

made up of the transition element only. In this approximation a comparison can be made between the Mo effect in Mo_2B and that of elemental Mo.

The isotope effect in Mo has been measured by Matthias *et al.*¹⁶ and by Bucher and Palmy.¹⁷ Both measurements agree with each other for $\alpha = -0.37 \pm 0.04$ except for a constant temperature difference which may be due to thermometry. The error quoted is from the latter measurement. This figure is, within error limits, comparable to the Mo in Mo_2B effect found in the present experiment of $\alpha = -0.42 \pm 0.02$. If we consider then that both Mo in Mo_2B and elemental Mo have isotope effects of about $\alpha = -0.4$, the analogous situation for W_2B and W would be an $\alpha = -0.5$. This predicted isotope effect in tungsten would then be the same as in the nontransition elements.

A large isotope effect in tungsten is consistent with what appears to be a systematic variation of α across the transition elements symmetrical around column VI.

Thus α is small for Zr ($\alpha=0$),²⁰ Ru ($\alpha=0$),²¹ and Os ($\alpha=0.21$)²²; then rising at Re ($\alpha=-0.36$)²³ to a large value at Mo and W. This behavior is in line with other physical quantities such as T_c , cohesive energy and melting points that are roughly symmetrical around column VI.^{4,24}

ACKNOWLEDGMENTS

I am grateful to Bernd Matthias for his advice and encouragement throughout this experiment. I am indebted to John Maita of Bell Telephone Laboratories for two very useful specific-heat measurements.

²⁰ E. Bucher, J. Muller, J. L. Olsen, and C. Palmy, *Phys. Letters* **15**, 303 (1965).

²¹ T. H. Geballe, B. T. Matthias, G. W. Hull, Jr., and E. Corenzwit, *Phys. Rev. Letters* **6**, 275 (1961).

²² R. A. Hein and J. W. Gibson, *Phys. Rev.* **131**, 1105 (1963).

²³ E. Maxwell, Myron Strongin, and T. B. Reed, *Phys. Rev.* **166**, 457 (1968).

²⁴ B. T. Matthias, *Science* **144**, 378 (1964).

Pressure Dependence of the Superconducting Transition Temperature

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A theory of the superconducting transition temperature using a simple model for the electron-phonon interaction has been used to calculate the pressure dependence of the transition temperature for nontransition metals. The pressure dependence of the Debye temperature and phonon frequencies is included by using a Grüneisen model. The theory is compared to experiment for aluminum, lead, zinc, cadmium, indium, and tin, and the agreement is generally quite good. The results have been used to predict the critical pressures at which $T_c=0$; and for the cases of zinc, cadmium, and possibly aluminum, it should be possible to carry out experiments where T_c is pushed below presently measurable temperatures. The empirical $T_c=f(P)$ relations published in the literature are discussed and compared with the present results.

IN roughly the last ten years, there has been a great deal of work on the effect of pressure on superconductors. There have been various experimental investigations¹⁻¹⁷ of the behavior of the superconducting

transition temperature (T_c) as well as a number of phenomenological analyses^{4,5,12,13,16,18} which have tried to describe the systematics of the behavior of T_c with pressure. There has, however, been no serious attempt to try to understand the pressure dependence from a detailed consideration of the interactions involved. In this paper the pressure dependence of T_c for nontransi-

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¹ P. F. Chester and G. O. Jones, *Phil. Mag.* **44**, 1281 (1953).

² L. D. Jennings and C. A. Swenson, *Phys. Rev.* **122**, 459 (1961).

³ D. H. Bowen and G. O. Jones, *Proc. Roy. Soc. (London)* **A254**, 522 (1960).

⁴ Heinrich Rohrer, *Helv. Phys. Acta* **33**, 675 (1960).

⁵ J. L. Olsen and H. Rohrer, *Helv. Phys. Acta* **33**, 872 (1960).

⁶ M. Garfinkel and D. E. Mapother, *Phys. Rev.* **122**, 459 (1961).

⁷ Werner Buckel and Wolfgang Gey, *Z. Physik* **176**, 336 (1963).

⁸ N. B. Brandt and N. I. Ginzburg, *Zh. Eksperim. i Teor. Fiz.* **44**, 1876 (1963) [English transl.: *Soviet Phys.—JETP* **17**, 1262 (1963)].

⁹ D. H. Bowen, *High Pressure Physics and Chemistry*, edited by R. S. Bradley (Academic Press Inc., New York, 1963), Chap. 5. V.

¹⁰ J. L. Olsen, E. Bucher, M. Levy, J. Muller, E. Corenzwit, and T. Geballe, *Rev. Mod. Phys.* **36**, 168 (1964).

¹¹ M. Levy and J. L. Olsen, *Solid State Commun.* **2**, 137 (1964).

¹² N. B. Brandt and N. I. Ginzburg, *Usp. Fiz. Nauk.* **85**, 485 (1965) [English transl.: *Soviet Phys.—Usp.* **8**, 202 (1965)].

¹³ M. Levy and J. L. Olsen, *Physics of High Pressures and the Condensed Phase*, edited by A. van Itterbeek (North-Holland Publishing Co., Amsterdam, 1965), Chap. 13.

¹⁴ Jörg Wittig, *Z. Physik* **195**, 228 (1966).

¹⁵ N. B. Brandt and N. I. Ginzburg, *Zh. Eksperim. i Teor. Fiz.* **50**, 1260 (1966) [English transl.: *Soviet Phys.—JETP* **23**, 838 (1966)].

¹⁶ T. F. Smith and C. W. Chu, *Phys. Rev.* **159**, 353 (1967).

¹⁷ D. Köhnlein, *Z. Physik* **208**, 142 (1968).

¹⁸ V. L. Ginzburg, *Zh. Eksperim. i Teor. Fiz.* **44**, 2104 (1963) [English transl.: *Soviet Phys.—JETP* **17**, 1415 (1963)].

tion metals is calculated from an explicit microscopic formulation of the electron-phonon interaction. The results agree well with the available data and allow predictions as to what should happen at higher pressures.

The theory used contains the isotropic spherical model for the electron-phonon interaction which was successful in accounting for the electron concentration dependence of T_c in lanthanum selenide.¹⁹ The parameters entering the calculation are the valence, lattice parameter (a_0), Debye temperature (Θ_D), band mass, and strength of the core repulsion in the point-ion pseudopotential.²⁰ The first three are, of course, well known for the elements. The band mass (m_B) is determined from the specific-heat effective mass²¹ (m^*) and T_c by using McMillan's equation²²

$$T_c = \frac{\Theta_D}{1.45} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*}\right) \quad (1)$$

and

$$m^* = m_B(1+\lambda),$$

where λ is the electron-phonon coupling constant and μ^* the Morel-Anderson Coulomb repulsion.²³ One can eliminate λ and find

$$m_B = m^* \frac{1 - 0.62\mu^* - 1.04 \ln^{-1} 0.69 \Theta_D / T_c}{1 + 0.38\mu^*}. \quad (2)$$

The calculation of μ^* involves the known parameters, valence, a_0 and Θ_D , as well as the band mass m_B . The value of m_B is varied until a self-consistent value is found from Eq. (2) and the Morel-Anderson expression²³ for μ^* .

The pseudopotential used includes a δ -function repulsion at the nucleus in the point-ion potential which is taken directly from Harrison.²⁰

The one additional correction that must be made comes from the use of a jellium phonon spectrum in the calculation of λ . This spectrum is still used but the phonon frequencies are corrected for by a factor (see Ref. 19)

$$\sigma = \omega_j / \omega_q,$$

where ω_j is a jellium phonon frequency and ω_q should be a corresponding "real" phonon frequency determined in some way (e.g., by the measured sound velocity or Debye temperature). In this paper, however, σ is considered an undetermined parameter and is evaluated by fitting the theory to the measured zero pressure T_c to obtain the proper zero-pressure result.

¹⁹ P. E. Seiden, Phys. Rev. **168**, 403 (1968).

²⁰ W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

²¹ J. G. Daunt, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam, 1955), Vol. I, p. 202.

²² W. L. McMillan, Phys. Rev. **167**, 331 (1968).

²³ P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962).

PRESSURE DEPENDENCE

What I will actually calculate will be the volume dependence of T_c since this has a more fundamental meaning from the point of view of the theory of superconductivity. The experimental values of pressure to which the results will be compared will be converted to volume using the experimentally determined pressure dependence of volume.²⁴⁻³⁰

The parameters having a volume dependence are a_0 , Θ_D , and ω_q . The dependence of a_0 on volume for the cubic materials is, of course, trivial, for noncubic materials it is not so simple because the c/a ratio is not constant with pressure. This fact has been neglected here so that $a_0 \sim V^{1/3}$ is used in all cases. For the volume dependence of the phonon frequencies and Θ_D the Grüneisen³¹ approximation is used. The Grüneisen constant (γ) is given by

$$d \ln \omega = -\gamma d \ln V,$$

which is integrated to give

$$\omega = \omega_0 (V/V_0)^{-\gamma},$$

and similarly for Θ_D :

$$\Theta_D = (\Theta_D)_0 (V/V_0)^{-\gamma}.$$

This expression is used directly for the volume dependence of Θ_D . For the phonon frequencies, however, the volume dependence will be included in the parameter σ which also includes the factor ω_j . The volume dependence of ω_j is contained in the factor

$$\omega_j^2 \sim \frac{N q^2}{k_s^2} \sim \frac{V^{-1} V^{-2/3}}{V^{-1/3}} = V^{-4/3},$$

where N is the number of ions/cm³, q is the phonon wave vector, and k_s is the Fermi-Thomas screening constant. Therefore σ is taken to vary as

$$\sigma = \sigma_0 (V/V_0)^{\gamma-2/3}.$$

²⁴ P. W. Bridgman, Proc. Am. Acad. Arts Sci. **74**, 425 (1942); **76**, 1 (1945); **76**, 9 (1945); **76**, 55 (1948); **76**, 71 (1948); **77**, 189 (1949).

²⁵ M. H. Rice, R. G. McQueen, and J. M. Walsh, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6.

²⁶ R. G. McQueen and S. P. Marsh, J. Appl. Phys. **31**, 1253 (1960).

²⁷ L. V. Al'tshuler, S. B. Kormer, A. A. Bakanova, and R. F. Trunin, Zh. Eksperim. i Teor. Fiz. **38**, 790 (1960) [English transl.: Soviet Phys.—JETP **11**, 573 (1960)].

²⁸ S. B. Kormer, A. I. Funtikov, V. D. Urtin, and A. N. Kolesnikova, Zh. Eksperim. i Teor. Fiz. **42**, 686 (1962) [English transl.: Soviet Phys.—JETP **15**, 477 (1960)].

²⁹ L. V. Al'tshuler, A. A. Bakanova, and R. F. Turin, Zh. Eksperim. i Teor. Fiz. **42**, 91 (1962) [English transl.: Soviet Phys.—JETP **15**, 65 (1962)].

³⁰ H. G. Drickamer, R. W. Lynch, R. L. Clendenen, and E. A. Perez-Albuerna, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 19.

³¹ C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1966), 3rd ed., p. 183.

The pseudopotential core repulsion and the band mass are assumed to be volume-independent.

The strength of the volume dependence is then given by the Grüneisen parameter γ . The value of γ is not well known, especially at low temperatures, so it will be used as an adjustable parameter to fit the measured volume dependence of T_c . The values of γ

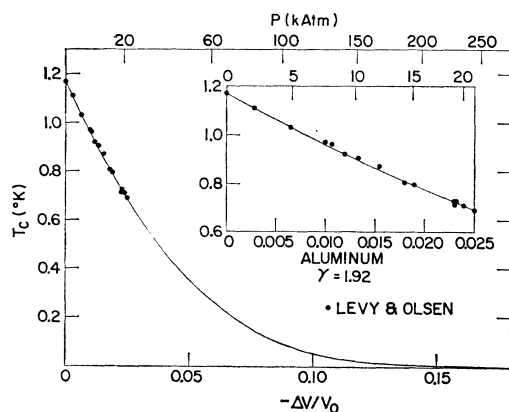


FIG. 1. Volume and pressure dependence of T_c for aluminum.

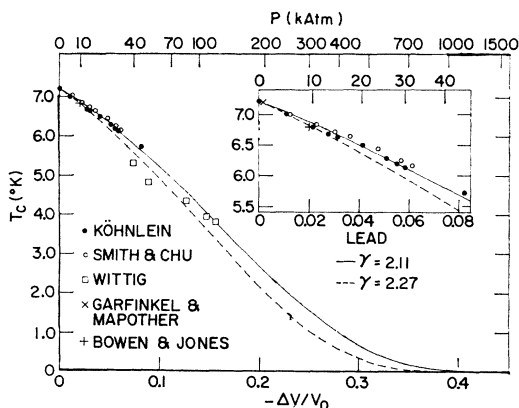


FIG. 2. Volume and pressure dependence of T_c for lead.

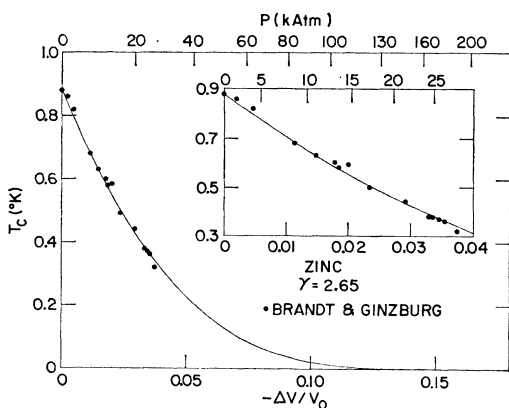


FIG. 3. Volume and pressure dependence of T_c for zinc.

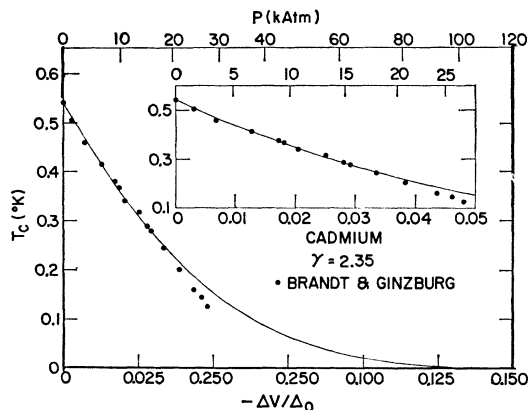


FIG. 4. Volume and pressure dependence of T_c for cadmium.

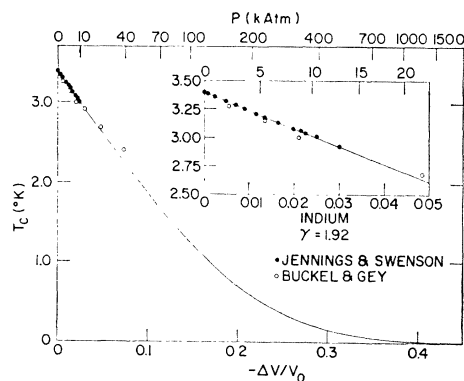


FIG. 5. Volume and pressure dependence of T_c for indium.

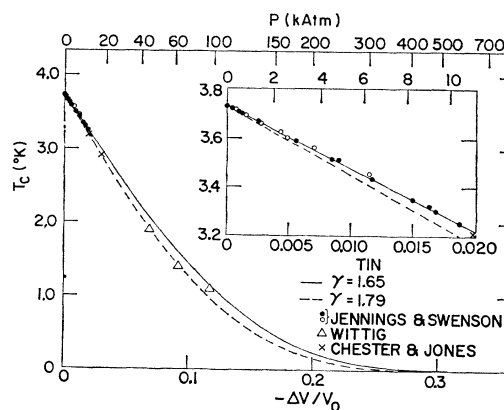


FIG. 6. Volume and pressure dependence of T_c for tin.

so determined will then be compared to the various measured values determined by other means.

The results are shown in Figs. 1–6. T_c is plotted as a function of $\Delta V/V_0$ ($\Delta V = V - V_0$) for aluminum, lead, zinc, cadmium, indium, and tin. The general agreement between theory and experiment is good; however, the experiments have not yet been taken far enough out of the region of linear behavior in $\Delta V/V_0$. The values of γ

used are given in Table I along with the measured values of γ . The values determined by fitting the pressure dependence lie within the range of measured values for all the metals except zinc and tin. For cadmium, although the value for γ is in the observed range, T_c appears to continue downward linearly beyond the point where the theory would predict (Fig. 4). The difficulty with these metals may lie in the failure to take the change in c/a into account but is most likely due to the fact that the isotropic jellium phonon spectrum is a worse approximation for noncubic metals than for cubic metals.

The measurements of Wittig¹⁴ should be most significant in comparing theory with experiment since they extend furthest into the nonlinear region. However, since the consistency of these data with the low-pressure data of others is not good, there is some doubt as to how really reliable are these data. In any case, for Pb and Sn two curves are plotted, one fitting the low-pressure data and the other Wittig's data.

Using the theoretical curves one can get a prediction of the volume and pressure at which T_c will go to zero. Table II gives the critical pressure and volumes for which $T_c = 5 \times 10^{-3}$ °K, which is the order of the lowest practical measurements at present (although perhaps not in conjunction with pressure measurements), and the values for which $T_c = 0$, that is, when the Coulomb repulsion equals the attractive electron-phonon interaction so that the net interaction ceases to be attractive. These pressures are generally quite high but are within the range of accessible low-temperature high-pressure experiments for zinc and cadmium and perhaps even aluminum. These estimates should probably be lower

TABLE II. Critical values and pressures.

	γ	$T_c = 5 \times 10^{-3}$ °K		$T_c = 0$ °K	
		$-\Delta V/V_0$	P (katm)	$-\Delta V/V_0$	P (katm)
Al	1.92	0.143	200	0.329	860
Pb	2.11	0.425	1200	0.587	5000 ^a
	2.27	0.387	900	0.543	3400
Zn	2.65	0.122	120	0.290	660
Cd	2.35	0.125	92	0.317	700
In	1.92	0.429	1600 ^a	0.758	50 000 ^a
Sn	1.65	0.297	410	0.540	3800
	1.79	0.269	320	0.484	2400

^a Extrapolated values from existing $V = f(P)$ data at lower pressures.

limits since at high pressures γ decreases as pressure increases.²⁶⁻²⁸ This should not seriously affect the values for the lowest critical volumes and pressures since at these modest values the changes in γ are small. The data for cadmium, in fact, suggest that the critical volume and pressure should be even less than that given in Table II.

EMPIRICAL RELATIONS FOR PRESSURE DEPENDENCE OF T_c

There have been a number of empirical relations for the volume and pressure dependence of T_c that have been constructed from observation of the consistencies in the data between different elements.

Smith and Chu¹⁶ pointed out that for a great majority of the data one can write

$$\frac{T_c(V)}{T_c(V_0)} = 1 + K \frac{\Delta V}{V_0}.$$

This relation can be obtained from the present theory by expanding in a Taylor series about V_0 . From Figs. 1-6 it is clear that the theory does indeed give a linear region in $\Delta V/V_0$ for small $\Delta V/V_0$. As pointed out previously, the data do not yet extend appreciably into the nonlinear region; however, considering the form of the interaction¹⁹ it is not reasonable to expect this linear dependence to continue for large $\Delta V/V_0$.

A second relation was suggested by Rohrer.^{4,5,12,13} If we take the BCS³² equation

$$T_c = \Theta_D e^{-1/N(0)U},$$

we can differentiate T_c/Θ_D with respect to V and obtain

$$\frac{d \ln(T_c/\Theta_D)}{d \ln V} = \ln \frac{\Theta_D}{T_c} \frac{d \ln[N(0)U]}{d \ln V}.$$

If the derivative on the right-hand side is now evaluated from the experimental pressure-dependence data, one

TABLE I. Grüneisen parameters.

	Present work	Grüneisen relation			Slater-Bridgman relation (a)	Shock wave dynamic (b)	Dugdale-McDonald
		Lattice Room temp.	Electronic Low temp.	low temp.			
Al	1.92	2.18 ^a	2.6 ^c	1.8 ^c	1.96		1.87 ^d
		2.35 ^{e,f}	2.3 ^c	2.0 ^c			2.09 ^g
Pb	2.11	2.84 ^a	2.6 ^c	1.7 ^c	1.12	2.77	2.03 ^b
	2.27	2.65 ^a	2.4 ^c	0.8 ^c			2.64 ^b
							2.46 ^g
Zn	2.65	2.05 ^a			2.15	2.45	2.12 ^b
							2.11 ^b
Cd	2.35	2.30 ^a	2.7 ^c	0.7 ^c	2.10	2.32	2.34 ^b
		2.34 ^e					2.22 ^b
In	1.92	2.48 ^a			1.60		
Sn	1.65	2.27 ^a			1.85	2.11	1.95 ^b
	1.79	2.15 ^b					2.01 ⁱ

^a Karl A. Gschneidner, Jr., in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 16.

^b See Ref. 26.

^c G. K. White, in *Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962*, edited by R. O. Davies (Butterworths Scientific Publications Ltd., London, 1963), p. 394.

^d See Ref. 28.

^e K. Andres, *Physik Kondensierten Materie* 2, 294 (1964).

^f D. B. Fraser and A. C. Hollis Hallett, in *Proceedings of the Seventh International Conference on Low-Temperature Physics, 1960*, edited by G. M. Graham and A. C. Hollis Hallett (University of Toronto Press, Toronto, 1960), p. 689.

^g See Ref. 27.

^h See Ref. 29.

ⁱ J. J. Gilvarry, *J. Chem. Phys.* 23, 1925 (1955).

³² J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* 108, 1175 (1957).

TABLE III. Comparison with Rohrer's model.

	ϕ Ref. 13	γ	λ	μ^*	ϕ Eq. (3)
Al	3.7	1.92	0.392	0.104	2.7
Pb	2.0	2.11	1.080	0.082	1.6
Zn	2.2	2.65	0.383	0.087	4.0
Cd	3.2	2.35	0.363	0.085	3.5
In	2.3	1.92	0.688	0.087	1.8
Sn	2.3	1.65	0.574	0.089	1.6

finds that it is a constant, so that

$$\frac{d \ln(T_c/\Theta_D)}{d \ln V} = \phi \ln(\Theta_D/T_c),$$

where

$$\phi = \frac{d \ln[N(0)U]}{d \ln V} \simeq 2.5.$$

In the present theory the equivalent of $N(0)U$ is approximately [Eq. (1)]

$$N(0)U \rightarrow \frac{\lambda - \mu^*}{1 + \lambda}.$$

Using the dependence on volume discussed in the previous section, an explicit expression can be found for ϕ :

$$\phi = (2\gamma - \frac{4}{3}) \frac{\lambda}{1 + \lambda} \frac{1 + \mu^*}{\lambda - \mu^*}. \quad (3)$$

Table III shows the value of these parameters along with the Levy-Olsen¹³ values for ϕ . They are all in the same range and vary around an average value of about 2.5. It is difficult to read any significance into Eq. (3) and it appears that the reason for the relative constancy of ϕ is just the nature of the result; γ is of the same order for all the elements and since, in general, $\lambda \leq 1$ and $\lambda \gg \mu^*$ the factor involving λ and μ^* is of the order of 0.75 ± 0.25 , so that ϕ is relatively insensitive to the variation of these parameters.

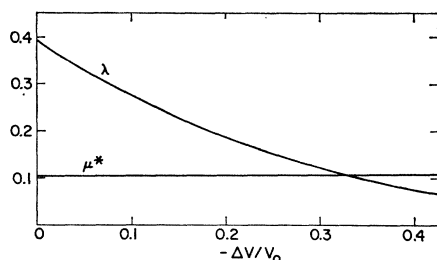


FIG. 7. Volume dependence of the electron-phonon and Coulomb repulsion coupling constants in aluminum.

The third form suggested by Ginzburg,¹⁸ based upon the theory of second-order phase transitions, is

$$T_c = a e^{-b/(P_c - P)},$$

where P_c is a critical pressure for the destruction of superconductivity. The present theory does not fall easily into an expression of this form. For cadmium, however, which is the metal to which Ginzburg's expression has been applied,¹² it can be seen that the form is reasonable. For cadmium we can simplify Eq. (1) to

$$T_c \sim e^{-1/(\lambda - \mu^*)}. \quad (4)$$

Now from Fig. 7 it is seen that the pressure dependence of μ^* is negligibly small compared to λ , so that μ^* can be replaced by λ_c , that is, the λ at which $T_c = 0$. Then using a power law for λ (which is the case in the present theory where $n = 2\gamma - \frac{4}{3}$),

$$\lambda = \lambda_0 (V/V_0)^n,$$

and Bridgman's relation²⁴ for volume as a function of pressure,

$$V/V_0 = 1 - \alpha P + \beta P^2,$$

one gets

$$\lambda \simeq \lambda_0 (1 - n\alpha P)$$

limited to linear terms in P (P_c for cadmium is 80 katm, so that this is not too bad). Then Eq. (4) becomes

$$T_c \sim \exp\left(\frac{-1}{\lambda_0(1 - n\alpha P) - \lambda_0(1 - n\alpha P_c)}\right) = \exp\left(\frac{-1/n\alpha\lambda_0}{P_c - P}\right),$$

the Ginzburg form.

CONCLUSIONS

The theory accounts very reasonably for the observed pressure dependence of T_c . However, the presently available data are mostly in the linear region, so that a really good test is not yet possible. It would be of interest to have higher pressure measurements in the cases of Zn, Cd, and Al, where it should be possible to get into the nonlinear range. In the case of the hexagonal metals, it should even be possible to decrease T_c to zero (at least below presently attainable temperatures). One could improve the calculations in a number of ways; in particular, it is possible to account for the fact that $\gamma = f(P)$ and to use a more reasonable model for the properties of a noncubic lattice. Upon the appearance of more extensive data these improvements would be well worth undertaking. The discussion of the various empirical models shows why they reasonably fit the cases to which they have been applied but shows up their limitations as relations which one can use for prediction into unknown regions.