EFFECT OF LATTICE DISORDER ON THE SUPERCONDUCTING TRANSITION TEMPERATURE*

J. W. Garland†
Department of Physics, University of Illinois, Chicago, Illinois,
and Argonne National Laboratory, Argonne, Illinois

and

K. H. Bennemann
Department of Physics and Astronomy, University of Rochester, Rochester, New York,
and Argonne National Laboratory, Argonne, Illinois

and

F. M. Mueller
Argonne National Laboratory, Argonne, Illinois
(Received 31 July 1968; revised manuscript received 9 September 1968)

A theory is presented to explain the dependence of the superconducting transition temperature T_c on the changes in the phonon frequency spectrum and electronic density of states which result from lattice disorder. Numerical calculations of T_c are presented for films composed of crystalline granules, for films composed of amorphous granules, and for homogeneous amorphous metals. The calculations are in good agreement with experimental values of T_c.

Experiments[1,2] on disordered films of a variety of metals and on disordered dilute Sn-Cu alloys[3] have shown that the superconducting transition temperature T_c increases with increasing lattice disorder. None of the explanations proposed[4,5] for the enhancement of T_c in superconducting films has been applicable to all experimental situations discussed in this paper. Although no calculations are presented for the case of very thin films,[4] the theory proposed here is applicable to films composed of small metallic crystallites,[1,6] films composed of amorphous metallic granules,[1,2,6] and homogeneous amorphous superconducting alloys. In particular, a two-parameter model for granular films of nearly-free-electron metals yields numerical values for the enhancement of T_c which are in good agreement with the experimental values found by Buckel and Hilsch[1] and von Minnigerode.[2]

The theory proposed here is based on the assumption that the average amplitude of ionic vibrations is larger in a disordered lattice than a perfect crystal. For disordered films which consist of small crystalline granules,[6] this increase in the average amplitude of ionic vibrations results from the many ions which are in lattice positions of reduced symmetry near the surface of the granules. Since these ions are held in place by weaker ionic forces than those found in a bulk crystal, they undergo localized ionic vibrations of larger amplitude and lower frequency than those found in a bulk crystal. As a result, the formation of granules (1) increases the average amplitude of ionic vibrations and decreases the average phonon frequency $\langle\omega_{\text{ph}}\rangle$, and (2) broadens the peaks in the phonon density of states $D(\omega)$. For homogeneous amorphous metals, the increased average amplitude of ionic vibrations results from the weakened forces acting on all of the ions. In this case, the first effect is usually more important than the second. Both the effects found in homogeneous amorphous metals and those found in crystalline granular films occur in the case of disordered films which consist of amorphous granules.

The increase in the average amplitude of the ionic vibrations increases the average electron-phonon coupling constant. This increases both T_c and the phonon contribution[7] λ to the electron mass renormalization constant $Z(0)=(1+\lambda)Z_e$. Here, Z_e is the Coulomb mass renormalization constant.[8] Note that λ is approximately given by[7] $\lambda \approx [N(0)/M\langle\omega_{\text{ph}}^2\rangle]\langle J^2\rangle$, where $N(0)$ is the electronic band density of states at the Fermi level, M is the ionic mass, $\langle\omega_{\text{ph}}^2\rangle$ is the average squared phonon frequency, and $\langle J^2\rangle$ is the average over the Fermi surface of the squared matrix element of the electron-ion deformation potential $J(\vec{q})$. From this expression for λ it is clear that λ increases with decreasing $\langle\omega_{\text{ph}}\rangle$, provided that $N(0)$ remains constant.

Lattice disorder also leads to changes in electronic band structure. The primary effect of these changes is to smear out any structure in the band density of states $N(E)$. All important structure in $N(E)$ disappears in amorphous films and alloys of simple metals. However, the smearing of structure in $N(E)$ is relatively small in granular films and leads to only small changes in T_c, λ, Z_e, and the Coulomb pseudopotential[8,9] $U_c \equiv K_e{}^*$ for simple metals.

Although smearing out of structure in $D(\omega)$ can produce only small changes in λ, it can substantially reduce T_c. This reduction of T_c follows from the form of the integral equation for the superconducting energy gap $\Delta(\omega)$.[8] Any peaks in $D(\omega)$ are mirrored in $\Delta(\omega)$, which multiplies $D(\omega)$ in the equation for T_c. Thus, the equation for T_c is not linear in $D(\omega)$. This reduction of T_c is verified by detailed calculations,[10] which yield the approximate equation

$$\ln\left(\frac{\langle\omega_{\mathrm{ph}}\rangle}{1.26T_c}\right)=\frac{1+\lambda}{A(1-0.5\mu^*)\lambda-\mu^*}. \tag{1}$$

Here, A is a constant of order unity. It is independent of λ, $\langle\omega_{\mathrm{ph}}\rangle$, and the reduced Coulomb pseudopotential $\mu^* \equiv Z_e{}^{-1}U_c$, but depends on the functional form of the product $D(\omega)\alpha^2(\omega)$, where $\alpha(\omega)$ is the rms electron-phonon coupling constant for phonons of frequency ω. Hence, A depends upon crystal structure, as is seen from the computed values[10] listed in Table I, and, in general, is reduced by lattice disorder. Note that Eq. (1) is similar in form to the McMillan equation.[7] The small differences between Eq. (1) and the McMillan equation arise primarily from differences in the calculation of $\alpha^2(\omega)$. We calculated $\alpha^2(\omega)$ from known pseudopotentials $V_p(\vec{q})$ and phonon spectra rather than assuming a model for $\alpha^2(\omega)$. Note that the difference found[10] between the values of A for Hg and for Pb is confirmed by calculations of McMillan.[7] Also, note that the value of μ^* is affected only negligibly by lattice disorder.

Equation (1) yields the expression

$$\ln\left(\frac{T_c}{T_{c0}}\right)=\delta\ln\langle\omega_{\mathrm{ph}}\rangle+\frac{1+\lambda}{A(1-0.5\mu^*)\lambda-\mu^*}-\frac{1+\lambda+\delta\lambda}{(A+\delta A)(1-0.5\mu^*)(\lambda+\delta\lambda)-\mu^*} \tag{2}$$

for the logarithmic change in T_c as a function of the changes $\delta\ln\langle\omega_{\mathrm{ph}}\rangle$, δA, and $\delta\lambda$ introduced by lattice disorder and of the quantities,λ, A, and μ^*. Given the experimental value of $g \equiv \ln(\langle\omega_{\mathrm{ph}}\rangle/1.26T_c)$ and the calculated values of A and μ^*,[9] one can determine λ from Eq. (1). Also, from the approximate expression for λ given above, one finds $\partial\ln\lambda/\partial\ln\langle\omega_{\mathrm{ph}}\rangle \approx -2$. Thus, in the absence of band-structure effects, the ratio T_c/T_{c0} is given as a function of only two unknowns, δA and $\delta\ln\langle\omega_{\mathrm{ph}}\rangle$.

Table I. Numerical values of the quantities used in calculating T_c for disordered superconductors. Values given for A, $\gamma_G{}^{\mathrm{calc}}$, and $\partial\ln\lambda/\partial\ln N(0)$ are taken from Ref. 10. Except where otherwise noted, values for g, μ^*, $\gamma_G{}^{\mathrm{exp}}$, and $\delta\ln v$ are taken from Refs. 7, 9, 11, and 18, respectively. Values of λ were calculated from Eq. (1), using the above values of A, g, and μ^*. Values of $N_{bs}(0)/N_{fe}(0)$ were calculated as in Ref. 7, using our values of λ.

Metal	g	A	λ	μ^*	γ_G^{exp}	γ_G^{calc}	$\frac{N_{bs}(0)}{N_{fe}(0)}$	$\frac{\partial\ln\lambda}{\partial\ln N(0)}$	$\delta\ln v$
Al	5.54	0.90	0.41	.10	2.5	2.7	1.06	~1.1	.065
Hg	2.48	0.76	1.54	.09	2.2	2.2	0.84	~1.0	.037
In	3.12	0.85	0.84	.09	2.35	2.4	0.96	~1.1	.020
Pb	2.31	0.90	1.22	.09	2.6	2.2	0.90	~1.1	.035
Sn	3.62	0.80	0.75	.09	2.2	2.3	0.85	~1.1	.023
Tl	3.13	0.85	0.81	.08	2.7	1.0	0.69	~1.1	.022
Zn	5.52	0.76	0.48	.08	2.0	1.6	0.65	~1.3	.047
Cd	5.93	0.76	0.45	.08	2.2	~1.9	0.55	~1.1	.040
Ga	5.34	0.80	0.46	.08	1.45[b]	1.6	0.48	~1.4	-.032
Th	4.44[a]	0.90	0.56	.12	1.0	~1.2	-	-	-

[a] Handbook of Chemistry and Physics (Chemical Rubber Company, Cleveland, Ohio, 1967), 48th ed.
[b] Ref. 12.

We now propose a model for the determination of the fractional changes $(\delta \ln A)_{gr}$ and $(\delta \ln\langle\omega_{ph}\rangle)_{gr}$ induced by the formation of granules. We assume that the character and degree of disorder was the same in each of the seven different crystalline granular films studied by Buckel and Hilsch.[1] Thus we assume the ratio $\beta \equiv (\delta \ln A)_{gr}/(\delta \ln\langle\omega_{ph}\rangle)_{gr}$ to have been a universal constant for these films. Then, we make three different hypotheses as to the variation of $(\delta \ln\langle\omega_{ph}\rangle)_{gr}$ from one film to another. First, we choose $(\delta \ln\langle\omega_{ph}\rangle)_{gr}$ to be a constant, η_1. Then, guided by our physical picture of the effects of the formation of granules, we attempt to improve this approximation by assuming $(\delta \ln\langle\omega_{ph}\rangle)_{gr}$ to be proportional to $\langle\gamma_G\rangle \equiv \partial \ln\langle\omega_{ph}\rangle/\partial \ln v$. As a second hypothesis we approximate $\langle\gamma_G\rangle$ by the value $\gamma_G{}^{\exp}$ of the Grüneisen constant determined[11,12] by velocity-of-sound measurements, and choose $\eta_2 \equiv (\delta \ln\langle\omega_{ph}\rangle)_{gr}/\gamma_G{}^{\exp}$ to be a constant. However, this choice for $\langle\gamma_G\rangle$ does not properly take account of the volume dependence of $\omega(\vec{q})$ for the short-wavelength phonon modes primarily responsible for superconductivity. In order to meet this objection, we use the experimentally determined volume dependence[13,14] of T_c to find values $\gamma_G{}^{calc}$ for $\langle\gamma_G\rangle$, and choose $\eta_3 \equiv (\delta \ln\langle\omega_{ph}\rangle)/\gamma_G{}^{calc}$ to be constant for our third hypothesis. To calculate $\langle\gamma_G\rangle$, we note that the volume dependence of λ and, hence, of T_c is given by $\partial \ln\lambda/\partial \ln v = 2\langle\gamma_G\rangle - \delta_0$, where the correction factor δ_0 is of order unity and has been calculated elsewhere.[10]

The exact degree of disorder is not known for the films which we consider. Thus, we treat both the ratio β and, depending on the approximation used, either η_1, η_2, or η_3 as parameters. For each of the three approximations, the two parameters β and η_1 are chosen to fit the experimental results[1] $\ln(T_c/T_{c0}) = 0.00$ for Pb and $\ln(T_c/T_{c0}) = 0.82$ for Al. The values found, $(\delta \ln\langle\omega_{ph}\rangle)_{gr} \approx 0.1$ and $\delta A \approx -0.6$, are within the range expected for granules of diameter $d \lesssim 100$ Å or platelets of thickness $d \lesssim 50$ Å.

Given these values and the values of g, A, λ, μ^*, $\gamma_G{}^{\exp}$, and $\lambda_G{}^{calc}$ listed in Table I, we now evaluate $\ln(T_c/T_{c0})$ for crystalline granular films of Hg, In, Sn, Tl, Zn, Cd, and Th.[15] As is shown in Table II and as is expected on physical grounds, the third approximation, $(\delta \ln\langle\omega_{ph}\rangle_{gr} \propto \gamma_G{}^{calc}$, yields the best agreement with experiment. With no free parameters, our values for $\ln(T_c/T_{c0})$ calculated in that approximation agree, as demonstrated in Fig. 1, with the experimental values of Buckel and Hilsch[1] for crys-

Table II. Experimental and theoretical values of $\ln(T_c/T_{c0})$. T_c and T_{c0} are the values of the transition temperature in the disordered state and the bulk crystalline state, respectively.

Metal	Crystalline Granular Films					Films Composed of Amorphous Granules		Homogeneous Amorphous Samples	
	Experimental Values		Theoretical Values				Theory		Theory
	(Buckel & Hilsch[1])	(Abeles et al[1])	$\eta_1 = -.135$ $\beta = .50$	$\eta_2 = -.054$ $\beta = .50$	$\eta_3 = -.050$ $\beta = .52$	Expt.	$\eta_3 = -.050$ $\beta = .52$	Expt. (von Minnegerode[2,3])	$\eta_3 = -.050$ $\beta = .52$
Al	0.82	0.95	0.82[a]	0.82[a]	0.82[a]	1.6[b]	~1.5	-	~1.1
Hg	-0.06	-	-0.06	-0.05	-0.05	-	~0.3	-	~0.5
In	0.20	0.1	0.16	0.15	0.15	-	~0.3	-	~0.2
Pb	0.00	0.0	0.00[a]	0.00[a]	0.00[a]	-	~0.0	-	~0.0
Sn	0.23	0.1	0.23	0.21	0.21	0.7[b,c]	~0.7[c]	0.60[e]	~0.6[e]
Tl	0.10	-	0.15	0.16	0.07	-	~0.5	-	~0.5
Zn	0.44	-	0.68	0.56	0.42	-	~2.4	-	~2.4
Cd	-	-	0.78	0.69	0.56	-	~2.7	-	~2.8
Ga	-	-	-			2.1[d]	~2.5	-	~2.6
Th	-	-	0.50	0.23	0.22	-	-	-	-

[a] These values were set equal to the experimental values in order to fix the two parameters of our model for granular films.

[b] Ref. 2.

[c] Here, T_c is for disordered $Sn_{0.92}Cu_{0.08}$, and T_{c0} is for pure crystalline Sn.

[d] Buckel and Hilsch, Ref. 1.

[e] Here, T_c is for disordered $Sn_{0.90}Cu_{0.10}$, but T_{c0} is for pure crystalline Sn.

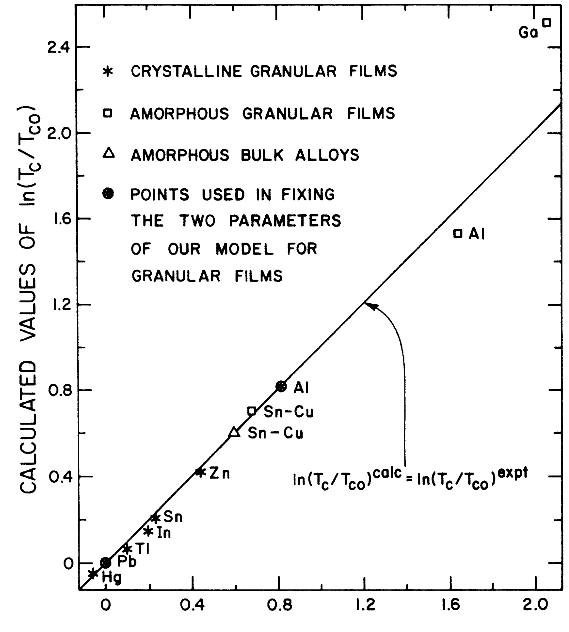

FIG. 1. Calculated versus experimental values of $\ln(T_c/T_{c0})$. Calculated values are taken from the approximation $\delta \ln\langle\omega_{\text{ph}}\rangle \propto \gamma_{\text{G}}{}^{\text{calc}}$; the values for Al and Pb for crystalline granular films were set equal to the experimental values in order to fix the two parameters of our model for granular films.

talline granular films of Hg, In, Sn, Tl, and Zn within an rms error of 0.03.

Since crystallization can be suppressed by impurities, as has been shown for Al[2] and Sn,[2,3] we also calculate $\ln(T_c/T_{c0})$ for films composed of amorphous granules and for homogeneous amorphous metals. We approximate the softening of the lattice which accompanies the transition from the crystalline state to the amorphous state by that softening which would accompany an expansion δv in molar volume equal to the change δv_m upon melting and write $\delta \ln\langle\omega_{\text{ph}}\rangle = -\langle\gamma_{\text{G}}\rangle \delta \ln v$. The disordered nature of the amorphous state greatly reduces the dependence of $(\delta \ln\lambda)_v \equiv (2\langle\gamma_{\text{G}}\rangle - \delta_0)\delta \ln v$ upon the functional form of $J(\vec{q})$ and allows one to neglect the correction factor δ_0. We approximate the electronic density of states $N(0)$ in the amorphous state by the free-electron density of states $N_{fe}(0)$ and calculate its value $N_{bs}(0)$ in the crystalline state from the coefficient γ of the electronic specific heat, using the approximate formula $N_{bs}(0) \approx 3\gamma/2\pi^2 k_{\text{B}}{}^2(1+\lambda)$.[16] Using the estimated[10] values of $\partial \ln\lambda/\partial \ln N(0)$ given in Table I, assuming $\partial \ln\langle\omega_{\text{ph}}\rangle/\partial \ln N(0) \approx -0.5$,[17] and using the values of $\delta \ln v$ [18] and of $N_{bs}(0)/N_{fe}(0)$ given in Table I, we calculate the changes $(\delta \ln\langle\omega_{\text{ph}}\rangle)_a \approx 0.5 \ln[N_{bs}(0)/N_{fe}(0)] - \gamma_{\text{G}}{}^{\text{calc}} \delta \ln\nu$ and $(\delta \ln\lambda)_a \approx [\partial \ln\lambda/\partial \ln N(0)] \ln[N_{bs}(0)/N_{fe}(0)] + 2\gamma_{\text{G}}{}^{\text{calc}} \times \delta \ln\nu$ which accompany the transition to an amorphous state. Then, estimating $A \approx 0.85$ and $\mu^* \approx 0.09$ in the amorphous state, we find $\ln(T_c/T_{c0})$ for the homogeneous amorphous state from Eq. (2), using $\delta \ln\langle\omega_{\text{ph}}\rangle = (\delta \ln\langle\omega_{\text{ph}}\rangle_a$, $\delta \ln\lambda = (\delta \ln\lambda)_a$, and $\delta A \approx 0.85 - A$. Finally, assuming that such films have a granular structure similar to that of crystalline granular films, we find $\ln(T_c/T_{c0})$ for films composed of amorphous granules by setting $\delta \ln\langle\omega_{\text{ph}}\rangle = (\delta \ln\langle\omega_{\text{ph}}\rangle)_a + (\delta \ln\langle\omega_{\text{ph}}\rangle)_{\text{gr}}$, $\delta \ln\lambda = (\delta \ln\lambda)_a + (\delta \ln\lambda)_{\text{gr}}$, and $\delta \ln A \approx \ln(0.85/A) + (\delta \ln A)_{\text{gr}}$ in Eq. (3). The resultant values of $\ln(T_c/T_{c0})$ are given in Table II for both amorphous granular films and homogeneous amorphous metals. However, these values are not expected to be nearly so accurate as were the values of $\ln(T_c/T_{c0})$ for crystalline granular films.

In addition to the amorphous Ga films prepared by Buckel and Hilsch,[1,6] presumably amorphous films of Al and Sn have been prepared by von Minnigerode[2] by introducing oxygen and Cu impurities, respectively. As is shown in Table II, our values of $\ln(T_c/T_{c0})$, which have been corrected for the effect of the impurity Cu ions on λ and on $\langle\omega_{\text{ph}}\rangle$ for the Sn-Cu film, are in good qualitative agreement with experiment for Al, Ga, and Sn.

Also, the transition temperature T_c has been measured[3] by Strieder and by von Minnigerode for both ordered and disordered bulk Sn-Cu alloys for Cu concentrations from zero to approximately 20%. The Cu impurities reduce $\langle\omega_{\text{ph}}\rangle$, λ, and T_c for the ordered alloys, but increase T_c for the disordered alloys. This increase in T_c is linear in the concentration c of Cu impurities for $c \ll 0.1$ and reaches its maximum value, $T_c = 6.8°\text{K}$, at $c = 0.1$. We interpret this variation of T_c as a function of c as indicating that the Cu impurities induce localized disorder about each Cu site with the regions of disorder overlapping as c is increased until one obtains a nearly amorphous state at $c = 0.1$. Our calculated value $T_c/T_{c0} = 1.8$ for the ratio of the transition temperature in disordered bulk $\text{Sn}_{0.90}\text{Cu}_{0.10}$ alloys to that in pure crystalline Sn is in excellent agreement with the experimental value[3] $1.83 = 6.8/3.72$.

Calculated values of $\ln(T_c/T_{c0})$ are presented in Table II for both crystalline and amorphous granular films and for homogeneous amorphous samples of all simple metals. However, these calculated values might not be in quantitative agreement with experiments performed by different groups, since the degree of lattice and disorder and, hence, δA and $\delta \ln\langle\omega_{\rm ph}\rangle$ depend sensitively on the method of sample preparation and could vary from experiment to experiment.

Band-structure effects, which are important for the case of transition metals, limit our calculations of T_c/T_{c0} to the case of simple metals (and Th[16]). However, qualitatively we can say that T_c should be (1) strongly enhanced in disordered films of transition metals such as W which are characterized by small values of λ and $N(0)$, (2) not greatly affected for metals such as V and Nb, and (3) depressed for metals such as $\mathrm{Nb_3Sn}$ or the V_3X compounds which are characterized by very large values of $N(0)$.

The excellent agreement between our calculated values for T_c/T_{c0} and the experimental values of Buckel and Hilsch,[1] von Minnigerode,[2,3] and Strieder[3] suggests several conclusions:

(1) The formation of granules in disordered films of simple metals significantly affects T_c only by softening the lattice near the surface of each granule. Such softening increases the average amplitude of localized ionic vibrations; this enhances T_c. However, it also smears out any structure in $D(\omega)$; this tends to depress T_c.

(2) For a given lattice disordering, both the fractional increase in the amplitude of ionic vibrations and the fractional smearing out of $D(\omega)$ are proportional to $\gamma_{\rm G}{}^{\rm calc}(\approx -\partial\langle\omega_{\rm ph}\rangle/\partial v)$, the Grüneisen constant which enters into the determination of $\partial T_c/\partial v$.

(3) Both softening of the ionic lattice and changes in band structure caused by lattice disorder contribute to changes in T_c for nearly amorphous samples.

We wish to thank Professor Buckel for stimulating our interest in this problem and Dr. von Minnigerode for communicating his results prior to publication.

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*Based on work performed under the auspices of the U. S. Atomic Energy Commission.

†Alfred P. Sloan Foundation Fellow. Work supported in part by the Alfred P. Sloan Foundation.

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[15] Although Th does not possess a nearly-free-electron band structure, both the experimentally observed value of $\partial T_c/\partial v$ for Th and the band-structure calculations of F. M. Mueller (to be published) indicate that the formation of small crystallites should introduce only small band-structure effects in the calculation of $\ln(T_c/T_{c0})$ for Th.

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