

# Effect of Isotopic Composition on Electrical Resistance of Lithium\*†

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The electrical resistance of solid metallic lithium containing varying proportions of lithium-6 and lithium-7 was measured between 4.2° and 295°K. For the isotopically pure substances, the main features of the behavior agree with the predictions of the Bloch-Grüneisen law, the characteristic temperature being inversely proportional to the square root of the mass. The deviation in the details is just that found for most other metals. For the isotopically impure substances, the behavior of the resistance as a function of temperature can be described just as that of an isotopically pure substance with a mass dependent on the isotopic composition. In fact, the temperature dependence of resistance for all compositions, including the pure isotopes, can be repre-

sented as a universal curve by use of appropriate scaling factors depending on average isotopic mass. From the present data the arithmetic mean cannot be preferred over the harmonic mean isotopic mass, and hence one cannot decide between certain theoretical proposals concerned with the effect of isotopic impurities on lattice vibration spectra. On the other hand, it appears definite that no need exists to invoke a scattering mechanism that looks upon isotopes as introducing imperfections in the lattice; rather, their presence merely modifies the lattice vibration spectrum. The effect of the martensitic transition at low temperatures is barely, if at all, discernible.

## I. PRELIMINARY CONSIDERATIONS

SOME insight into the complicated problem of electrical conduction in metals can be gained through use of isotopic mass as a probe. To this end we have studied the electrical resistance of the separated stable isotopes Li<sup>6</sup> and Li<sup>7</sup> in the temperature range 4°–300°K. In addition we have studied "isotopic alloys" made from varying proportions of the isotopes. Lithium was chosen because its crystalline and electronic structure is simple, and because its stable isotopes have a large relative mass difference and are available in reasonable quantity. Section II of the present article describes the experimental procedures in our study. Section III gives the results obtained with isotopically pure substances and with isotopic alloys. The Bloch-Grüneisen equation<sup>1</sup> gives, as is well known, the main features of the interaction of conduction electrons with lattice vibrations in producing the intrinsic electrical resistivity in metals. This equation is usually written in the form

$$\rho(T) = 4A(\Theta/T)^{-5}J_5(\Theta/T), \quad (1)$$

where  $\rho(T)$  is the intrinsic resistivity at the absolute temperature  $T$ . The function  $J_5$ , one of the Debye integrals, is tabulated in the literature.<sup>2</sup> The parameters  $\Theta$  and  $A$  are characteristic of the material. The constant  $\Theta$  has the form of a characteristic temperature defined through the relation  $k\Theta \equiv \hbar\omega_c$ , where  $\omega_c$  itself is a characteristic angular frequency related to the isotopic mass  $M$  and to an effective spring constant  $b$  through the condition  $\omega_c^2 = b/M$ . The constant  $A$  is dependent upon such quantities as the lattice param-

eters, the interatomic force fields, the Fermi level, and other characteristics of the electronic and crystal structure. For isotopes of the same element, however,  $A$  is dependent only on the isotopic mass, the other quantities mentioned differing negligibly between isotopes.

Figure 1 is a plot of Eq. (1) for two isotopes of atomic mass 6 and 7. The effect of isotopic mass in separating the middle portions of the curves is evident. At low temperatures the curves come together as the resistivity for each isotope approaches zero. The resistivities separately go to zero as  $T^5$ , but their ratio approaches the square of the ratio of the masses, that is,  $(7/6)^2 = 1.36$ . As the temperature increases, the ratio of the resistivities decreases, becoming about 1.02 for an element like lithium at room temperature, and approaching unity at higher temperatures when equipartition sets in and quantum effects disappear. In this region the resistivity becomes proportional to  $T$ . Such behavior at limiting values of  $T$  has of course a wider basis of validity than that furnished by the detailed derivation of the Bloch-Grüneisen equation.<sup>3</sup> In the first portion of Sec. IIIb we investigate the adequacy of the form of the function appearing in Eq. (1). As with most other metals,<sup>4</sup> and natural lithium in particular,<sup>5</sup> we find that the equation gives the general features of the course of the resistance variation with temperature, but fails quantitatively in the intermediate regions.

In the usual presentation of the Bloch-Grüneisen formula, the normalized resistivity  $\rho(T)/\rho(\Theta)$  is written as a function of the reduced temperature  $T/\Theta$ , in keeping with Eq. (1). For making comparisons between different elements, this viewpoint is eminently satisfactory. For making comparisons between isotopes of the same element, however, a slightly different method

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<sup>1</sup> F. Bloch, Z. Physik **59**, 208 (1930).

<sup>2</sup> E. H. Sondheimer, Proc. Roy. Soc. (London) **A203**, 75 (1950); A. M. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1953).

<sup>3</sup> See, e.g., J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1960).

<sup>4</sup> See, e.g., E. Grüneisen, Ann. Phys. **16**, 530 (1933).

<sup>5</sup> F. M. Kelly and D. K. C. MacDonald, Can. J. Phys. **31**, 147 (1953).

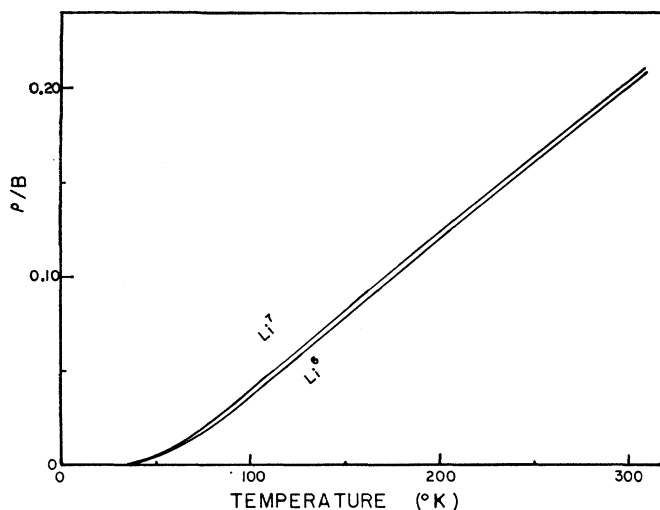


FIG. 1. Intrinsic resistivity as a function of absolute temperature for isotopes of mass 6 and 7, according to the Bloch-Grüneisen equation. Here  $\rho(T)$  has been divided by  $B$ , a constant fixed by the knowledge of the resistivity at some given temperature. The characteristic temperature  $\Theta$  has been taken as 345°K for  $\text{Li}^7$ .

suggests itself. We first rewrite Eq. (1) in the form

$$\rho(T)/\Theta = B(\Theta/T)^{-5}J_5(\Theta/T), \quad (2)$$

by noting that  $A$  varies inversely as  $M\Theta$ , and that  $M\Theta^2$  is constant for isotopes of the same element, to give a constant  $B$  which does not change between isotopes. Now we recall that the form of the Bloch-Grüneisen function is unsatisfactory in its details; yet, the idea persists that  $T/\Theta$  might be a particularly suitable variable for characterizing interactions with lattice vibrations. There is, of course, considerable independent support for this idea, as will be outlined later. We seek, then, a law stating that  $\rho/\Theta$  is a universal function of  $T/\Theta$  for isotopes of the same material, even though the form of the function is not specified. In the latter portion of Sec. IIIb we establish the validity of such a law for the separated isotopes of lithium.

We now turn our attention to isotopic alloys. It is by no means evident *a priori* in what respects an isotopic alloy behaves like an isotopically pure species having the average mass of the alloy. The theoretical analysis for all transport properties is so complicated, and the experimental results on other transport properties are so resistant to systemization, that measurements of electrical resistance of isotopic alloys promise to be significant in elucidating this behavior. The results permit of a gratifying simple interpretation, showing that for electrical resistance the effect of isotopic impurities can be taken into account merely by replacing the mass in an isotopically pure substance by the average mass of the isotopic mixture. This finding has important theoretical and practical significance. Section IIIc contains the results and discussion on this topic.

Section IV summarizes the work.

## II. EXPERIMENTAL CONSIDERATIONS

The experimental difficulties that arise with lithium contrast strongly with the theoretical advantages that obtain in choosing it as a material for study. Lithium has high chemical reactivity and low electrical resistivity. To get accuracy in the determination of resistivity, the resistance of the specimen must not be excessively low, and its cross-sectional area must not be excessively small. The length of specimen necessary to get accurately measurable resistances, and the thickness of specimen necessary to get accurately known stable cross-sectional areas, demand amounts of material which at the time of planning the experiment were judged to be excessive. Hence we decided to measure only resistances relative to the resistance at a standard temperature  $T_0$ , taken for convenience as 20°C. Measurements need to be made then merely of resistance and of temperature, accurate knowledge of physical dimensions not being required.

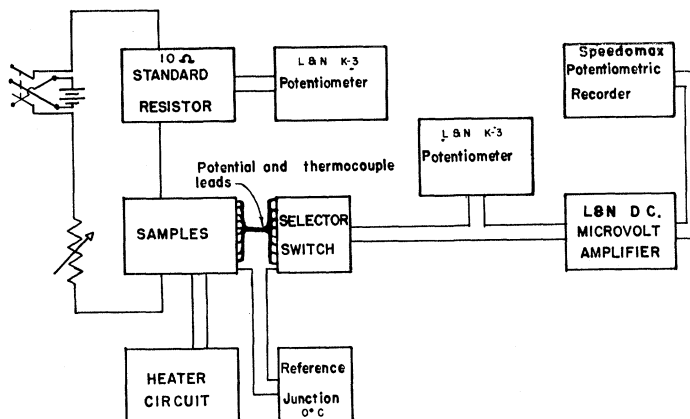
### Samples

The pure isotopes were obtained from Oak Ridge National Laboratory.<sup>6</sup> The supplier's isotopic analyses (in atomic percent) were  $(99.3 \pm 0.1)\% \text{Li}^6$ ,  $(0.7 \pm 0.1)\% \text{Li}^7$  for "lithium-6" and  $(99.99 \pm 0.01)\% \text{Li}^7$ ,  $(0.01 \pm 0.01)\% \text{Li}^6$  for "lithium-7." The supplier's chemical analyses gave only a few thousandths of an atomic percent impurity for any elements except calcium and zinc in "lithium-6," and except strontium in "lithium-7." For these exceptions the concentration of the impurities was a few hundredths of a percent. The materials were further purified by redistillation. Subsequent analysis was not made, but experience with this process<sup>7</sup> has

<sup>6</sup> We are grateful to Dr. P. S. Baker and his colleagues at Oak Ridge National Laboratory for their aid in procuring and purifying the enriched isotopes.

<sup>7</sup> P. S. Baker, F. R. Duncan, and H. B. Greene, *Science* **118**, 778 (1953).

FIG. 2. Block diagram of measuring circuit.



shown that purification by an order of magnitude occurs for most elements.

Natural lithium was obtained from Lithium Corporation of America, in their "low-sodium" grade. The isotopic composition of natural lithium is given in the literature as 7.52%  $\text{Li}^6$ , 92.48%  $\text{Li}^7$ . The chemical analysis, as given by the supplier, showed only a few thousandths atomic percent impurity, except for nitrogen, present to 0.03%. The natural lithium was not purified further.

The test specimens were prepared by scraping off the outer contaminating coatings that appeared on lumps of metal kept in oil, and then loading the cleaned sample into a mechanical press that extruded the lithium metal through a circular die. These operations were carried out at room temperature in an atmosphere of dry carbon dioxide. Samples about 25 cm long and 1 mm thick were extruded, to be fastened into a sample holder to be described presently. The resistance of a typical specimen at room temperature was about 25 mohm, decreasing to perhaps a thousandth of this value at liquid-helium temperature.

The isotopic alloys were made by melting together weighed amounts of the separated isotopes. The material was floated in heated oil, to form a single globule upon melting. A thin coating that formed on the metal was strong enough to permit deformation of the globule with a stainless-steel rod to ensure thorough mixing. Although the weighings are accurate to 0.1%, the possibility of unequal consumption of metal in producing the thin film makes  $\pm 1\%$  a more realistic estimate of the accuracy of isotopic composition for these alloys. After cooling, the alloys were treated just like the pure isotopes in the preparation of specimens.

In each run three specimens were used. Two were the test specimens, and the third was a dummy on which a thermocouple was placed.

#### Measurement of Temperature

The temperature was measured with copper-constantan thermocouples calibrated against an N.B.S.-certified

platinum resistance thermometer in the range 20°–300°K. The boiling point of helium at atmospheric pressure was taken as a low reference temperature. Neither the measurements of the temperature nor of the intrinsic resistance are very accurate between 4.2° and 20°K, and no data are presented for this region. The thermal emf was measured on a self-balancing potentiometer, after most of the signal had been backed off with a precision potentiometer and the remainder amplified with a linear dc microvolt amplifier. We believe that the over-all accuracy in temperature measurement is better than 0.2°K.

#### Measurement of Resistance

In earlier work<sup>8</sup> in our laboratory, wherein measurements did not go below liquid-air temperatures, the resistance was measured with a precision Kelvin double bridge. For the present studies, down to liquid-helium temperature, the thick current leads necessary for high accuracy with this bridge introduce excessive heat leakage. Hence we chose an ammeter-voltmeter method, in which the current is measured by the  $IR$  drop across a standard resistor, and the voltage is measured by a potentiometer. With this method both the current and the potential leads can be thin. The leads from the different specimens are brought to an external selector switch, as shown in Fig. 2, a block diagram of the electrical measuring circuit.

#### Test Chamber

The test chamber, placed in a special glass Dewar immersed in liquid air contained in a larger metal Dewar, consists of a brass cylinder holding the specimens and ancillary apparatus. The two ends of the specimens themselves were fastened with copper nuts and screws to a Teflon sample holder. These screws served as current contacts, wires of spring-brass serving as potential contacts. All the leads were wrapped

<sup>8</sup> D. D. Snyder and D. J. Montgomery, Phys. Rev. **109**, 222 (1958).

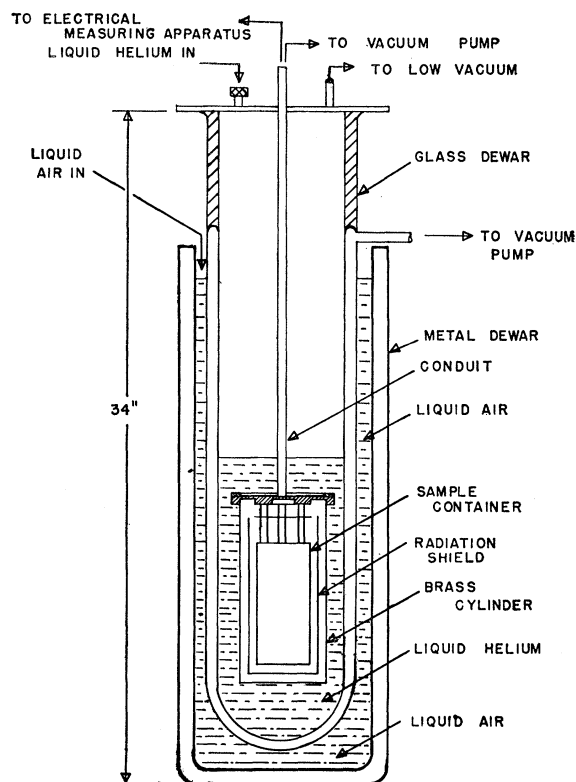


FIG. 3. Cross-sectional view of cryostat assembly.

around an aluminum torus acting as a heat exchanger, and then were passed through an aluminum can constituting an isothermal sample container. The sample

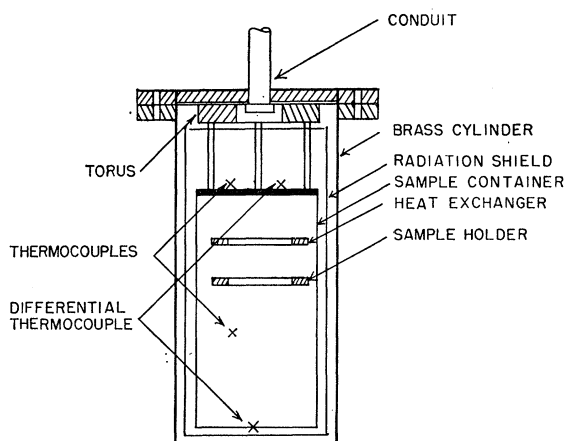


FIG. 4. Sketch of measuring chamber. At the top of the sketch is the central stainless steel conduit to which is soldered a brass plate. From the rim of this plate is suspended a brass cylinder acting as the outer wall of the chamber. On the bottom of the plate is an aluminum torus serving as a heat exchanger. Through notches in the torus are passed several turns of the leads (not shown). Three vertical Teflon standoff insulators carry the sample container, which is surrounded by an aluminum-foil radiation shield. Within the container are another heat exchanger and the sample holder, sketched in Fig. 5. The locations of the thermocouples are indicated by crosses.

container was insulated thermally from the top of the test chamber by three Teflon standoff insulators. The leads were next wrapped around another heat exchanger, an aluminum torus fastened to the top of the test chamber. They then passed through a thin-walled stainless-steel conduit acting as a mechanical support and as a vacuum line to the test chamber. The conduit is sealed at the top with resin cast around the leads, and is connected to the external vacuum system through a side tube. Figures 3, 4, and 5 show some details of the apparatus.

### Experimental Procedure

Following cleaning and extruding, the specimens were mounted carefully on the screws in the sample holder, and the potential contacts were made. The aluminum sample container and the radiation shield were placed around the sample, the assembly then being inserted into the brass cylinder. The cylinder was clamped against the cover carrying the stainless-steel conduit, with a lead gasket under the cover to give a vacuum-tight seal. The test-chamber assembly was then removed from the dry box and placed in the double-Dewar assembly. To prevent possible chemical reaction with carbon dioxide or with impurities in the dry-box atmosphere, the filling gas was pumped out.

For measurements below 80°K, the test chamber was precooled to liquid-air temperature by introducing helium gas as an exchange medium into the glass Dewar and into its vacuum jacket. After equilibration, the vacuum jacket was pumped out, and liquid helium was poured into the glass Dewar through a transfer

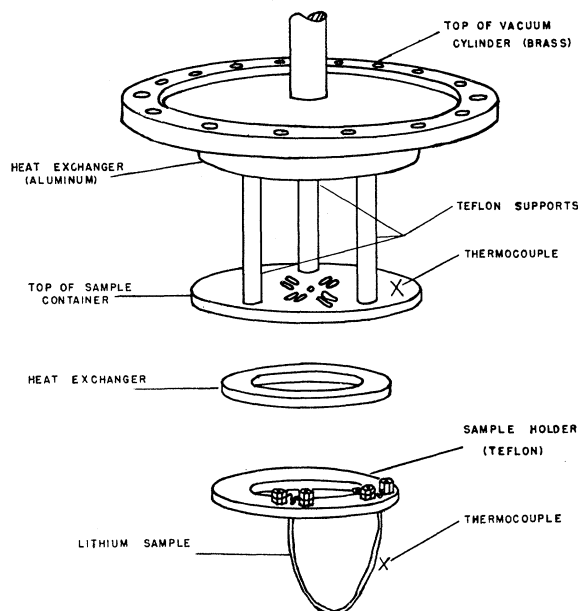


FIG. 5. Detail of sample holder and heat exchanger. (To avoid confusion, the leads are not shown.)

tube. A desired temperature was obtained by manual adjustment of the heaters, or by natural warming alone when the rate of heat leak was suitable. With the aid of the selector switch, the self-balancing potentiometer alternately recorded signals from the samples and from the thermocouples. The chart records were subsequently analyzed to get resistance as a function of temperature for the specimens under investigation.

### III. RESULTS AND DISCUSSION

#### a. Residual and Normalizing Resistances

Table I gives the measured *total resistance*  $R'$  for all the specimens at room temperature  $T_0 = 293.1^\circ\text{K}$ , and at liquid-helium temperature,  $4.2^\circ\text{K}$ . The total resistance  $R'(4.2^\circ\text{K})$  is due virtually completely to impurities, and may be taken to be almost exactly the *residual resistance*. The *intrinsic resistance*  $R(T)$  is then defined as the total resistance  $R'(T)$  minus the residual resistance  $R'(4.2^\circ\text{K})$ . The intrinsic resistance  $R(293.1^\circ\text{K})$  may be considered as the *normalizing resistance*, that is, the resistance by which each  $R(T)$  is divided to give the *normalized intrinsic resistance*  $R(T)/R(T_0)$ .

The ratio of residual resistance to room-temperature resistance is about 1 or 2 parts per thousand. So low a ratio for a metal as reactive as lithium indicates the high chemical purity of the material, and constitutes a tribute to the skill and care of our suppliers. It gives confidence also that our results cannot be much in error because of a possible failure of Matthiessen's rule. The ratio for the isotopic alloys is somewhat higher than that for the pure isotopes or for natural lithium. This increase is to be expected in view of the additional handling necessary to prepare the alloys.

#### b. Effect of Isotopic Mass in Pure Isotopes

Figure 6 shows the normalized intrinsic resistance  $R(T)/R(T_0)$  for "Li<sup>6</sup>" (99.3% Li<sup>6</sup>) and "Li<sup>7</sup>" (99.99% Li<sup>7</sup>), as a function of absolute temperature  $T$ . The

TABLE I. Residual and room-temperature resistances for lithium specimens.

Material	Specimen number	Residual resistance $R'(4.2^\circ\text{K})$ (mohm)	Room-temp. resistance $R'(293^\circ\text{K})$ (mohm)	$R'(4.2^\circ\text{K})/R'(293^\circ\text{K})$
"Li-6"	1a	0.0412	23.63	$1.74 \times 10^{-3}$
"Li-7"	1b	0.0350	23.44	$1.49 \times 10^{-3}$
"Li-6"	2a	0.0416	23.82	$1.75 \times 10^{-3}$
Li-nat	2b	0.0280	24.20	$1.16 \times 10^{-3}$
Li-nat	3a	0.0233	23.29	$1.00 \times 10^{-3}$
"Li-7"	3b	0.0318	23.68	$1.34 \times 10^{-3}$
"Li-6"	4a	0.0385	23.90	$1.61 \times 10^{-3}$
"Li-7"	4b	0.0206	16.37	$1.26 \times 10^{-3}$
75% Li-7	5a	0.0355	15.94	$2.23 \times 10^{-3}$
75% Li-7	5b	0.0345	15.03	$2.30 \times 10^{-3}$
50% Li-7	6a	0.0350	19.44	$1.80 \times 10^{-3}$
25% Li-7	6b	0.0378	21.70	$1.74 \times 10^{-3}$

curves approach the horizontal axis as  $T$  approaches zero, actually reaching it at  $T = 4.2^\circ\text{K}$  because we have ignored the very small intrinsic resistance at very low temperatures. At the standard temperature  $T_0 = 293.1^\circ\text{K}$  the curves cross at unity ordinate. The *resistivities*, of course, are not expected to coincide at  $T_0$ , but rather to remain separated by a percent or two as suggested by Eq. (1). We shall return to this point.

The adequacy of the Bloch-Grüneisen function may be tested by considering the resistance of each isotope separately, or by examining the ratio of the resistances of the isotopes. For the former, one traditionally calculates the apparent characteristic temperature  $\Theta$  necessary to make the experimental values agree with the theoretical ones. The constancy of  $\Theta$  with respect to temperature gives a measure of the goodness of fit of the formula. For natural lithium, Kelly and MacDonald have made this test.<sup>5</sup> They found a marked variation in  $\Theta$  over the temperature range  $4^\circ$ – $300^\circ\text{K}$ . The Bloch-Grüneisen equation is, of course, derived under the assumption of constant volume, whereas

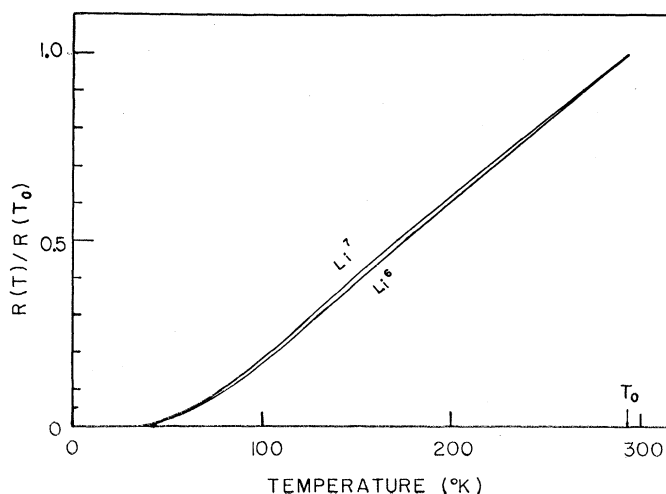


FIG. 6. Intrinsic resistance as a function of absolute temperature for lithium-6 and lithium-7, as determined experimentally. Here the intrinsic resistance  $R(T)$  has been normalized by dividing it by  $R(T_0)$ .  $T_0$  has been taken as room temperature,  $20^\circ\text{C}$ .

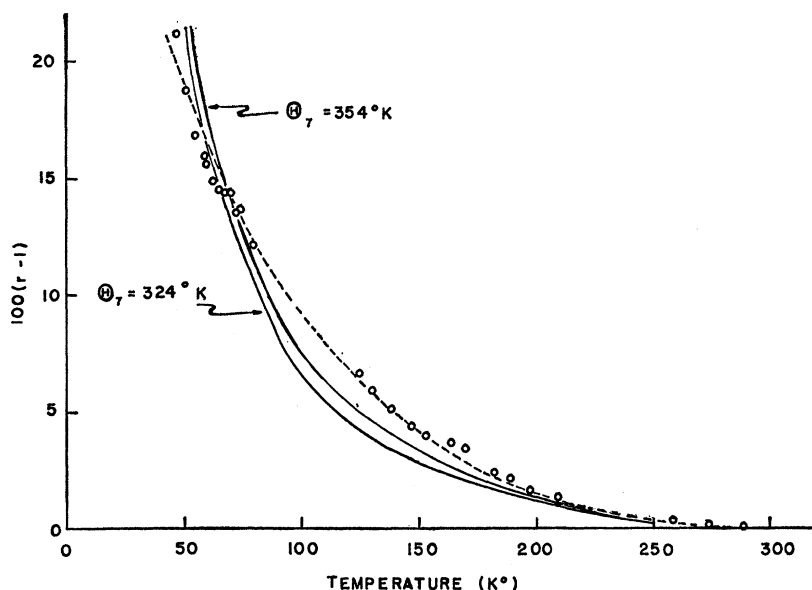


FIG. 7. Comparison of experimental results with theory. The ordinate is percent excess over unity of the ratio of normalized intrinsic resistivity for lithium-7 to that for lithium-6. The abscissa is absolute temperature. The dashed line is an average curve drawn through the experimental points. The solid lines are curves calculated according to the Bloch-Grüneisen law for two values of the parameter  $\Theta$  for lithium-7.

experiments are made at constant pressure. But correcting for this difference does not remove the variation. Our results for  $\text{Li}^6$  and for  $\text{Li}^7$  differ only slightly from theirs for natural lithium, and in fact (as we shall see) can be reduced to the same curve by use of appropriate scaling factors. Consequently, it is not worthwhile to repeat this test for our data.<sup>9</sup>

Instead we choose to compare the temperature dependence of the ratio of measured normalized resistances for  $\text{Li}^7$  and  $\text{Li}^6$ , with this ratio as computed from Eq. (1). This test is not so stringent as the traditional one, but its significance is perhaps more directly understood. Figure 7 is a plot of the percentage excess over unity of this ratio as a function of temperature. Points are shown only down to temperatures of about 50°K. At lower temperatures the scatter becomes so great that the representation is almost without meaning. The reasons for the scatter, we believe, are primarily experimental errors. Although these are small in themselves, their effect is magnified by the necessity for subtracting the residual resistance from the total resistance to get the intrinsic resistance. In the absence of systematic error, taking the ratio further increases the scatter. The dashed line is an average curve through the experimental points. The solid lines are calculated from Eq. (1) for two values of the parameter  $\Theta$  for  $\text{Li}^7$ . These values have been chosen to bracket the values obtained in the traditional analysis. The course of the curve is not highly sensitive to the value of this parameter, and the fit over the whole range cannot be improved much by adjusting it. From Fig. 7 we see

again how the Bloch-Grüneisen formula gives the main features of the behavior, but fails in detail.

Even though the detailed fit is not satisfactory, certain steps in the derivation of Eq. (1) suggest that a reduced resistivity of some kind might be a universal function of a reduced temperature,  $T/\Theta$ . Indeed, the Bloch-Grüneisen equation is frequently presented in this form. Improvements in the derivation lead to the same notion.<sup>3</sup> As a matter of fact, the argument has general support from dimensional arguments. We note first of all that the equation of motion for  $q_i$ , the displacement of the  $i$ th atom, in an isotopically pure substance will have the form  $M d^2 q_i / dt^2$  equals a function dependent on other coordinates and on certain parameters, but independent of time and isotopic mass. Hence the solution for the equations can contain mass  $M$  and time  $t$  only in the combination  $t/M^{1/2}$ . It follows immediately that all frequencies must be proportional to  $M^{-1/2}$ . Next we employ a less rigorous argument based on conventional dimensional analysis. It can be shown under reasonable assumptions that the variation in electrical resistivity between separated isotopes of the same element can go only as  $M^{1/2}$  times a function of the dimensionless variable<sup>10</sup>  $\hbar\omega_c/kT$ . But since  $\hbar\omega_c = k\Theta$ , and  $\Theta$  is proportional to  $M^{-1/2}$ , we can write  $\rho(T) \sim \Theta f(T/\Theta)$ , where the constant of proportionality is identical between isotopes, and  $f$  is some function determined by the details of the interaction.

We seek then to verify this relation by constructing a universal curve for  $\rho(T)/\Theta$  as a function of  $T/\Theta$ . Such a construction is indeed possible for  $\text{Li}^6$  and  $\text{Li}^7$ . The details of the verification are most easily presented

<sup>9</sup> J. Dugdale, D. Guban, and K. Okumura, in similar experiments with  $\text{Li}^6$ , have actually made such a comparison, with the expected result [Proc. Roy. Soc. (London) A263, 407 (1961)]. Our experimental values for normalized resistance agree closely with theirs. We wish to express our gratitude to them for their kindness in making their data available to us before publication.

<sup>10</sup> Usually this dependence is expressed in terms of the variable  $\Lambda^*$  [see, e.g., J. de Boer, Physica 14, 149 (1948)]. Although such a choice is logically unexceptionable, and indeed is equivalent to ours, we consider it not so appropriate for solids.

in conjunction with the work on isotopic alloys, of which the pure isotopes can be considered limiting cases. We accordingly postpone the verification.

### c. Effect of Isotopic Composition in Isotopic Alloys

Measurements of the normalized intrinsic resistances for isotopic alloys of atomic composition 25% Li<sup>6</sup>-75% Li<sup>7</sup>, 50% Li<sup>6</sup>-50% Li<sup>7</sup>, and 75% Li<sup>6</sup>-25% Li<sup>7</sup> (as well as natural lithium, 7.5% Li<sup>6</sup>-92.5% Li<sup>7</sup>) gave results<sup>11</sup> lying on smooth curves more or less uniformly spaced between the curves for 100% Li<sup>6</sup>-0% Li<sup>7</sup> and 0% Li<sup>6</sup>-100% Li<sup>7</sup> shown in Fig. 6. The detailed data are presented in Table II. Since the theory for isotopically impure materials is much more complicated than that for isotopically pure ones—and this theory in turn is none too good—it does not appear worthwhile to try to force isotopic alloys into the framework of the Bloch-Grüneisen formula. Instead we content ourselves with searching for a universal relation for  $\rho/\Theta$  as a function of  $T/\Theta$ , where  $\Theta$  is now calculated from the isotopic mass averaged in some fashion.

Theory is a fairly good guide here: Prigogine<sup>12</sup> has shown, in a first-order perturbation calculation, that the frequency spectrum for an isotopically impure monatomic substance has the same form as that for a pure substance having an isotopic mass equal to the arithmetic mean of the mixture; and Pirenne,<sup>13</sup> by a variational calculation applicable to any order, has shown that the first-order correction for isotopic impurities is of the same kind as that given by Prigogine, except that the arithmetic mean is to be used instead of the harmonic mean. Hence, if we assume that no new scattering mechanism enters importantly when isotopic impurities are introduced, we should expect to find a relation of the form of Eq. (3).<sup>14</sup>

Since we do not know the resistivities themselves, we cannot test directly our conjecture that  $\rho/\Theta$  is a universal function of  $T/\Theta$  for isotopic alloys. Instead we test the temperature dependence of the normalized resistances, in the following manner.

Recall Eq. (3), wherein we may incorporate the constant with the function  $f$ :

$$\rho(T)/\Theta = f(T/\Theta). \quad (3)$$

Next note that  $R(T)$  is proportional to  $\rho(T)$ , the constant of proportionality being a geometrical factor  $G$  appropriate to each specimen. The factor varies slightly

TABLE II. Normalized intrinsic resistivities,  $R(T)/R(T_0)$ , of lithium isotopic alloys.  $T_0 = 293.1^\circ\text{K}$ .

$T(^{\circ}\text{K}) \backslash x$	0-100	25-75	50-50	75-25	Natural	100-0
20	0.001	0.001	0.001	0.001	0.001	0.001
40	0.009	0.010	0.011	0.011	0.011	0.011
60	0.039	0.042	0.044	0.046	0.046	0.045
80	0.096	0.101	0.104	0.106	0.107	0.108
100	0.170	0.174	0.178	0.183	0.185	0.186
120	0.254	0.260	0.264	0.269	0.272	0.271
140	0.344	0.348	0.352	0.356	0.359	0.360
160	0.433	0.436	0.440	0.444	0.446	0.447
180	0.522	0.523	0.527	0.530	0.532	0.534
200	0.608	0.607	0.610	0.612	0.617	0.620
220	0.692	0.691	0.694	0.696	0.703	0.703
240	0.777	0.777	0.778	0.780	0.783	0.783
260	0.862	0.862	0.863	0.863	0.863	0.866
280	0.946	0.945	0.945	0.946	0.946	0.947
300	1.028	1.029	1.028	1.028	1.029	1.029

with temperature, owing to thermal expansion, but it changes in nearly the same way for all specimens. We accordingly take it as constant:

$$R(T) = G\rho(T). \quad (4)$$

We shall refer the behavior for each composition  $x$  to that for a standard composition  $s$ , say "Li<sup>6</sup>." The characteristic temperature  $\Theta_x$  for the alloy of variable composition  $x$  is related to that for the alloy of standard composition by

$$\Theta_x = \alpha_x \Theta_s; \quad (5)$$

here

$$\alpha_x^2 \equiv \bar{M}_s / \bar{M}_x, \quad (6)$$

where  $\bar{M}_s$  is the average isotopic mass of the standard alloy, and  $\bar{M}_x$  that of the test alloy.

We see from Eqs. (3) and (4) that

$$\begin{aligned} f_x(\Theta_x/T) &= \rho_x(T)/\Theta_x \\ &= [R_x(T)/G_x\Theta_x][G_x\rho_x(T_0)/R_x(T_0)] \\ &= [R_x(T)/R_x(T_0)][\rho_x(T_0)/\Theta_x]; \end{aligned} \quad (7)$$

similarly, with use of Eq. (5),

$$\begin{aligned} f_x(\Theta_x/\alpha_x T) &= [R_x(\alpha_x T)/R_x(T_0)][\rho_x(T_0)/\Theta_x] \\ &= f_x(\Theta_s/T), \end{aligned} \quad (8)$$

and

$$f_s(\Theta_s/T) = [R_s(T)/R_s(T_0)][\rho_s(T_0)/\Theta_s]. \quad (9)$$

We seek then to compute the ratio of  $f_x/f_s$  for the same value of the arguments; if our conjecture is valid, the ratio will be unity over the temperature range concerned. Division of Eq. (8) by Eq. (9) gives this quantity, but the result contains the ratio of the resistivities at  $T_0$ . In the absence of direct knowledge of this ratio, we proceed by assuming the functions  $f_x$  and  $f_s$  to be equal at some point, say  $\Theta_s/T_0 = \Theta_x/\alpha_x T_0$ :

$$f_x(\Theta_x/\alpha_x T_0) = f_s(\Theta_s/T_0). \quad (10)$$

<sup>11</sup> R. G. Leffler and D. J. Montgomery, Bull. Am. Phys. Soc. **5**, 540 (1960).

<sup>12</sup> I. Prigogine, Physica **20**, 383, 516 (1954).

<sup>13</sup> J. Pirenne, Physica **24**, 73 (1958).

<sup>14</sup> This situation is quite in contrast with that obtaining for thermal conductivity in insulators. The intrinsic electrical resistivity arises only through perturbation terms in the electron-phonon interaction, whereas thermal conductivity arises only through perturbation terms in the phonon-phonon interaction. The theory for the isotopic effect in thermal conductivity becomes complicated and obscure.

TABLE III. Departure from unity (in percent) of ratio  $w_s(x, T)$  for isotopic alloys of lithium.

$T(^{\circ}\text{K}) \backslash x$	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	Natural	1
40	+10.0	+11.8	+7.2	-3.4	+3.0
60	+2.4	+2.7	+2.2	+1.0	-1.8
80	+1.5	+1.9	+1.4	+0.2	+0.4
100	+0.3	+0.5	+1.0	+0.7	+0.9
120	+0.4	+0.6	+0.2	+0.9	+0.2
140	-0.8	+0.2	+0.3	+0.4	+0.3
160	+0.8	-0.1	0.0	+0.2	+0.1
180	+0.2	0.0	0.0	+0.2	+0.4
200	-0.6	-0.5	-0.4	+0.3	+0.7
220	-0.3	-0.2	-0.1	+0.7	+0.2
240	-0.1	-0.1	-0.1	+0.2	+0.2
260	-0.2	-0.2	0.0	+0.1	+0.1
280	-0.1	-0.1	0.0	0.0	0.0
300	-0.1	0.0	0.0	0.0	0.0

Then

$$w_s(x, T) \equiv \frac{f_x(\Theta_s/T)}{f_s(\Theta_s/T)} = \frac{R_x(T_0)}{R_x(\alpha_x T_0)} \frac{R_x(\alpha_x T)}{R_x(T_0)} \bigg/ \frac{R_s(T)}{R_s(T_0)} \quad (11)$$

gives the desired expression.<sup>15</sup>

The question remains as to the method of calculation of the average isotopic mass  $\bar{M}$ . According to Prigogine, one should take

$$\bar{M} \equiv \sum c_i M_i, \quad (\text{arithmetic mean}) \quad (12a)$$

where  $c_i$  is the atomic fraction of the  $i$ th isotope of mass  $M_i$ . According to Pirenne, one should take

$$1/\bar{M}' \equiv \sum c_i/M_i. \quad (\text{harmonic mean}) \quad (12b)$$

The difference between the two means disappears at 0%-100% and 100%-0%, of course, and for masses of 6 and 7 is equivalent to a difference of almost 4% in isotopic composition around the 50%-50% point.

We have used the data on which Table II is based to calculate the ratio  $w_s(x, T)$  referred to "Li<sup>6</sup>" (actually containing  $0.007 \pm 0.001$  atomic fraction Li<sup>7</sup>) for the nominal compositions  $\frac{1}{4}$ ,  $\frac{1}{2}$ ,  $\frac{3}{4}$ , natural, and 1 (actually,  $0.25 \pm 0.01$ ,  $0.50 \pm 0.01$ ,  $0.75 \pm 0.1$ ,  $0.925$ , and  $0.9999 \pm 0.0001$  Li<sup>7</sup>). The ratio was computed at 20-degree intervals from 40° to 300°K for both the arithmetic mean mass and the harmonic mean mass. The departure from unity of this ratio in percent—that is,  $(w_s - 1) \times 100$ —is given in Table III, where the arithmetic mean mass only has been used. From 300° to 80°K, the departure does not exceed 1%, and is usually much smaller than this. At 80°K and below, the departure rises to some 10%; but here the values of  $f_s$  and  $f_x$  themselves differ by only a fraction of a part

<sup>15</sup> Since  $\alpha T_0$  lies beyond the range of measurement, it is necessary to extrapolate the curves for  $R_x(T)$ . The curves are very nearly straight at  $T_0 = 293.1^{\circ}\text{K}$ , and it is safe to take only the linear term in the Taylor expansion for  $R_x(T)$ :  $R_x(\alpha_x T_0) = R_x(T_0)\{1 + (\alpha_x - 1)T_0 d[R_x(T)/R_x(T_0)]/dT\}$ . We can then replace the first factor on the right-hand side of Eq. (11) by the reciprocal of the term in braces above. (Of course, one could match the curves for some other temperature.)

per thousand, close to the limits of precision of the experiments.

When the harmonic-mean mass instead of the arithmetic-mean mass is taken in computing the average mass used in getting  $\alpha$ , the results are not changed significantly. The maximum difference between the two means corresponds to a difference of about 4% in isotopic composition. Now the over-all difference in  $w_s$  for 100% change in composition is only some 1 to 10% down to 80°K. Hence the maximum difference in  $w_s$  between the two methods of computing the mean will be only some 0.04 times 0.01 to 0.1, that is, at most a few parts per thousand. These differences are at the limit of precision of the experiment, and hence preclude a definite statement of the preferability of one mean over the other.

We consider then that the departure from unity in the ratio  $w_s(x, T)$  displayed in Table III is sufficiently small, both for pure isotopes and for isotopic alloys, that we may give credence to the theoretical arguments advanced earlier, and we assert that the dependence of the electrical resistivity  $\rho$  on isotopic composition  $x$  and absolute temperature  $T$  for a given element is of the form  $\rho(T)/\Theta = f(\Theta/T)$ , where  $\Theta$  is proportional to  $\bar{M}^{-1}$ , and  $\bar{M}$  is an average isotopic mass not far from the arithmetic mean. Moreover, we suggest that simple relations of this type are to be sought in other phenomena where first-order phonon interactions are controlling.

That  $\rho(T)/\Theta$  is a function of  $T/\Theta$  has useful consequences. First, the behavior of the absolute resistivity  $\rho_x(T)$  of an element with respect to temperature  $T$  and isotopic composition  $x$  is determined by knowledge of the absolute resistivity  $\rho_y(T_0)$  of any given composition  $y$  at any given temperature  $T_0$ , together with knowledge of the temperature dependence of the relative resistance of a specimen of the given composition,  $R_y(T)/R_y(T_0)$ . For it follows directly that

$$\begin{aligned} \rho_x(T)/\Theta_x &= f(\Theta_x/T) = f(\alpha_x \Theta_y/T) \\ &= f[\Theta_y/(T/\alpha_x)] = \rho_y(T/\alpha_x)/\Theta_y, \end{aligned}$$

or

$$\rho_x(T) = \alpha_x \rho_y(T/\alpha_x),$$

where we recall that  $\alpha_x \equiv (\bar{M}_y/\bar{M}_x)^{\frac{1}{2}}$ , and  $\rho_y(T) = \rho_y(T_0)[R_y(T)/R_y(T_0)]$  very nearly. For example, from the measured resistivity of lithium-natural at, say, 20°C, which we may estimate from the older literature as about 9.25  $\mu\text{ohm-cm}$ , and the data of column 5 of our Table II, the resistivity 20°C for Li<sup>6</sup> may be computed to be 9.12  $\mu\text{ohm-cm}$ , and for Li<sup>7</sup> 9.26  $\mu\text{ohm-cm}$ .<sup>16</sup>

Second, for certain studies the utility of isotopic mass is extended by permitting it to be treated as a

<sup>16</sup> The ratio of the room-temperature resistance of lithium-6 to that of lithium-natural is 0.985 in the above computation. J. Dugdale, D. Guggan, and K. Okumura have kindly communicated to us their results on the direct measurement of the absolute resistivity of lithium-6 and lithium-natural, which give a ratio of 0.986 at 20°C.



variable appearing in a given function and defined over a continuous domain, rather than on a few points only.

The existence of allotropic modifications would seem to complicate analyses of this sort. Temperature hysteresis makes most physical properties multiple-valued functions, and hence the history of the specimen must be specified. Even then, there is some question as to whether the transition temperature  $T_c$  follows the law  $T_c \bar{M}^{1/2} = \text{const.}$  In our experiments the precision in the region of the martensitic transition in lithium ( $\sim 80^\circ\text{K}$ ) was not high enough to pick up definite manifestations of the transition.<sup>17</sup> Certain irregularities in our data below  $80^\circ\text{K}$  might be attributable to a modification of the crystal structure. But all of our data were taken with temperature increasing from  $4.2^\circ\text{K}$ , and it is likely that hysteresis would have produced anomalies at temperature considerably above the transition temperature  $80^\circ\text{K}$ . We can state only that the effect of the martensitic transition is not discernible in our measurements.

#### IV. SUMMARY

##### a. Isotopic Mass

By studying the temperature dependence of the intrinsic resistance, normalized with respect to room-temperature resistance, of isotopically pure specimens  $\text{Li}^6$  and  $\text{Li}^7$  in the range  $4^\circ$ – $300^\circ\text{K}$ , it was established that

(1) the Bloch-Grüneisen equation gives the qualitative features of the temperature dependence of resistance; and

(2) the resistivity  $\rho$  divided by a characteristic temperature  $\Theta$ , a parameter inversely proportional to the

<sup>17</sup> See, e.g., D. L. Martin, *Physica* **25**, 1193 (1959).

square root of the isotopic mass  $M$ , is a universal function of  $T/\Theta$ ; or, which is the same thing, of  $TM$ .<sup>3</sup>

##### b. Isotopic Composition

By studying the temperature dependence of the normalized intrinsic resistance of isotopic alloys made with varying proportions of  $\text{Li}^6$  and  $\text{Li}^7$  in the range  $4^\circ$ – $300^\circ\text{K}$ , it was established that

(1) the general course of the temperature dependence of the resistance of isotopic alloys can be described only semiquantitatively by the Bloch-Grüneisen equation; and

(2) the resistivity  $\rho$  divided by a characteristic temperature  $\Theta$ , a parameter inversely proportional to the square root of the average isotopic mass  $\bar{M}$ , is a universal function of  $T/\Theta$  (or of  $T\bar{M}^{1/2}$ ). The data do not permit a preference to be established between arithmetic-mean mass and the harmonic-mean mass.

##### c. General Considerations

(1) The electrical resistivity of solid isotopic alloys of any composition, including the limiting case of pure isotopes, can be obtained from knowledge of the temperature dependence of the absolute resistivity of a single alloy, by means of a simple scaling factor, the square root of the ratio of the average masses, applied to the resistivity and to the temperature.

(2) Isotopic impurities do not seem to act as additional scattering sources, but serve only to modify the lattice-vibrational spectra.

(3) The existence of allotropic modifications should complicate the behavior of electrical resistance in lithium, but such an effect was not discernible in our experiments.

## Range of Heavy Ions in Solids\*

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The ranges of N, Ne, Ar, Kr, and Xe ions in Be, B, C, and Al have been measured to  $\pm 10\%$  for incident ion energy 50–500 kev. A monoenergetic ion beam from an electrostatic accelerator strikes a thick target of the absorber, and the penetration depth is determined by a momentum analysis of monoenergetic protons elastically scattered from the target and the embedded atoms. An expression relating the penetration depth to the actual path length is derived. A linear range-energy behavior is found for Ar, Kr, and Xe ions; for N and Ne ions  $dE/dX$  increases with ion energy. The experimental ranges are 20% shorter than theoretical values based on energy loss by elastic nuclear collisions. By including electronic contributions to the stopping process, good agreement with experiment is achieved.

#### I. INTRODUCTION

BOHR laid the foundation for a theoretical description of the energy loss of heavy ions of low velocity in his 1948 paper,<sup>1</sup> and his analysis of the stopping

process in terms of elastic nuclear collisions has since been extended by Nielsen<sup>2</sup> and by Lindhard and Scharff.<sup>3</sup> In spite of the increased use of accelerated heavy ions in recent years, there are very few experi-

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<sup>1</sup> N. Bohr, *Kgl. Danske Videnskab. Selskab., Mat.-Fys. Medd* **18**, No. 8 (1948).

<sup>2</sup> K. O. Nielsen, in *Electromagnetically Enriched Isotopes and Mass Spectrometry*, edited by M. L. Smith (Academic Press Inc., New York, 1956), p. 68.

<sup>3</sup> J. Lindhard and M. Scharff, *Phys. Rev.* **124**, 128 (1961).