ing evidence that is the correct model for this case. We have looked at some lead–tin alloys, solid solution alloys, where first of all the transition is frequency dependent. The higher the frequency at which you make your measurement the higher the apparent transition temperature; this is because frequency and conductivity are interchangeable in this mechanism. If you make the measurements by a ballistic galvanometer technique the transition will occur about 0.02°K degrees lower than the measurement at 18 cps. Finally on the same alloys Shiffman, Cochran, and Garber have made specific heat measurements and find that the transition occurs at a temperature still lower than that determined by the ballistic galvanometer. So the only reasonable explanation is that you have a distribution of filaments which show up first in the ac technique, next in the ballistic technique when they close, and finally at some lower temperature the bulk matrix goes superconducting which is what specific heat measurement shows.

COLES: Dr. Park will be presenting detailed comparison of magnetization curves and ac transition for Sn–In alloys which show effects quite similar to those mentioned by Dr. Maxwell.

T. H. GEBALLE, *Bell Telephone Laboratories:* With respect to Maxwell's comment on the transition temperatures being different when measured different ways, we have data on 1% Fe in Ti. The ac transition and the heat capacity transition as measured by Phillips at Berkeley occur over the same temperature interval. There is no direct evidence for the existence of any beta phase.

Superconductivity under Pressure

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The effect of pressure p on the critical field H_c of superconductors has been extensively investigated experimentally, and the general features are well understood. It is found that $\partial H_c/\partial p$ depends in a simple way upon the shape of the critical field curve and upon the pressure derivatives of T_c and of the normal state electronic specific heat.

The pressure dependence of the electronic specific heat is a function of the sensitivity of the electronic band structure to volume changes, and is independent of the superconductive properties of the metal. The pressure dependence of T_c, on the other hand, is a characteristic of the mechanism of superconductivity, and should be predictable from the theory of superconductivity.

An examination of the well-known expression

$$T_c = 0.85\,\theta_D \exp\left[-1/N(0)V\right] \qquad (1)$$

for the transition temperature given by Bardeen, Cooper, and Schrieffer shows that the volume dependence of T_c is a function of the volume dependences of the Debye temperature θ, of the electronic density of states at the Fermi surface $N(0)$, and of the interaction parameter V.

The volume dependence of θ is given by the Grüneisen constant γ_G, and the volume dependence of $N(0)V$ has been shown by Rohrer[1] to obey a remarkably simple empirical law in superconductors which are not transition metals or rare earths. In the metals for which data were available to Rohrer (In, Sn, Hg, Pb, Al) he found that

$$\partial \ln N(0)V/\partial \ln v = 2.5 \pm 0.5\,. \qquad (2)$$

Thallium, which is exceedingly anisotropic in its properties, was found to be an exception, however.

It was also found that this simple relation broke down for the transition metals for which the pressure dependence was known, and we have pointed out[2,3] that this failure is in some way connected with the absence of an isotope effect in osmium and ruthenium noticed by Geballe, Matthias, Hull, and Corenzwit,[4] and by Geballe and Matthias.[5]

The nature of this connection remains uncertain, however, and we have thought it useful to collect pressure effect data on additional metals in order to help establish its nature. The form of the expression obtained by differentiation of (1) with respect to volume makes it particularly desirable to examine other metals with small values of T_c/θ.

We have recently investigated the change in tran-

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[2] K. Andres, J. L. Olsen, and H. Rohrer, IBM J. Res. Develop. **6**, 84 (1962).

[3] E. Bucher and J. L. Olsen, *Proceedings of the 8th International Conference on Low Temperature Physics, 1962.*

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

[5] T. H. Geballe and B. T. Matthias, IBM J. Res. Develop. **6**, 256 (1962).

TABLE I. Pressure effect in Mo, Th, and Ga.

Metal	$\partial T_c/\partial p$ (deg dyn^{-1} cm^2 $\times 10^{11}$)	$\partial \ln (T_c/\theta)/\partial \ln v$	κ (dyn cm^{-2} $\times 10^{-11}$)	T_c (°K)	θ_D (°K)	γ_G[a]
Mo	-0.1 ± 0.1	4	26.	0.91	425	1
Th	-1.7 ± 0.2	8.3	5.8	1.33	142	1
Ga	-1.8 ± 0.3	10.3	5.0	1.09	240	2

[a] Estimated.

sition temperature with pressure using an ice bomb method to create the pressure in Ga, Mo, and Th, and Andres[6] has been able to deduce $\partial T_c/\partial p$ for the face centered cubic phase of Lanthanum from thermal expansion data.

Our new results are summarized in Table I together with the values of the various constants used to calculate $\partial \ln (T_c/\theta)/\partial \ln v$. It should be noted that in some cases the tabulated values of κ required to calculate $\partial \ln (T_c/\theta)/\partial \ln v$[7] are old and unreliable. The changes in T_c with pressure in the transition metals are small and it is difficult to obtain specimens of sufficient purity to show really sharp transitions. In consequence the probable errors of the results are fairly large.

Table II contains a complete collection of known values of $\partial \ln T_c/\partial \ln v$, and of values of $\varphi =$

$$\partial \ln N(0) V/\partial \ln v$$

calculated using the expression

$$\frac{\partial \ln (T_c/\theta)}{\partial \ln v} = \ln \frac{0.85\,\theta}{T_c} \left\{\frac{\partial \ln N(0) V}{\partial \ln v}\right\} = \ln \frac{0.85\,\theta}{T_c}\varphi . \quad (3)$$

We also list the deviations ζ from the full isotope effect where ζ is defined by

$$T_c \propto M^{-0.5(1-\zeta)} . \quad (4)$$

ζ has only been observed experimentally for three transition metal superconductors, but Swihart[8], Morel and Anderson[9] and Garland[10] have recently made calculations which give ζ for those metals where this property is known, and predicting ζ for a number of other superconductive metals.

It will be seen that $\partial \ln N(0) V/\partial \ln v \equiv \varphi \approx 2.5$, where $\zeta = 0$ while it is -2 for ruthenium where $\zeta = 1$. For molybdenum, where $\zeta = 0.25$[11] $\varphi \approx +0.5$. There thus appears to be some correlation between φ and ζ. This trend is seen clearly in Fig. 1, where we have plotted φ against Garland's values of ζ.

[6] K. Andres, Phys. Kondens. Materie (to be published).
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TABLE II. Pressure effect and isotope effect.

Metal	$\partial \ln (T_c/\theta)/\partial \ln v$[a]	$\ln (\theta/T_c)$	φ	ζ_{Garland}[b]	ζ_{obs}
Nb	1.5	3.3	.45	...	...
Pb	5.3	2.7	2.0	0.06	0
La (fcc)	6.7	3.2	2.3	...	...
V	− 0.6	4.3	− .14	0.7	...
Ta	3	4.1	.52	0.3	...
αHg	5	2.8	1.8	0.07	0
βHg	7.5	3.2	2.4	...	...
Sn	9.1	4.0	2.3	0.12	0
In	8.0	3.5	2.3	...	...
Tl	0	3.7	0	0.11	0
Re	5.8	5.5	1.1	0.4	...
Th	8.3	4.7	1.8	...	...
Al	22	5.9	3.7	0.31	...
Ga	10.3	5.4	1.9	...	...
Zn	12	5.6	2.2	0.20	0
Mo	4	6.2	.65	0.3	0.25
Cd	19	5.9	3.3	0.27	0
Ru	−16	6.7	−2.4	1.0	1.0

[a] Data from Table I and from various authors. For detailed references see Refs. 6 and 7.
[b] See Ref. 11.

If this is a real effect, then we would expect to observe a normal isotope effect in lanthanum and thorium, and a partial one in niobium. Since, unfortunately, each of these metals only has one reasonably abundant stable isotope, our values of φ may be the only experimental check on any future theoretical estimate of ζ.

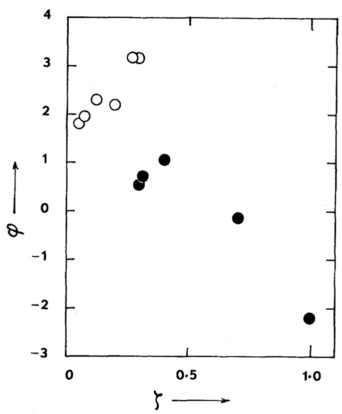

FIG. 1. Plot of experimental values of $\varphi = \partial \ln N(0)\, V/\partial \ln v$ against Garland's value of ζ. ● transition metals, ○ other metals.

Table II shows that φ does not vary much among the simple nontransition elements. If this is so, then it is to be expected that it will be approximately constant for a given metal under a wide range of pressure unless some new areas of Fermi surface overlap are established at the Brillouin zones by high pressures. In this case we may integrate (3) taking φ as a constant and obtain

$$\ln (T_c/\theta) \propto v^{-\varphi}. \quad (5)$$

We may therefore expect that the $T_c - v$ relation will no longer be linear, but that T_c will only approach zero asymptotically with decreasing volume instead of falling to zero at a particular pressure.

We chose aluminium as a particularly suitable substance in which to look for this effect. Measurements have now been made to pressures of 20 000 atm which reduce T_c to 0.71° K. We find that there is a clear deviation from linearity, and that this deviation is in fact that predicted by our expression (5).

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Orbital Paramagnetism and the Knight Shift in Transition Metal Superconductors

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INTRODUCTION

One of the consequences of the BCS[1] microscopic theory of superconductivity is that the spin susceptibility of the conduction electrons will vanish exponentially as the reduced temperature, T/T_c approaches zero.[2] (This is shown in Fig. 1.) This follows from the fact that all states are chosen to be eigenstates of the total spin and that the ground state of the superconductor is one for which the expectation value of the spin is zero. Since the remaining states are removed in energy by an amount Δ (the energy gap) it requires, as a minimum, an amount of energy 2Δ to excite a Cooper pair to those states for which $\langle |S_Z| \rangle \neq 0$.

It is, therefore, of some interest to measure the temperature dependence of the spin paramagnetism

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[2] K. Yosida, Phys. Rev. **110**, 769 (1958).