

TABLE I.  $g$ -Value of  $\text{NiOF}_2\text{O}_3$ .

Form of specimen	Wave-length	
	7.5 cm	3.2 cm
Disk	$2.05 \pm 0.07$	$2.26 \pm 0.02$
Sphere	$2.02 \pm 0.10$	$2.26 \pm 0.02$

field accurately when the 3-mm sphere was used, owing to the marked drop of the  $Q$ -value of a resonance cavity.

The  $g$ -value of  $\text{NiOF}_2\text{O}_3$  obtained is shown in Table I.

It was ascertained experimentally that the wave-length becomes shorter as the  $g$ -value becomes greater. Kittel<sup>6</sup> has discussed such a frequency dependence on the  $g$ -value for some metals, but the phenomenon should be studied further using a semiconductor, which has a deeper skin-depth.

<sup>1</sup> W. H. Hewitt, Jr., Phys. Rev. **73**, 1118 (1948).

<sup>2</sup> Recently published in Sci. Rep. RTU.

<sup>3</sup> C. Kittel, Phys. Rev. **73**, 155 (1948).

<sup>4</sup> E. W. Gorter, Nature **165**, 789 (1950).

<sup>5</sup> H. G. Beljers and D. Polder, Nature **165**, 800 (1950).

<sup>6</sup> C. Kittel, Phys. Rev. **76**, 743 (1949).

## Microwave Spectroscopic Evidence for Internal Rotation in Methyl Silane

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WHILE thermodynamic evidence for the existence of internal rotation in molecules is conclusive, there are some questions as to the nature of the hindering potential barrier. This has recently been emphasized by Blade and Kimball,<sup>1</sup> who introduced a shape parameter into an assumed potential barrier, and found that the best modern thermodynamic data were inadequate for distinguishing between widely different barrier shapes and heights. Raman and infra-red spectroscopic studies have also proved somewhat inconclusive—partly because of the limited resolution obtainable in the visible and infra-red regions of the spectrum. Fortunately, microwave absorption lines associated with different stages of torsional vibration can be resolved easily. By careful intensity measurements of these absorption lines, it seems possible to determine the energy levels and therefrom the barrier height and shape rather accurately.

Probably the lightest symmetric-top molecule which is capable of internal rotation and of absorbing in the microwave region is  $\text{H}_3\text{C}-\text{SiH}_3$  (methyl silane). We find that the  $J=0 \rightarrow 1$  transition of this molecule has the interesting appearance shown in Fig. 1a. Here the more highly excited levels of torsional oscillation are seen to be split into two components, in agreement with the theory of internal rotation.<sup>2</sup> The spectrum of the deuterated compound (Fig. 1b) has a similar appearance, except for the relative intensities of the two components of a doublet. The statistical weight associated with each of these components, which depends on the nuclear spin of the two sets of equivalent nuclei, can be found by calculating the weight for each end of the molecule separately, as if it were rotating with perfect freedom, and then multiplying the two weights together to get that for the state of hindered rotation.

In the notation of reference 2, the two components of the normalized statistical weight  $g_I$  are  $3/4$  and  $3/8$  for  $\text{CH}_3\text{SiH}_3$ , giving a total of  $9/8$ , while for  $\text{CH}_3\text{SiD}_3$  the component weights are  $11/18$  and  $8/18$ , giving a total of  $19/18$ . For molecules with large nuclear spins of the equivalent nuclei, the component weight factors  $g_I$  would be  $1/3$  and  $2/3$  respectively.

In order to study the splitting for molecules with over-all axial rotation, we examined the spectrum corresponding to the transition  $J=1 \rightarrow 2$ ,  $K=1 \rightarrow 1$ . In agreement with the prediction of Koehler and Dennison for this case,<sup>3</sup> these torsional vibrational levels appeared to be split into three components.

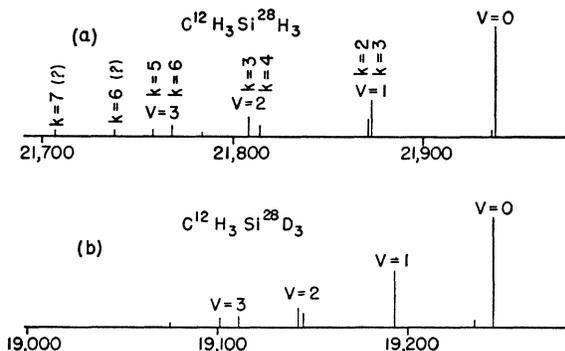


FIG. 1. The  $J=0 \rightarrow 1$  transitions in methyl silane.

The rotational constants  $B_0$  for different isotopic species of methyl silane are found to be:

$\text{CH}_3\text{Si}^{28}\text{H}_3$ —10,968.96 Mc	$\text{CH}_3\text{Si}^{28}\text{D}_3$ —9622.78 Mc
$\text{CH}_3\text{Si}^{29}\text{H}_3$ —10,885.54 Mc	$\text{CH}_3\text{Si}^{29}\text{D}_3$ —9572 Mc
$\text{CH}_3\text{Si}^{30}\text{H}_3$ —10,806.53 Mc	$\text{CH}_3\text{Si}^{30}\text{D}_3$ —9525 Mc.

Stark effect measurements show that this molecule has a dipole moment of 0.73 Debye.

Intensity measurements were attempted on absorption lines corresponding to different stages of torsional vibration and internal rotation. We used sinusoidal Stark effect modulation at 85 kc, two stages of 85 kc amplification, and then a calibrated r-f attenuator. Comparing two lines with the same statistical weight, the intensity ratio provided a measure of the corresponding energy level spacing, at the rate of  $15.6 \text{ cm}^{-1}$  per decibel of attenuation (temperature of dry ice). Preliminary values of the energy level spacings above the ground level are:

Level	$V=1$	$V=2$	$V=3, k=5$	$V=3, k=6$
Energy ( $\text{cm}^{-1}$ )	183	313	415	465

These values are consistent with Blade and Kimball's two-parabola potential, where  $V_0/V_{\cos} = 1$ ,  $V_0 = 460 \pm 80 \text{ cm}^{-1}$ . With improvements to eliminate standing waves in the absorption cell, we believe that the barrier shape and height can be determined within  $20 \text{ cm}^{-1}$ .

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<sup>1</sup> E. Blade and G. E. Kimball, J. Chem. Phys. **18**, 630 (1950).

<sup>2</sup> D. K. Coles, *Advances in Electronics*, Vol. II (Academic Press, New York, 1950), p. 335.

<sup>3</sup> J. S. Koehler and D. M. Dennison, Phys. Rev. **57**, 1006 (1940).

## An Empirical Correlation Among Superconductors

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THE recent experimental results of Maxwell<sup>1</sup> and of Reynolds, Serin, Wright, and Nesbitt<sup>2</sup> on the change in the superconducting transition temperatures of Hg and Sn with change in isotopic mass has served to re-emphasize the important role of the lattice in determining electronic superconductivity, a feature of the phenomenon which was also evident from the marked observable effects of mechanical stress on the transition temperatures.<sup>3</sup> Moreover, these experiments on isotopic changes, being such that one clearly evident parameter is varied, afford an elegant check on theory, such as has been carried out for example recently by Bardeen<sup>4</sup> and Froehlich.<sup>5</sup>

On the other hand, the electronic character of the phenomenon also shows certain regularities among the superconducting pure metals and in view of the increased recent theoretical attention

TABLE I. Tabulated data for the superconductors.\*

Element	$T_c$ (°K)	$V$ (cc)	$(\gamma \times 10^4)^{**}$	$(\gamma \times 10^4)^{***}$	$\Theta$ (°K)
"Soft" Superconductors					
Pb	7.22	18.2	7.1 <sup>a, b</sup>	—	90 <sup>i</sup>
Hg	4.15	13.4	3.75 <sup>a</sup> —4.5 <sup>c</sup>	—	96 <sup>i</sup>
Sn	3.71	16.2	3.45 <sup>a</sup> —3.95 <sup>b</sup>	4.0 <sup>d</sup>	185—260 <sup>i</sup>
In	3.38	15.8	3.5 <sup>b</sup> —3.6 <sup>e</sup>	—	110
Tl	2.4	17.3	2.8 <sup>b</sup> —3.4 <sup>c</sup>	—	90—100 <sup>i</sup>
Al	1.15	10.1	2.59 <sup>e</sup>	3.48 <sup>f</sup>	390—420 <sup>i</sup>
Ga	1.12	11.75	0.8 <sup>g</sup> —1.5 <sup>g</sup>	—	240
Zn	0.95	9.15	1.36 <sup>e</sup>	1.25 <sup>h</sup> —1.5 <sup>i</sup>	290—320 <sup>i</sup>
Cd	0.54	13.0	0.75 <sup>g</sup>	—	170 <sup>j</sup>
"Hard" Superconductors					
Th	1.3	20.5	7.1 <sup>k</sup>	—	170 <sup>j</sup>
Ta	4.4	10.9	14.1 <sup>l</sup>	—	240 <sup>j</sup>

\*  $T_c$  is the transition temperature,  $V$  is the atomic volume,  $\gamma$  is the normal electronic specific heat coefficient, and  $\Theta$  is the Debye temperature.

\*\*  $\gamma$  is given in units of cal./mole-deg.<sup>2</sup>. The values in this column for the soft superconductors are obtained from magnetic measurements of the threshold curves.

\*\*\*  $\gamma$  is given in units of cal./mole-deg.<sup>2</sup>. The values in this column for the soft superconductors are obtained from calorimetric measurements.

<sup>a</sup> J. G. Daunt and K. Mendelsohn, Proc. Roy. Soc. A160, 127 (1937).

<sup>b</sup> Daunt, Horseman, and Mendelsohn, Phil. Mag. 27, 754 (1937).

<sup>c</sup> A. D. Misener, Proc. Roy. Soc. A174, 262 (1940).

<sup>d</sup> W. H. Keesom and P. H. Van Laer, Physica 5, 193 (1938).

<sup>e</sup> J. G. Daunt and C. V. Heer, Phys. Rev. 76, 1324 (1949).

<sup>f</sup> J. A. Kok and W. H. Keesom, Physica 4, 835 (1937).

<sup>g</sup> Results to be reported subsequently.

<sup>h</sup> W. H. Keesom and J. N. van den Ende, Proc. Amst. Akad. Sci. 35, 143 (1932).

<sup>i</sup> A. A. Silvidi and J. G. Daunt, Phys. Rev. 77, 125 (1950).

<sup>j</sup> Burton, Grayson-Smith, and Wilhelm, *Phenomena at the Temperature of Liquid Helium* (Reinhold Publishing Corporation, New York, 1940), p. 347.

<sup>k</sup> Calculated from Eq. (2) using Schoenberg's data, reference 7.

<sup>l</sup> From calorimetric data of Keesom and Desirant, reference 8.

paid to the problem of superconductivity it is thought worth while to point out one empirical correlation which concerns the electronic structure.

Recent measurements<sup>6</sup> of the magnetic properties of pure Ga and Cd in the superconducting state below 1°K have completed all the data necessary for the calculation of the electronic specific heat of the normal state ( $C_{el} = \gamma T$ ) for all the known "soft" superconductors. In Table I, the Sommerfeld  $\gamma$ -values have been tabulated together with other pertinent data for the superconductors. It is to be noticed that the  $\gamma$ -values increase approximately linearly with increasing transition temperature,  $T_c$ , such that

$$\gamma = AT_c \quad (1)$$

where  $A \approx 1 \times 10^{-4}$  cal./mole-degree<sup>2</sup>. Al, however, appears to be exceptional, but in view of its high Debye temperature as compared with the other soft superconductors, it may not be strictly permissible to class it in the same grouping.

No similar complete data can be tabulated for the hard superconductors since with the possible exceptions of thorium measured magnetically by Schoenberg<sup>7</sup> and of Ta measured calorimetrically by Keesom and Desirant,<sup>8</sup> either their observed magnetic threshold curves do not represent a reversible equilibrium boundary between the normal and superconductive states thus allowing no reliable derivation of  $\gamma$  or no calorimetric observations at low temperatures have been made. The pertinent data for Th and Ta are included in Table I, the  $\gamma$ -value for Th being calculated from Schoenberg's data<sup>7</sup> using the equation that can be derived for  $\gamma$  from Gorter and Casimir's thermodynamical theory<sup>9</sup> assuming a parabolic magnetic threshold curve, namely

$$\gamma = (V/8\pi)(dH_c/dT)^2 T = T_c. \quad (2)$$

From Table I it can be deduced that if the  $\gamma$ -values of Ta and Th satisfied an equation of type (1), it would be with a value of the constant  $A$  more than three times larger than that for the soft superconductors. More data here would be of value; for example, calorimetric measurements of  $\gamma$  for such readily obtainable metals as Nb, V, and Ti would be of interest.

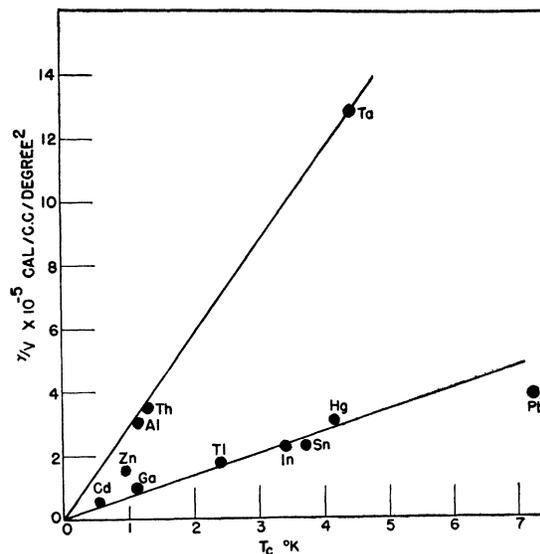


FIG. 1. Variation of  $\gamma/V$  with  $T_c$ , showing the division into "hard" and "soft" superconductors.

As a first approximation it would be expected that the interaction energy between the electrons responsible for the condensation into the superconductive state would increase with increasing number density of electrons and hence on the Sommerfeld theory<sup>10</sup> with the quotient  $\gamma/V$  where  $V$  is the atomic volume. It seemed to be of interest, therefore, to examine the empirical relationship between  $kT_c$  and  $\gamma/V$ . A plot of the experimentally observed values of  $\gamma/V$  against  $T_c$  is given in Fig. 1, for the elements listed in Table I, the  $\gamma$ -values being taken as the mean of those listed in the above tables. It will be seen that with exception of Zn the elements fall along two approximately straight lines, one for the soft superconductors and another for the hard superconductors (which group appears to include Al). The difference between the groups is not surprising in view of the known differences in their electronic band structures.

<sup>1</sup> E. Maxwell, Phys. Rev. 78, 477 (1950); 79, 399 (1950).

<sup>2</sup> Reynolds, Serin, Wright, and Nesbitt, Phys. Rev. 78, 487 (1950).

<sup>3</sup> G. J. Sizoo and H. K. Onnes, Leiden Communications, Nos. 133 and 180b; N. Alekseyevsky, J. Phys. U.S.S.R. 9, 147 (1945); B. Lasarew and A. Galkin, J. Phys. U.S.S.R. 8, 376 (1944).

<sup>4</sup> J. Bardeen, Phys. Rev. 79, 167 (1950).

<sup>5</sup> H. Froehlich, Phys. Rev. 79, 845 (1950).

<sup>6</sup> J. G. Daunt, to be reported later.

<sup>7</sup> D. Schoenberg, Proc. Camb. Phil. Soc. 36, 84 (1940).

<sup>8</sup> W. H. Keesom and M. C. Desirant, Physica 8, 273 (1941).

<sup>9</sup> C. J. Gorter and H. G. B. Casimir, Physica 1, 305 (1934).

<sup>10</sup> A. Sommerfeld, Zeits. f. Physik 47, 1 (1928).

## On the Cohesive Energy of Metallic Lithium

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ON the basis of the Wigner-Seitz atomic sphere approximation, Bardeen<sup>1</sup> has evaluated the first two terms of a series expansion for the energy  $E(k)$  of an electron with wave number  $k$  moving in the lattice of metallic Li. He found that  $E(k) = E_0 + E_2 k^2 + E_4 k^4 + \dots$ , where  $E_0 = -0.6635$  and  $E_2 = 0.6539$  for the experimentally determined lattice constant<sup>2</sup> of 3.4492 Å. Bardeen's calculations were based on the Li ion-core potential published by