

Resonances due to transmission were detected in samples up to  $150 \mu$  thickness, where the signal to noise after narrow-banding was about 3:1. A plot of the signal intensity versus thickness is shown in Fig. 2, where the slope corresponds to an attenuation length of  $16 \mu$ , in excellent agreement with the calculated value of  $\delta_e/\sqrt{2} = 15.5 \mu$ . Signals of equal magnitude were observed for both relative orientations of the cavities, verifying that the transmitted fields are circularly polarized.

Observation of spin resonances in metals other than the alkalis and beryllium has frequently been obscured by resonances from static impurities.<sup>2</sup> Resonance transmission should not be sensitive to the presence of static impurities and may aid in the search for spin resonance in other metals at low temperatures. Recent measurements in this laboratory of the relaxation time of conduction electrons in sodium indicate that  $T_2$  may be  $\geq 10^{-6}$  sec in the liquid hydrogen range.<sup>8</sup> Transmission experiments on thick samples of sodium may provide an alternative approach to the measurement of  $T_2$ . If resonance transmission can be observed in metals having anisotropic Fermi

surfaces, transmission experiments on single crystals may possibly be used to measure anisotropies in  $\delta_e$ .

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## THERMAL CONDUCTIVITY AT ELEVATED PRESSURE AND TEMPERATURE

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We report here some results obtained on the thermal transport properties of materials at pressures to 50 kbar and temperatures to  $600^\circ\text{C}$ . Phase diagrams of Bi and Te were determined using a differential thermal conductivity analysis<sup>1</sup> (DTCA) and are compared with data taken by other techniques. A theoretical method for determination of thermal conductivity at high pressure and temperature from experimental data is proposed and the results are used to compare qualitatively experimental and theoretical temperature gradients.

Although the idea of determining high-pressure phase boundaries using thermal conductivity changes has been presented before,<sup>1</sup> no method has been proposed which would have general applicability or permit the measurement of thermal conductivity. A coupling of the theoretical analysis and the generally applicable experimental technique reported here will permit simultaneous determination of both high-pressure phase

boundaries and thermal conductivities.

Experiments were performed using a tetrahedral anvil high-pressure apparatus and techniques which have been described previously.<sup>2,3</sup> The pyrophyllite tetrahedrons contained a cylindrical graphite heater, inside of which was placed the cylindrical sample and boron nitride container as shown in the inset of Fig. 1(b). A pair of chromel-alumel thermocouples served to monitor the temperature at the center of the sample ( $T_a$ ) and at a distance  $b$  from the center in the boron nitride ( $T_b$ ). DTCA measurements consist of observation of the temperature difference,  $\Delta T \equiv T_b - T_a$ , as a function of the center temperature,  $T_a$ . If the thermal conductivity of the sample,  $K_a$ , differs in magnitude each side of a phase boundary, the transition between phases will be reflected by a discontinuous shift in the temperature dependence of  $\Delta T$ . Examples of this behavior are shown by the solid curves in Fig. 2. The discontinuities observed correspond to melting

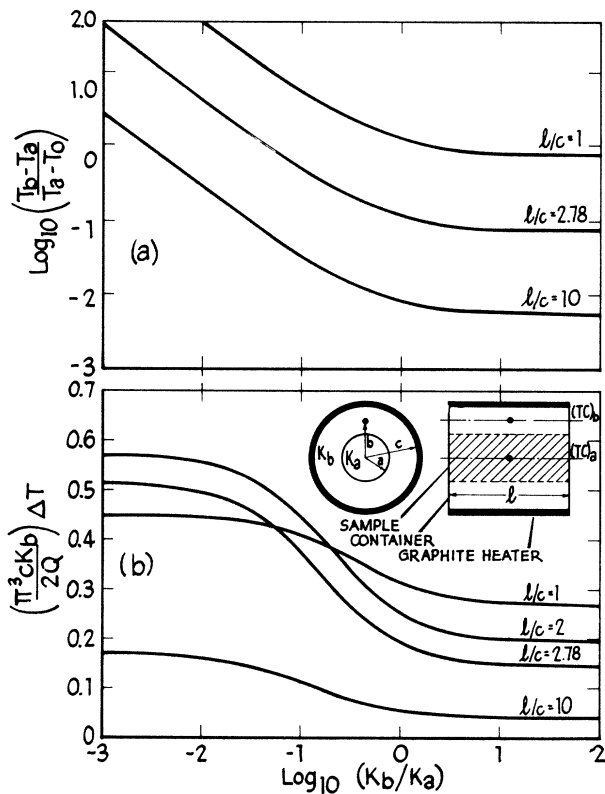


FIG. 1. (a) Theoretical dependence of  $R$  on the thermal conductivity ratio ( $K_b/K_a$ ). (b) Theoretical variation of  $\Delta T$  with ( $K_b/K_a$ ). Inset: high-pressure cell configuration where  $a=0.03$  in.,  $b=0.06$  in.,  $c=0.09$  in., and  $l=0.25$  in.

in each case.<sup>4,5</sup> Similar sharp displacements of  $\Delta T$  are observed at solid-solid transition boundaries, allowing a ready determination of pressure-temperature phase diagrams. Figure 3 shows the phase diagrams of Bi and Te found by this method. The DTCA data are compared with known data of indicated source<sup>6-8</sup> resulting from investigations using other techniques. We were unable to detect melting points of Te II which have been determined<sup>6</sup> by differential thermal analysis up to 50 kbar or the Bi III-IV transition indicated by Bridgman's volume measurements.<sup>9</sup>

We found DTCA to be simple and rapid compared to resistance measurements under pressure, as well as extending the application of our apparatus to electrical insulators. Preliminary measurements on Ba, S, Se, Bi, and Te indicate that the magnitudes of changes in  $\Delta T$  upon crossing a phase boundary are, in general, large and easy to measure.

Assuming the sample and container thermal conductivities ( $K_a$  and  $K_b$ ) are isotropic and

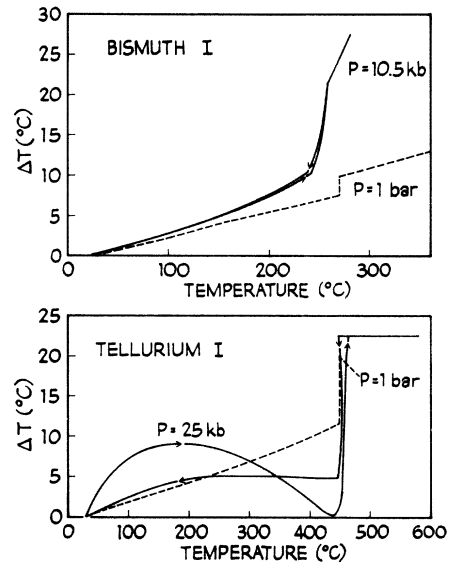


FIG. 2. Qualitative comparison of the experimental (solid curves) and theoretical (dashed curves) variation of  $\Delta T$  with temperature. Arrows indicate increasing and decreasing temperatures.

constant over the temperature range involved, the solution  $T(r, z)$  to Laplace's equation ( $\nabla^2 T = 0$ ) in cylindrical coordinates gives the theoretical temperature distribution in the high-pressure cell. Referring to the dimensions defined in Fig. 1(b), the appropriate boundary conditions are these: (1) a uniform radial heat flow  $Q$  at  $r=c$ ; (2) a constant temperature  $T_0$  at  $z=0$  and  $z=l$ ; and (3) a continuous temperature and radial heat flow at  $r=a$ . Using standard techniques<sup>10</sup>,  $T(r, z)$  was determined as a Fourier-Bessel expansion.

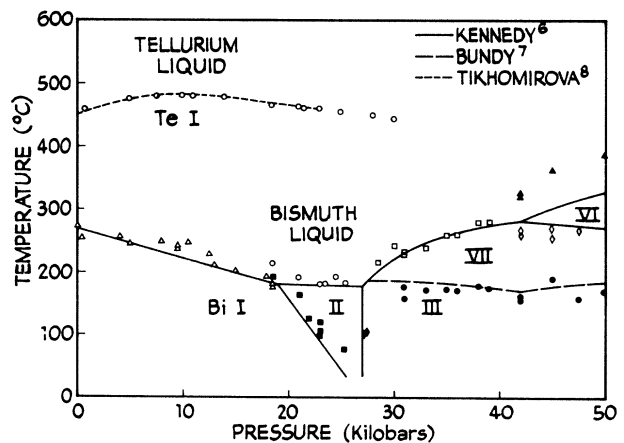


FIG. 3. Comparison of phase boundaries determined by DTCA with those determined by other techniques.

Then, using  $T(r, z)$  and the definitions

$$T_b \equiv T(b, l/2) \text{ and } T_a \equiv T(0, l/2),$$

the temperature differences,  $(T_a - T_b) = \Delta T$  and  $(T_a - T_0)$ , were obtained (for  $b/a = 2$  and  $c/a = 3$ ) in the forms

$$\Delta T = \frac{2Q}{\pi^3 c K_b} F(l/c, \gamma),$$

$$(T_a - T_0) = \frac{2Q}{\pi^3 c K_b} G(l/c, \gamma),$$

where  $\gamma = K_b/K_a$ . The values of the functions  $F$  and  $G$  for various values of  $l/c$  were calculated on an IBM 7090 computer with an estimated accuracy of 0.5%. The function  $F$  and the ratio  $R = (T_b - T_a)/(T_a - T_0)$  are shown in Fig. 1 for several values of  $l/c$ .

Since the ratio  $R$  is related to  $\gamma$  by the curves of Fig. 1(a), experimental measurement of the temperature dependence of  $R$  would yield the temperature dependence of  $\gamma$ . Then if the temperature dependence of the container thermal conductivity,  $K_b(T)$ , is known,  $K_a(T)$  can be calculated. In most practical cases, the pressure and temperature variation of  $K_b$  is very slight.<sup>11</sup> Thus, measurement of the three temperatures  $T_a$ ,  $T_b$ , and  $T_0$  will determine the thermal conductivity  $K_b$ . The curves for  $R$  in Fig. 1(a) also show that this method for measurement of thermal conductivity is most sensitive for  $\gamma < 1$ .

In a typical experiment the heat flow  $Q$  remains constant within 25% during a phase transition. Therefore, the curves in Fig. 1(b) indicate that the intervals defining the optimum cell configurations for DTCA measurements are  $2 \leq l/c \leq 5$  and  $0.01 \leq (K_b/K_a) \leq 2$ . Preliminary data show qualitative agreement with the theory concerning the relative magnitude of phase boundary shifts for different elements.

It was found experimentally that  $T_0 \approx 0.7T_a + 0.3(25)^\circ\text{C}$ . Then, using the atmospheric pressure thermal conductivity data for Bi<sup>4</sup> and Te,<sup>5</sup> along with the relationship between  $R$  and  $\gamma$  shown in Fig. 1(a), assuming a constant  $K_b$  of 0.036 cal/(cm sec °C),<sup>12</sup> theoretical curves for  $\Delta T$  were determined and are shown as the dashed lines in Fig. 2. A comparison of the theoretical and experimental curves indicates that the thermal conductivity at elevated pressure shows an apparent increase upon melting for both Bi I and Te I, as is observed at atmospheric pressure.<sup>4,5</sup> Our data also indicate that the thermal conductivity

of Bi II lies between that of Bi I and the liquid. The agreement between the experimental and theoretical curves of Fig. 2 is only qualitative for several reasons: (1) The theoretical boundary conditions are not met because elliptical distortion of the sample and container is unavoidable in our apparatus, the diameters of the thermocouples are about one-fifth the sample diameter, and the thermal conductivity of the pyrophyllite tetrahedrons is low [0.011 cal/(cm sec °C)], creating temperature gradients at the ends of the high-pressure cells; (2) the thermal conductivity of the sample is affected by pressure; and (3) the thermal conductivity of boron nitride is anisotropic.<sup>12</sup> However, with a piston-cylinder high-pressure apparatus, one should be able to eliminate the above-mentioned problems, approach the theoretically imposed boundary conditions, and measure the relative pressure and temperature dependence of the thermal conductivity of various substances.

The fact that DTCA exploits the inherent temperature gradients in high-pressure cells with internal heating mechanisms and requires relatively small samples, makes it useful in virtually all high-pressure devices whose maximum operating pressure is less than 100 kbar, e.g., tetrahedral-anvil, belt,<sup>13</sup> and piston-cylinder.<sup>14</sup> Previously, excluding the differential thermal analysis and volume measurements done in piston-cylinder devices, measurements in these devices have been largely restricted to electrical resistance determination. The DTCA technique presented, then, greatly enhances the usefulness of these devices by allowing studies of electrically insulating materials.

Quantitative or semiquantitative use of the theory presented for determination of thermal conductivity, along with the currently available high-pressure x-ray crystallographic data, will increase the knowledge of the relation between the crystal structure and the physical properties of materials.

A thorough investigation of the ramifications of the proposed theory and the demonstrated technique is in progress.

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## SEMICONDUCTOR-TO-METAL TRANSITION IN $V_2O_3$ †

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After Morin<sup>1</sup> had shown that several transition metal oxides exhibit an abrupt change with temperature from semiconducting to metallic behavior, Goodenough,<sup>2</sup> Mott,<sup>3</sup> and others<sup>4</sup> proposed qualitative models to account for the transition. In this Letter we will present the results of a generally applicable quantitative theory of semiconductor-to-metal transitions, and the results of new optical and transport measurements on  $V_2O_3$  which strongly support this theory.

Consider a crystal which at low temperatures is a normal semiconductor with valence and conduction bands separated by an energy gap  $E_g(T)$ . If this energy gap depends on the concentration of carriers excited into the conduction band,  $n_i$ , then, to first order in  $n_i$ ,

$$E_g(T) = E_g(0) - \beta n_i, \quad (1)$$

ignoring the explicit temperature dependence of  $E_g$ . Such a relation can be shown to be appropriate in an antiferromagnet where the energy gap arises from the difference in exchange potential for an electron of given spin on the sublattices of opposite magnetization. When an electron is excited across this gap, the net magnetization on either sublattice decreases, and thus the energy gap decreases with increasing number of carriers excited. For antiferromagnetism in narrow bands, Eq. (1) is found to hold even as  $n_i$  becomes relatively large; in this case, the constant  $\beta$  can be shown to be  $4E_g(0)/N$ , where  $N$  is the concentration of electrons in the valence

band.

However, the existence of antiferromagnetism is not a necessary condition for the applicability of Eq. (1). The relation can also be shown to be appropriate when an energy gap is caused by a crystal structure distortion to lower symmetry. This type of gap may arise from an energy gain due to chemical binding—the lower band can be thought of as a bonding band, the upper an antibonding band. Excitation of an electron across the energy gap decreases the gap because the excited electron no longer contributes to the chemical binding. It is more difficult to evaluate the constant  $\beta$  when the gap is caused by crystalline distortion. For simple one-dimensional models with delta function or with Mathieu potentials,  $\beta$  has been evaluated as a function of the amount of distortion, the bandwidth, and the energy gap. It was found that  $\beta$  is more sensitive to the distortion than to the band parameters; for distortions of the order of 1% (such as is found in  $V_2O_3$ ), for these two models,  $\beta$  is quite close to the value of  $4E_g(0)/N$  obtained for antiferromagnetism.

For situations where Eq. (1) is valid, calculation of  $E_g$  as a function of temperature, taking into account Fermi-Dirac statistics, shows that, at a temperature  $T_t$ , there is a sharp collapse of the band gap, and therefore a sharp semiconductor-to-metal transition. The transition temperature can be evaluated in terms of  $E_g(0)$  and  $\beta$  in the limit where the bands are very narrow. In this case, a reasonable limit for  $d$  bands, it