from the Redlich–Teller product rule[3] since this rule gives the product of the ratios of the frequencies of the isotopically substituted molecules for each vibrational frequency and since the frequency must remain the same or increase on substitution of a lighter isotope.

The observed frequency ratios for the isotopic molecules are

$$1389/1318 = 1.053 \quad 1040/986 = 1.056 \quad 952/915 = 1.040$$
$$906/855 = 1.060 \quad 605/599 = 1.010$$

If the frequencies observed are fundamentals of B_2S_3, then it can be shown that the D_{3h} and $D_{\infty h}$ structures are inconsistent with the observed shifts. The C_{2v} point group is not eliminated directly by the product rule. However, the most plausible assignment of the observed frequencies seems to favor the C_2 structure as the only chemically sound structure which is consistent with the observed isotope shifts. Other models, which require violation of classical valences, have been tentatively rejected.

If the C_2 model is correct, there should be nine infrared active fundamentals of which only five have been observed. The remaining four frequencies almost certainly belong to weaker bending modes and might be below the limit of detectability.

Visible and Ultraviolet Spectra of B_2S_3.—The electronic spectrum of the gas over B_2S_3 at 1000° was investigated in absorption from 3000 to 7400 Å. with a Bausch and Lomb 1.5 meter grating. A No. 2 photoflood and a xenon arc were used as light sources. Bands were observed in the regions 5400–7200, 3900–4200 and 3100–3500 Å. The red band system bears at least a superficial resemblance to the green system of B_2O_3.

Acknowledgment.—This work was in part supported by the Callery Chemical Company under a contract from the Bureau of Aeronautics, Department of the Navy.

MADISON, WISCONSIN

[3] G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Thallium–Tungsten Bronze: A Solid State Defect Structure[1]

BY M. J. SIENKO

RECEIVED APRIL 29, 1959

Thallium–tungsten bronzes, Tl_xWO_3, have been prepared ranging in composition from $x = 0.19$ to $x = 0.36$. Preparation methods included: (1) heating Tl_2WO_4, WO_3 and W; (2) vapor phase reaction of Tl and WO_3; (3) electrolysis of Tl_2CO_3 and WO_3 mixtures. Products were crystalline and powder diagrams could be indexed in the tetragonal system with a = 7.31 Å. and c = 12.80 Å. Electrical resistance measurements using a potential probe method on single crystals indicated metallic conduction with specific resistivity varying from 6.0×10^{-3} ohm-cm. at 25° to 9.0×10^{-3} ohm-cm. at 240°. Thermoelectric power at room temperature was −20 microvolts per degree referred to platinum, suggesting one free electron per thallium atom. A general model is proposed for the tungsten bronzes M_xWO_3 where M is viewed as giving rise to local energy levels in the forbidden gap between the conduction and valence bands of WO_3.

The tungsten bronzes,[2] M_xWO_3, in which M is a univalent metal and x lies between 0 and 1, represent an unusually interesting series of non-stoichiometric materials with properties ranging from metallic to semi-conducting depending on what M is. If M is sodium, the resulting sodium–tungsten bronze shows a linear increase of resistance with temperature and a Hall coefficient corresponding to one free electron per sodium atom[3]; if M is copper or silver, the resulting tungsten bronze shows an exponential decrease of resistance with rising temperature.[4] In both cases, magnetic susceptibility is low and independent of temperature. In attempting to set up a general model to account for these observations, we have been led to reject the older view of M_xWO_3 as a solid solution of WO_3 in hypothetical MWO_3 in favor of a model in which M_xWO_3 is viewed as a solid solution of M in WO_3. In this view M_xWO_3 is considered to be a solid state defect structure in which holes in a WO_3 network (conceivably greatly distorted from pure WO_3) are randomly occupied by M atoms with the M atoms more or less dissociated into M^+ ions and free electrons. The electrical and magnetic properties would then be explainable as functions of the tightness of binding of the electrons to the atoms M and to the host lattice. The striking chemical inertness invariably observed for metal–tungsten bronzes could be explained in terms of a "caging effect" of the WO_3 lattice on the ions M^+—only a negligible number of electrons could be removed from a metal–tungsten bronze crystal without building up an enormous space charge.

As part of a general program to determine necessary conditions for change-over from metallic to semi-conducting properties, we have tried to insert various metal atoms into the WO_3 lattice. It turns out to be extraordinarily difficult to achieve this with anything but the alkali metals and the copper subgroup metals. However, we have now succeeded in getting thallium in WO_3, and it is the preparation and properties of such a "thallium–tungsten bronze," Tl_xWO_3, that are described in this paper. The implications of these properties

[1] This research was supported in whole or in part by the United States Air Force under Contract No. AF 49(638)-191 monitored by the AF Office of Scientific Research of the Air Research and Development Command.

[2] See, for example, G. Hägg, *Z. physik. Chem.*, **B29**, 192 (1935); M. E. Straumanis and S. S. Hsu, THIS JOURNAL, **72**, 4027 (1950); A. Magneli and B. Blomberg, *Acta Chem. Scand.*, **5**, 377 (1951); L. E. Conroy and M. J. Sienko, THIS JOURNAL, **74**, 3520 (1952).

[3] E. J. Huibregtse, D. B. Barker and G. C. Danielson, *Phys. Rev.*, **84**, 142 (1951).

[4] L. E. Conroy and M. J. Sienko, THIS JOURNAL, **79**, 4048 (1957).

for setting up a general model for the bronzes are discussed.

Experimental Procedure and Results

Preparation.—Tl_xWO_3 has been prepared by three separate methods: (1) thermal, (2) vapor phase and (3) electrolytic. In the thermal method finely ground mixtures of Tl_2WO_4, WO_3 and W in a 3:8:1 molar ratio were heated in a vitreosil boat under argon for 160 hr. at 900°. The reaction can be written

$$3Tl_2WO_4(s) + 8WO_3(s) + W(s) \longrightarrow 12Tl_{0.3}WO_3(s) + 2.4Tl(g)$$

Frequently, it was convenient and, in fact, just as suitable to replace Tl_2WO_4 where called for by an equivalent amount of equimolar Tl_2CO_3 and WO_3. The crystals of $Tl_{0.3}WO_3$ produced were small (0.2 × 0.2 × 1 mm.) but invariably were in the shape of well-formed, blue-black, hexagonal prisms. Their size could be increased somewhat by a "thermal pumping" technique in which the temperature was periodically lowered to 500°.

In the vapor phase process, thallium and WO_3 vapors were brought together from separate sources in the vicinity of a colder surface on which crystals of $Tl_{0.2-0.3}WO_3$ could grow by condensation. The experimental set-up is shown in Fig. 1. Vitreosil boats—one containing a mixture of Tl_2CO_3 and W and the other, WO_3—were heated to 900° side by side in an evacuated tube under the tip of a stainless steel "cold finger" projecting in the center of the tube from a water-cooled head at the end of the tube. Crystals deposited at the cold surface were invariably perfectly shaped hexagonal prisms but rarely larger than 1 mm. in the longest dimension. Heating times of the order of 5 to 6 days were needed in order to produce reasonable crops of crystals.

The electrolytic method produced the largest crystals of Tl_xWO_3—some as large as 1.2 cm. in length and 0.3 × 0.3 cm. in cross-section—but habits were consistently malformed. Electrolysis was carried out under argon on fused mixtures of Tl_2WO_4 and WO_3 at 850° using platinum, gold or tungsten rods for the electrodes. A typical electrolytic cell consisted of a No. 2 Selas filtering crucible set inside a No. 2 porcelain crucible with 0.100″ diameter tungsten rods in the inner and outer crucibles. Asbestos-insulated holes drilled in the roof of the furnace supported the two electrodes. A typical charge consisted of 0.60 mole of Tl_2CO_3 and 1.05 mole of WO_3. Voltage drop at the electrodes was 2.5 v. with a current of 0.185 amp. corresponding to a current density of 0.12 amp. per cm.^{2}. After 4 hours of electrolysis, 7.6 g. of $Tl_{0.3}WO_3$ could be extracted from the cathode compartment.

Graphs of "current" *vs.* "potential drop between electrodes" showed on extrapolation a decomposition potential of 0.72–0.75 volt when Pt was used for the anode material and a decomposition potential of 0.10 v. when tungsten was the anode material. On the other hand, the identity of the cathode material had no influence on the polarization curves. It may well be that the rate-determining step with a platinum anode is the release of oxygen gas from oxidation of the melt whereas with a tungsten anode the rate-determining step is oxidation of the tungsten electrode.

In the vapor phase method, a homogeneous sample of bronze could easily be obtained by simply picking crystals off the cold surfaces. For the other two methods, fairly drastic methods were needed to separate Tl_xWO_3 from unchanged Tl_2WO_4, WO_3, W and SiO_2. Fortunately, the thallium bronzes proved to be as inert as their alkali or copper subgroup cousins. First step in purification was usually a leach with hot 5% Na_2CO_3 on an oscillating hot plate. Spent leach solution was decanted after every 4 hr. and replaced with fresh Na_2CO_3. Usually it took about 48 hr. to dissolve away the cement-like clinker of Tl_2WO_4 and WO_3 and leave the characteristic blue-black prisms of Tl_xWO_3. Most of the silica was then removed by flotation with tetrabromoethane, after which a long leach with 48% HF removed the last traces of SiO_2 and any W that might be present. (It is a remarkable fact that Tl_xWO_3 can remain in contact with 48% HF for as long as a month without any observable change.) Successive washings with NH_4OH, hot aqua regia, water and acetone completed the treatment.

Analysis.—For analysis Tl_xWO_3 was brought into solution by digestion in a molten mix consisting of 3 parts $NaNO_3$ to 1 part Na_2CO_3 by weight. Subsequent addition of concentrated HNO_3 to an aqueous solution of the fusion product precipitated H_2WO_4. After 12 hr. on the steam-bath, the solution had almost evaporated to dryness, producing large amounts of $NaNO_3$ in the process. More concentrated HNO_3 was added and the digestion continued for 3 hr. Filtration was through an ignited Selas crucible and was followed by washing with dilute HNO_3 and ignition at 900° for about 1 hr. Weighing was as WO_3. The per cent. WO_3 in the bronzes ranged from 75.8 to 85.6% corresponding, respectively, to $Tl_{0.36}WO_3$ and $Tl_{0.19}WO_3$. Invariably, the thallium-richer bronzes were the ones obtained by the electrolytic method at relatively higher current densities.

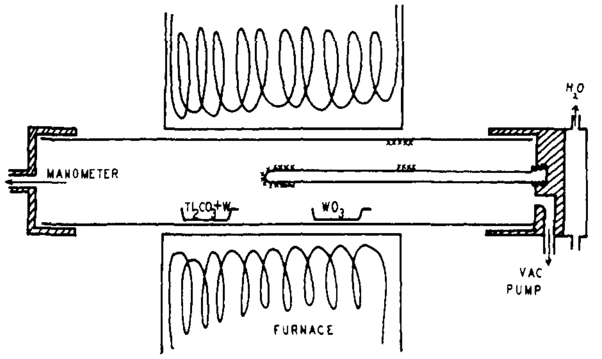

Fig. 1.—Vapor phase preparation of Tl_xWO_3.

Thallium content was determined by precipitating TlI from the supernatant liquid left above after the H_2WO_4 precipitation. Repeated addition of aqueous NH_3 and evaporation on the steam-bath was necessary first to reduce excessive nitrate content before adding KI. The observed thallium content usually was about 1% short of adding to the WO_3 percentage to make 100%. A similar 1% deficiency in thallium analysis was consistently observed for "pure" Tl_2CO_3 and Tl_2WO_4. Since the inherent accuracy of neither the tungsten nor the thallium analysis is very good—perhaps no better than 1% of total weight for each—the quoted composition limits as $Tl_{0.19-0.36}WO_3$ must be considered approximate. An independent analysis for oxygen content by reduction with hydrogen indicated that the oxygen-to-tunsten ratio was 3.1 ± 0.3.

Densities and X-Ray Measurements.—Densities were determined pycnometrically; at 25° they came to 7.6 ± 0.1 g. per cc. for $Tl_{0.19}WO_3$ and 8.13 ± 0.04 g. per cc. for $Tl_{0.36}WO_3$. X-Ray diagrams were obtained for the powders resulting from grinding up well-shaped crystals. Except for the crystals prepared by the electrolytic method, which showed faint additional lines that could not be indexed, the patterns were very similar and could be indexed in the tetragonal system with a = 7.31 Å. and c = 12.80 Å.

Electrical Resistance Studies.—Since electrical measurements on powders, especially with varying temperature, are frequently unreliable because of grain contact effects, it was necessary to investigate single crystals. To avoid contact resistances, a four-probe method was used with the arrangement shown in Fig. 2. Pairs of tungsten wires were pressure-clamped to opposite sides of a well-formed thallium–tungsten bronze crystal. The upper wires, which served to pass current through the crystal, had their con-

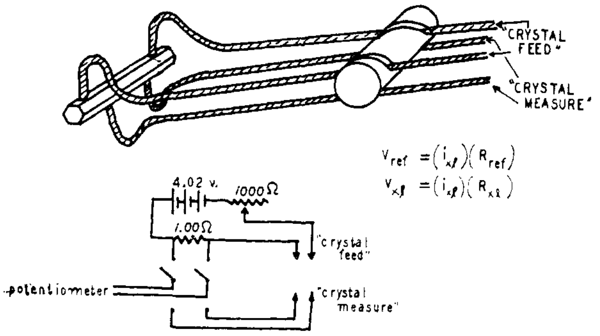

Fig. 2.—Four-probe method of measuring electrical resistance of Tl_xWO_3.

tact ends ground flat on a carborundum wheel so as to provide large contact area. The lower wires, which served as potential probes, were chemically pointed in molten sodium nitrite. Since the crystals are quite brittle, one needs to be very careful not to jiggle the potential probe contacts once they have been put in place; otherwise, holes are gouged in the prismatic faces. The white cylinder in the figure is a slotted piece of procelain which served to space the probes. Mica shims proved very useful in wedging the tungsten wires in the porcelain slots. This gave a very tight assembly which could be inserted into a Vycor tube so that the crystal rested at the mid-point of a horizontal combustion tube furnace. A chromel–alumel thermocouple equipped with 0° cold junction fitted in from the other end of the Vycor tube to the immediate vicinity of the crystal. The tube was evacuated and filled with argon for the measurements.

Electrical current-feed through the crystal was supplied by three mercury batteries. These have the advantage over ordinary dry cells of giving very steady voltages even when the current drain is several milliamperes. Current through the crystal was monitored by measuring the potential drop across a standard nichrome resistor in series with the crystal feed. A portable precision potentiometer capable of reading to one microvolt was used to measure the potential drop along the crystal and also to measure the reference voltage across the standard. Observed resistances as a function of temperature are shown in Fig. 3 for a crystal taken from an electrolytically prepared batch of $Tl_{0.20}WO_3$. It might be noted that, in contrast to crystal resistances of the order of 0.15 ohm, the contact resistance between the tungsten feed wires and the crystal amounted to 67 ohms—a powerful argument in favor of the potential probe method.

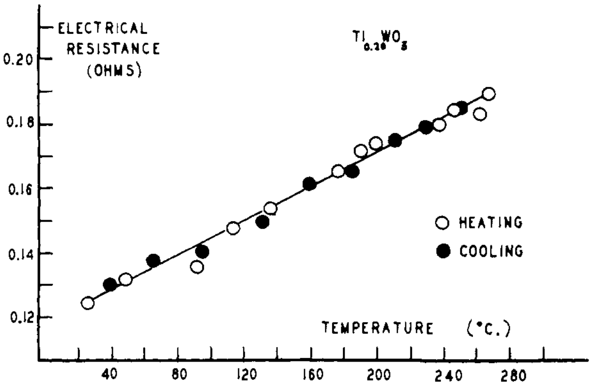

Fig. 3.—Electrical resistance as a function of temperature for a crystal taken from a preparation of $Tl_{0.20}WO_3$.

For calculating specific resistivity, cross-section dimensions of the crystal and probe separation were measured with a low-power microscope. Probe separation was 4.0 mm. and the hexagonal face was 1.5 mm. from side to side. It was assumed that the full-hexagonal cross-section of the crystal was electrically operative between the "crystal measure" probes, even though the "crystal feed" wires are not located at the ends of the crystal as would conventionally be the case. That this assumption is correct is supported by the observation that resistance studies carried out with the thermoelectric power set-up of Fig. 4 showed no significant difference from those with the set-up of Fig. 2. For the crystal described by Fig. 3, the specific resistivity increased from 6.0×10^{-3} ohm-cm. at 25° to 9.0×10^{-3} ohm-cm. at 250°. Several other crystals taken from the same preparation showed the same resistivity values within 5%.

For a given crystal, the resistance–temperature curve was easily reproducible within 1% on heating and cooling cycles between 25 and 250° for several consecutive cycles. However, if the crystal were heated above 300°, its electrical resistance began to increase more rapidly than linearly and on subsequent cooling did not return to its original value. Furthermore, when the crystal was maintained at 370° for any length of time, the resistance steadily increased with time. All of this was interpreted as a "boiling out" of the thallium from the WO_3 lattice—a boiling out that set in above 300°. It may be predominantly a surface effect, since it was observed that contact resistances were increased enormously by the above treatment. (When large amounts of Tl_xWO_3 are heated *in vacuo*, deposits of thallium are observed on the colder parts of the tube.)

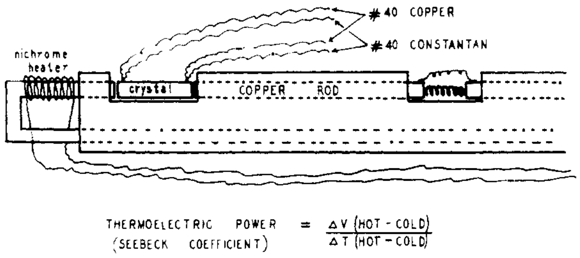

Fig. 4.—Experimental arrangement for determining Seebeck coefficient of thallium–tungsten bronze.

Thermoelectric Power Measurement.—In an attempt to determine whether the charge carriers for the above metallic type conduction are predominantly positive or negative, the thermoelectric power, or Seebeck coefficient, was measured by the set-up shown in Fig. 4. A crystal, about 4 mm. long, was clamped between two copper rods, one of which was spring-loaded. A nichrome heater wound around one copper rod served to heat the left end of the crystal while the copper rod at the right acted as a heat sink. Tiny copper and constantan wires were welded to the ends of the crystal to enable measurement of the thermal gradient-induced voltage difference between the hot and cold ends of the crystal and also to enable thermocouple measurement of the local temperatures. The body of the arrangement was a 2-hole porcelain insulator which did double duty as an electrical spacer and as a rigid support for introducing the assembly into a Vycor tube.

With a thallium–tungsten bronze crystal in the holder—the crystal was taken from the same batch as the ones used for the electrical resistance studies above—temperature differences of ten degrees were easily obtained between the hot and cold ends of the crystal. (The implication therefore is that the thermal conductivity of Tl_xWO_3 is quite low.) The voltage difference measured with a potentiometer between the two constantan leads amounted on the average to −0.015 millivolt per degree, with the constantan lead to the hot end being the more negative. Correcting for the thermoelectric power of constantan, for which the Seebeck coefficient referred to platinum is −0.035 mv. per degree, we calculate for thallium-tungsten bronze a Seebeck coefficient referred to platinum of −0.020 mv. per degree.[5]

Discussion

The linear dependence of electrical resistance on temperature indicates, at least in the temperature range studied, a metallic character for the thallium–tungsten bronze very much like the metallic character observed for the sodium–tungsten bronzes. Furthermore, the thermoelectric power, being of the same sign as that observed for *n*-type semi-conductors and for metals in which conduction is predominantly electronic, indicates that the charge carriers in Tl_xWO_3 are free electrons moving in some kind of conduction band. Assuming a simple inverse dependence of thermoelectric power on the logarithm of the electron density,[6] we can estimate from a comparison of the observed Seebeck coefficient to that of sodium that there are approximately 10^{22} free electrons per cc. of thallium–tungsten bronze. This compares with 3.4×10^{21} atoms of Tl per cc. of $Tl_{0.20}WO_3$, as calculated from the stoichiometry and the observed density of the bronze. The inference is that in the temperature range investigated all the thallium atoms are ionized to give thallous ions and free

(5) American Institute of Physics, "Temperature, Its Measurement and Control in Science and Industry," Reinhold Publ. Corp., New York, N. Y., 1941, p. 1308.

(6) W. Ehrenberg, "Electric Conduction in Semiconductors and Metals," Oxford University Press, London, 1958, p. 21.

electrons. It would seem then that the "electron gas" model previously proposed for the alkali tungsten bronzes would also apply to the thallium bronze.

In Fig. 5 we give a possible energy diagram for thallium–tungsten bronze which, by suitable adjustment of the parameters, can serve as a general model for the other bronzes, accounting either for semi-conductivity or for metallic conduction. The WO_3 conduction band, here shown to be completely empty of electrons, probably arises from an overlap of the 5 d orbitals of tungsten. The gap energy, E_g, between the top of the valence band and the bottom of the conduction band is estimated at 2.5 e.v. mainly on the basis of steep rises of absorption observed in the ultraviolet for WO_3 and for various tungstates. The gap energy is great enough so that at room temperature in pure WO_3 only a negligible number of electrons would be found in the conduction band. In the presence of added thallium atoms it is proposed that there are introduced in the forbidden gap local levels from which it might be relatively easy to excite electrons into the conduction band provided the ionization energy, E_i, is small enough compared to kT. In the case of $Tl_{0.20}WO_3$ and the sodium–tungsten bronzes, it would seem that E_i is essentially zero; so that at room temperature and above, the local levels have been completely emptied of electrons into the conduction band. Furthermore, if, as seems probable, the WO_3 conduction band arises from overlap of the three 5 dϵ orbitals of a tungsten atom, then the conduction band has many more levels than there are electrons from M atoms; hence, the conduction band behaves as an "almost empty one" and the "free electron" model is applicable. There is essentially no activation energy for the conduction process and the decreased conductivity at higher temperatures would presumably be due to decreasing mobility due to lattice scattering.

In the case of the semi-conducting bronzes, it would seem that the local levels are considerably deeper in the forbidden energy gap so that a finite activation energy is required for the conduction process. In $Cu_{0.77}WO_3$, for example, the observed activation energy for conduction[4] is 0.15 e.v. If we assign this value to the ionization energy E_i for Cu atoms, then we have to conclude that at room temperature only a negligible fraction of the copper atoms ionize to give free electrons in the conduction band and that this fraction increases exponentially with rising temperature. (Alternatively, the observed activation energy for conduction might be assigned as the energy required for an electron to jump from one copper atom to a neighbor—that is, the energy for conduction by a "hopping" process.[7] Such a "hopping" process in $Cu_{0.77}WO_3$ is quite possible since in this bronze the copper atoms are on the average only 4.3 Å. apart. With such close-spacing, it is almost certainly true that the local energy levels are not independent of each other. Antiferromagnetic interactions of this type could explain why only about 20% of the expected spinparamagnetism of neutral copper atoms shows up in the observed magnetic susceptibility[4] of copper–tungsten bronze.)

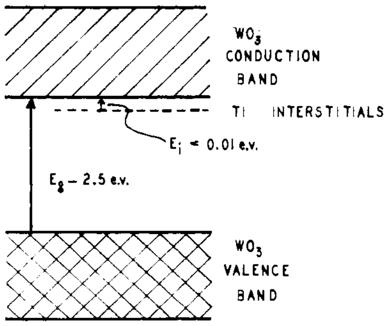

Fig. 5.—Possible energy relations in thallium–tungsten bronze.

If the local levels contribute to the conductivity by introducing an additional band in the forbidden gap—so-called "impurity banding"—then the situation is immeasurably more complex, even in a qualitative sense. However, for the sodium–tungsten bronzes, we have independent evidence that the sodium atoms do not form such an additional band. The evidence comes from a report[8] that there is essentially no Knight shift for the Na^{23} resonance in Na_xWO_3. Such an absence of a Knight shift could be explained by having (1) the conduction band made up of other than 3s functions of the sodium or (2) the conduction band made up of tungsten orbitals having a node at the sodium nuclei. As suggested above, the 5 dϵ orbitals of the tungsten seem to satisfy the latter condition—at least in the cubic tungsten bronzes and probably also in the hexagonal bronzes.

ITHACA, NEW YORK

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(7) N. F. Mott, *Can. J. Phys.*, **34**, 1364 (1956).

(8) R. G. Barnes, R. A. Hultsch and W. H. Jones, Jr., *Bull. Am Phys. Soc.*, [II] **4**, 166 (1959).