory,[25–27] one obtains, in the Ginzburg–Landau region for the upper critical field

$$\frac{dB_{c2}}{dT} = -\frac{12}{\pi^3}\frac{e\gamma\rho}{k_B} , \tag{4.2}$$

where γ is the Sommerfeld constant, ρ is the residual resistivity, k_B is the Boltzmann constant, and e is the electron charge.

The Sommerfeld constant corresponds to the density of states at the Fermi surface. The density of states, including both spin directions, is therefore

$$N_{B_{c2}} = \frac{\pi(dB_{c2}/dT)}{4k_B e\rho} . \tag{4.3}$$

Equation (4.3) is derived for weak-coupling superconductors, i.e., it is assumed that λ is small compared with 1. If we apply it for strong-coupling superconductors it yields a dressed density of states as we are going to point out below.

However, first we will discuss the meaning of the dressed density of states in more detail. The electron-phonon interaction changes the energy levels of the electrons (quasiparticles) (see, for example, Refs. 28 and 29). In the vicinity of the Fermi energy, the energy levels move closely together so that their density of states is enhanced by $1+\lambda$. At $T=0$ °K, λ is defined by

$$\lambda(0) = 2\int_0^\infty \alpha^2F(\Omega)\frac{d\Omega}{\Omega} , \tag{4.4}$$

where $\alpha^2F(\Omega)$ is measured in superconducting-tunneling experiments and describes the total transition probability for an electron to emit a phonon with the energy Ω.

Measurements of the cyclotron mass[29] yield this dressed density of states N_λ which is $1+\lambda$ times the bare density of states. The density of states is, however, only constant in the direct vicinity of the Fermi energy. For energies of the order of the important phonon frequencies above or below the Fermi energy, the density of states is strongly energy dependent. Therefore the definition of the dressed density of states is not unique. It depends on the physical problem and the energy range over which the energy-dependent density of states is averaged. This situation is similar to the definition of the effective mass of an electron in a periodic potential, where the effective mass depends on the actual problem. Eilenberger and Ambegaokar[30] investigated the relation between N_λ and $N_{B_{c2}}$. They showed that for strong-coupling superconductors the upper critical field can be calculated in a first approximation by using the renormalized density of states. In addition they found, however, that $N_{B_{c2}}$ and N_λ may differ by a factor of the order of unity. For pure Pb, they obtained 1.2 for the factor. Rainer, the author, and Eckhardt[31] calculated the initial slope of $B_{c2}(T)$ for amorphous Pb and Sn, using the values $\alpha^2F(\Omega)$, which have been measured by Knorr and Barth. Although the alloys of Knorr and Barth, $Pb_{0.90}Cu_{0.10}$ and $Sn_{0.90}Cu_{0.10}$, are not identical with our alloys, the result will be representative. The calculation yields the ratio $N_{B_{c2}}/N_b$, and allows a comparison with $1+\lambda$. For the Pb alloy we obtain $N_{B_{c2}}/N_b = 3.02$, whereas $1+\lambda$ has the value 3.01. For the Sn alloy the calculation results in $N_{B_{c2}}/N_b = 2.73$, whereas $1+\lambda$ has the value 2.84. The enhancement factor for the upper critical field agrees fairly well with the electron-phonon-enhancement factor at $T=0$ °K and we expect therefore for the amorphous superconductors that $N_{B_{c2}}/N_b \approx 1+\lambda$.

We calculate the dressed density of states $N_{B_{c2}}$ from the initial slope of the $B_{c2}(T)$ curve and the residual resistivity. The values are given in the fourth column of Table II. There does not exist

TABLE II. First three columns give the composition of the alloys, the residual resistivity, and the initial slope of the $B_{c2}(T)$ curves. The dressed density of states N_{Bc2}, which is calculated from ρ and dB_{c2}/dT according to Eq. (4.3) and the free-electron density of states N_{free}, are given in columns four and five. The following two columns contain the ratio of the two densities of states and $1+\lambda$, the electron-phonon-enhancement factor.

Alloy	ρ (10^{-6} Ωm)	$\frac{dB_{c2}}{dT}\left(\frac{\text{kG}}{\text{K}}\right)$	N_{Bc2} (10^{47} (Nm)$^{-1}$m^{-3})	N_{free}	$\frac{N_{Bc2}}{N_{\text{free}}}$	$1+\lambda(0)$
$Bi_{0.85}Tl_{0.15}$	1.60	11.2	2.5	1.34	1.85	(3.3)
Ga	0.285	3.05	3.8	1.4	2.7	3.1
$Sn_{0.86}Cu_{0.14}$	0.47	4.4	3.3	1.39	2.4	2.8
$Pb_{0.75}Bi_{0.25}$	0.78	9.6	4.37	1.33	3.3	3.76

any measurement of the bare density of states in amorphous superconductors. Therefore we need a theoretical model for its calculation. From electron defraction[2-4] and the residual resistivity, we know that the amorphous metals are similar to the corresponding liquid metals. It is an experimental fact that liquid nontransition metals are well described by the free-electron model. Even the Hall effect, which is very sensitive to small deviations from the Fermi sphere, gives in liquid metals the correct number of conduction electrons. The author[15] measured the Hall effect of the amorphous metals under investigation to check the validity of the free-electron model for the amorphous superconductors. For Sn and Ga the Hall constant agreed well with the free-electron model. Therefore for these metals we calculate the bare density of states according to the free-electron model. For Pb and Bi the Hall constant is only half as large as the free-electron model predicts. This might be caused by a trace of band structure, since the Hall effect is very sensitive to the balance of electrons and holes. The density of states, however, does not distinguish between electrons and holes and therefore might well obey the free-electron model. This is particularly plausible for Pb, for which the Fermi surface is almost spherical even in the crystalline phase. Therefore we make the assumption for Pb and Bi that their bare density of states may be calculated by the free-electron model too. Its validity will be examined by the experiment. N_{free} is given by (4.5) and tabled in the fifth column:

$$N_{\text{free}} = (m/\pi^2\hbar^2)(3\pi^2 n)^{1/3}, \quad n = z(L/A)\rho_d \qquad (4.5)$$

where n is the density of electrons per unit volume, m is the electron mass, z is the number of conduction electrons per atom, A is the atomic weight, L is Avogadro's number, and ρ_d is the density. z, A, and ρ_d have been averaged, according to alloy composition.

In the following column the ratio of the two density of states is entered. We want to compare this ratio with the electron-phonon-enhancement factor $1+\lambda$.

For most of the amorphous superconductors which are investigated in this paper the λ values are known from tunneling experiments. In Table III we collect some experimental results. One clearly finds deviations among the different publications, which are certainly not only due to the different compositions of the alloys. For example, one would expect that Bi with 5-at.% Pb is stronger coupling than pure Bi, in contrast to the experimental values. The reason may be that tunneling junctions with pure Bi present difficulties. The Bi tends to have a different structure on the oxide layer than on a quartz or sapphire substrate.[32] In addition these junctions show zero-point anomalies which complicate the evaluation.[33] Despite these problems, we average the values of λ and collect them in Table II. Their accuracy is of the order of 10–15%. $1+\lambda$ shows a good agreement with the experimental enhancement factor N_{Bc2}/N_{free} except for Bi. We would like to interpret the result in such a way that the bare density of states N_b in the amorphous metals Ga, $Sn_{0.86}Cu_{0.14}$, and $Pb_{0.75}Bi_{0.25}$ can be well described by the model for free electrons. If we talk with certain reservation about a Fermi body in these amorphous metals, it would be spherical and its diameter can be calculated with the free-electron model. However, the dressed density of states at the Fermi surface is enhanced by the factor $1+\lambda$.

At this point one should also discuss the reliability of the tunneling data. λ is calculated from $\alpha^2F(\Omega)$. The $\alpha^2F(\Omega)$ functions of amorphous superconductors, which are published in the literature,[8-11] always show rather high values at low energies in contrast to crystalline superconductors. This low-energy part contributes rather effectively to the value of λ because of the Ω^{-1} divergency

TABLE III. Electron-phonon-coupling term λ for the amorphous metals and their alloys. The references are given in the text.

Metal	$\lambda(0)$ Jackson	Leslie	Knorr
Bi	2.16 with 5-at.% Pb	2.46	•••
Ga	1.94	2.25	•••
Sn	•••	•••	1.84 with 10-at.% Cu
Pb	2.45 with 5-at.% Bi	•••	2.01 with 10-at.% Cu
$Pb_{0.75}Bi_{0.25}$	•••	2.76	•••

of the denominator. The evaluation of the tunneling characteristic at low energies is, however, rather uncertain[34] and one often puts $\alpha^2F(\Omega)=0$ in the energy region between 0 and 1 meV.[35] This reduces the value of λ by 0.2–0.4 and even improves the agreement with the B_{c2} measurements.

In amorphous $Bi_{0.85}Tl_{0.15}$ the ratio N_{Bc2}/N_{free} does not agree with the value $1+\lambda$ for pure Bi from the tunneling experiments. This discrepancy might be explained in part by the fact that the density of states is not determined for pure amorphous Bi. For an amorphous Bi film with 2-at.% Tl we found a density of states of 3.16×10^{47} $(\text{Nm})^{-1}$ m^{-3}. This yields the experimental enhancement factor 2.2. This value is still smaller than $1+\lambda$ for amorphous Bi. This discrepancy is perhaps associated with the experimental problems of the tunneling data of amorphous Bi that we discussed above. Another possibility is that Bi does not obey the free-electron model.

We neglected in our consideration the mass enhancement due to the Coulomb interaction. Its contribution is only of the order of 0.1 or 3%.[36]

C. Temperature Dependence of B_{c2}

In Figs. 4–7 the experimentally determined values of the upper critical field of $Bi_{0.85}Tl_{0.15}$, Ga, $Sn_{0.86}Cu_{0.14}$, and $Pb_{0.75}Bi_{0.25}$ are plotted as a function of the temperature. We want to compare these experimental points with the theory of B_{c2}. A survey of the magnetic behavior of type-II superconductors is given by Fetter and Hohenberg.[37] The upper critical field of weak-coupling superconductors with small mean free path has been calculated for all temperatures by Maki,[38] Helfand and Werthamer,[39] and Caroli, Cyrot, and de Gennes.[40] They found

$$\ln\frac{T_{c0}}{T}=\Psi\left\{\frac{1}{2}+\frac{1}{2}\,\frac{\pi k_B B_{c2}}{3e\gamma\rho T}\right\}-\Psi\left(\tfrac{1}{2}\right), \qquad (4.6)$$

where Ψ is the digamma function.

The broken line in Figs. 4–7 is calculated according to Eq. (4.6). The initial slope at T_{c0} is fitted to the experimental points. Equation (4.6) neglects the spin of the electrons and the spin-orbit coupling. These contributions have been examined by Maki[41] and Werthamer, Helfand, and Hohenberg.[42] They showed that the initial slope at T_{c0} is not changed by the inclusion of the electron-spin and the spin-orbit coupling. However, the values of B_{c2} at low temperatures are reduced. Therefore the broken lines in Figs. 4–7 give an upper limit for the theoretical B_{c2} values. This remains valid when an anisotropic impurity scattering is included. Eilenberger[43] calculated the upper critical field for different scattering processes. He showed that for superconductors with $\kappa>10$ the B_{c2} values for s scattering and forward scattering differ only by a few percent. The B_{c2} values for forward scattering lie always below those for s scattering. The broken line remains the upper theoretical limit for B_{c2}. We find, however, that the metals $Bi_{0.85}Tl_{0.15}$ and $Pb_{0.75}Bi_{0.25}$ with extremely small mean free path show an upper critical field which exceeds the theoretical limit at low temperature by about 10%. For $Sn_{0.86}Cu_{0.14}$ this effect is much smaller, whereas for Ga, B_{c2} lies in the theoretically expected region. We suggest that the strong electron-phonon coupling in amorphous superconductors causes these large B_{c2} values at low temperature. A numerical calculation of the upper critical field with realistic $\alpha^2F(\Omega)$ functions by Rainer, the author, and Eckhardt[31] yield just first results. For amorphous superconductors the calculated strong-coupling values for $B_{c2}(T)$ exceed these in weak-coupling theory at low temperature just as in the experiment. Therefore we suggest that the temperature dependence of B_{c2} and its deviation from the weak-coupling theory reflects the strong-coupling behavior of amorphous superconductors.[44]

D. Comparison with Other Experiments

Lazarev, Lazareva, Semenenko, Tutov, and Goridov[45] have measured the upper critical field of amorphous Bi and Be. For amorphous Bi they found values for dB_{c2}/dT which lie between 20 and 30 kG/°K. These values are by a factor 2–3 larger than the results of our experiments. However, the estimated film thickness in the paper of Lazarev *et al.* is of the order of 100 Å and the transition temperature lies about 1 °K below the transition temperature of thick Bi films. Unfortunately we do not have any information about the residual resistivity of these thin films. Therefore a quantitative comparison with our experiments or with the theory is not possible. It is well known that the residual resistivity of thin condensed films is no longer independent of the film thickness but increases with decreasing thickness. This may be the reason for the large critical field. However, we would expect that the transition curves of such thin films would be very smeared due to the contribution of superconducting fluctuations. Therefore the evaluation would be difficult. Danner and Baumann[46] measured the upper critical field of amorphous Ga in the temperature range between $0.7T_{c0}$ and T_{c0}. Here they found a linear dependence between B_{c2} and T. From their results one obtains $dB_{c2}/dT=3.6$ kG/°K. This value is of the same order of magnitude as our result. For an exact comparison we would need the residual resistivity of their Ga films.

V. CONCLUSION

In this paper we measured the upper critical

field of the amorphous metals $Bi_{0.85}Bl_{0.15}$, Ga, $Sn_{0.86}Cu_{0.14}$, and $Pb_{0.75}Bi_{0.25}$ and determined their density of states. The density of states is clearly larger than the free-electron model predicts. The electron-phonon interaction is responsible for this enhancement. The ratio N_{Bc2}/N_{free} agrees for Ga, $Sn_{0.86}Cu_{0.14}$, and $Pb_{0.75}Bi_{0.25}$ with the value $1+\lambda$ which is known from tunneling experiments. Therefore the bare density of states in these amorphous metals obeys the free-electron model and their dressed density of states is enhanced by the factor $1+\lambda$. The temperature dependence of the upper critical field does not agree with the theory of Werthamer, Helfand, and Hohenberg. It is suggested that the strong-coupling behavior of the amorphous metals is responsible for this discrepancy.

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