

THE EFFECT OF ISOTOPIC COMPOSITION ON THE
ELECTRICAL RESISTANCE OF LITHIUM

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Richard Gordon Leffler
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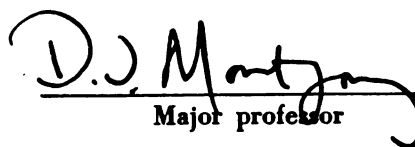
THE EFFECT OF ISOTOPIC COMPOSITION
ON THE ELECTRICAL RESISTANCE OF LITHIUM

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ABSTRACT

THE EFFECT OF ISOTOPIC COMPOSITION ON THE ELECTRICAL RESISTANCE OF LITHIUM

by Richard Gordon Leffler

The electrical resistance of solid metallic lithium containing varying proportions of lithium-6 and lithium-7 was measured between 4.2°K and 295°K . For the isotopically-pure substances, the main features of the behavior agree with the predictions of the Bloch-Grueneisen 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. This portion of the work represents an extension and refinement of our earlier work, and a confirmation of subsequent work by others. For the isotopic alloys, 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 represented as a universal curve, by use of appropriate scaling factors. The temperature-scaling factor is determined merely by some kind of average isotopic mass. For isotopic alloys of lithium, there is very little numerical difference between the arithmetic mean and the harmonic mean of the isotopic masses and it is impossible to decide from the present experiments which average is preferable and thereby choose between certain theoretical proposals concerned with the effect of isotopes on lattice-vibration spectra.

On the other hand, the results show clearly that there is no need at all to invoke a scattering mechanism that looks upon isotopes as impurities in the lattice. The effect of the martensitic transition of lithium at low temperatures is barely, if at all, discernible.

THE EFFECT OF ISOTOPIC COMPOSITION ON THE
ELECTRICAL RESISTANCE OF LITHIUM

By

Richard Gordon Leffler

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INTRODUCTION

Over three decades ago Dirac could write ". . . The underlying physical laws necessary for the mathematical theory for a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. . . ." (1) In that large part of physics is included solid-state theory, which is almost always concerned with energy changes small compared with the rest energy. The number of particles demanding simultaneous treatment is so enormous that indeed direct solution of the quantum mechanical equations appears hopelessly beyond reach. In the usual way, then, models of varying degrees of crudeness have been developed to handle different problems. For transport phenomena in crystals, specifically for electronic conduction in metals, the standard treatment is to begin with a model of a perfect crystal lattice on which the ion cores are located, with a certain number of electrons unattached to specific atoms and free to move about among the ion cores. Thermal energy appears as vibrations of the lattice, and as kinetic energy of the electrons. For mathematical treatment, the quantized vibrations are considered as a phonon gas, and the electrons are represented by wave packets. In this treatment the individual ion cores and the individual electrons disappear, being replaced by collective models.

Even after this profound simplification, the mathematical difficulties in handling any realistic model remain insuperable. Further approximations must be made, and it becomes important then to test the predictions of the simplified theory to gain some idea of the overall soundness of the simplified theory and of its region of validity.

Quite soon after the birth of modern quantum theory, Bloch (1930) (2) derived an expression for the temperature dependence of the electrical resistance of a pure metal insofar as the resistance arises from thermal vibrations of an otherwise perfect lattice. The expression was decidedly successful, and with this splendid beginning, one might have hoped for rapid progress in refining this Bloch-Grueneisen formula, as it came to be called in view of Grueneisen's study and explanation of it (3). However, the mathematics remained intractable, and an absolute calculation could not be made. Hence we must say that despite the generally satisfactory picture given in the Bloch treatment, present theory does not permit an assessment of its validity for the details of electronic conduction in metals. We need to make use of experiment, therefore, to test various aspects of the derivation.

The Bloch formula can be separated into a constant (calculable from certain parameters of the metal), times a function of the temperature and of another such constant usually written as a characteristic temperature. When the form of the function is tested rough agreement is obtained; but the function fails to describe the details of the temperature variation of resistivity for a given metal. Of course such behavior is to be expected, for, among other things, the lattice-vibration frequency spectrum and the shape of the Fermi surface are grossly simplified. Because of the complexity of this part of the calculation, the deviations of the experimental results from the theoretical do not shed much light on the places where the derivation is the most inadequate. In particular, we cannot be sure whether the deviations are due to inadequacy of the model, or to the mathematical simplifications necessary to effect calculation.

On the other hand, an investigation of the dependence of the constants on the metal parameters can lead to more fruitful results.

Specifically, if the atomic mass is varied, all other parameters remaining essentially the same, simple predictions are possible about certain features of these constants. Mathematically, we are saying simply that it is easier to study resistivity as a function of the atomic mass rather than as a functional of the atomic field, lattice vibration spectrum, and so on.

The present thesis is concerned with testing the validity of the Bloch picture by using isotopic mass as a probe. The details of this analysis are given in the theory section. In the first part we shall see that in isotopically-pure crystals the effect of atomic mass is just as would be predicted from the theoretical picture, and we are thereby given additional confidence that the shortcomings in the form of the function are due simply to over simplification in the mathematical treatment. This result was foreshadowed by earlier work in our laboratory (4), and recently by results of Dugdale and his collaborators at the National Research Council at Ottawa (5).

In the second part we consider the effect of isotopic composition--that is, the effect of varying the amount of one isotope of a given element relative to that of another isotope of the same element. This problem is much more complicated theoretically than the corresponding one for an isotopically-pure substance. One scheme proposes that mass imperfections (isotopes of different mass) act in much the same way as field imperfections (that is, as chemical impurities, which give different atomic fields). The mass excess of each atom is considered as a deviation from the average density of the solid, and acts as a perturbation to give the basis for a correction formula. We find this picture completely unconvincing. It seems to us that the only effect of varying the isotopic mass is to change the lattice-vibration spectrum, and not at all to introduce a new scattering mechanism. If our surmise is correct, the resistivity of isotopic alloys of Li-6 and Li-7 should lie

between the resistivities of pure Li-6 and Li-7. If the other picture is correct, the resistivity of isotopic alloys should always be higher than those of the pure isotopes.

In the present experiments, a direct comparison of this sort is not possible, since resistivities were never calculated, in view of the difficulty in knowing the dimensions of the sample accurately. Nevertheless, the examination of the temperature dependence of the relative resistivities failed to show any evidence of a new mechanism of scattering. Hence we conclude merely that the frequency spectrum of the isotopic alloys is intermediate between those for the pure isotopes making up the alloy. This conclusion is in keeping with the predictions of Prigogine (6) and of Pirene (7), who showed that to the first order the frequency spectrum is modified only by scaling the frequency in the ratio of the square root of the average mass. Prigogine takes the direct mean of the masses, and Pirene the harmonic mean. For Li-6 and Li-7, however, there is insufficient difference between the two methods of averaging to permit a choice.

In summary, the present work first of all extends the range and increases the precision of the measurements of Snyder on the resistance of metals, and corroborates the measurements of Dugdale et al. on the same subject. Thereby the qualitative soundness of the Bloch-Grueneisen picture of electrical conductivity in metals is confirmed. Secondly, the present work shows that the effect of isotopic composition can be explained by merely modifying the lattice-vibration spectrum, in accordance with the theories of Prigogine and of Pirene, without introducing any scattering through the apparent disorder of a random mixing of isotopes on lattice sites. If this interpretation is correct, serious modification of the analysis of experiments on heat conductivity may be required.

THEORETICAL CONSIDERATIONS

To picture first in a simple way the origin of electrical resistivity consider a perfect three-dimensional lattice with ions stationary at the lattice sites. Valence electrons which are nearly free are moving at random about the lattice ions, and it is seen from symmetry that no net transport of charge takes place. If a uniform electric field is applied, the free electrons will be accelerated and an arbitrarily large current would flow if there were no forces to obstruct the electrons. But if the ions are thermally agitated the deviation from perfect periodicity will cause collisions to occur between the ions and the electrons. The electrons are thus scattered and the current is thereby limited.

Historically, Weber (8) attempted in 1875 to account for the passage of electricity through metals by assuming that a molecule was composed of a number of electrically-charged particles, some of which would break away from the molecule and be captured by neighboring molecules. His goal was to account for the empirical evidence due to Wiedemann and Franz (9) (1853) that the ratio of electrical and thermal conductivities at a given temperature is the same for all metals. No real progress could be made, however, until after the discovery of the electron. Drude (10) (1900) was able to give a theoretical derivation of the Wiedemann-Franz law by means of the simple picture of an electron gas moving among fixed ions. The electrons, upon acceleration by an external electric field, were considered to collide with the ions with a certain relaxation time between collisions. His expression for electrical conductivity is

$$\sigma = ne^2\tau/m$$

where σ is the electrical conductivity, n is the number of charge carriers, τ is the relaxation time, and $-e$ and m are the charge and the mass of an electron respectively. Drude considered only average velocities and average drift velocity. He predicted not merely the form of the Wiedemann-Franz law, but also an excellent value for the numerical constant. However, the observed dependence of σ on temperature could not be reconciled with the picture.

Lorentz (11) improved the calculation by introducing distribution functions for the electrons. A full statistical treatment, following Maxwell and Boltzmann, together with a generalization about the dependence of relaxation time on velocity enables him to get the correct temperature dependence for σ , but only at the cost of good numerical agreement. Later, another objection appeared. The Lorentz theory required also that about one electron per atom be free to move about within the metal; but these electrons should contribute to the specific heat, and hence give to metals a much higher specific heat than to insulators, in contradiction to the Law of Dulong and Petit (12). Not until 1928 when Sommerfeld (13) applied the work of Pauli, Fermi, and Dirac to transport phenomena, was this difficulty of the Drude-Lorentz theory reconciled.

The problem was now on a quantum-mechanical basis, and Bloch (1930) (2) made the next contribution by showing that electrons having energies lying in certain bands can move through a perfect periodic crystal lattice freely, and that it is imperfections in the lattice that are responsible for electrical resistance. The effect of thermal motion increases with temperature, of course. Impurities and lattice defects of various other types give rise to stationary imperfections whose effects are usually small. These effects are nearly independent of temperature, and they provide the major contribution to electrical resistivity at low temperatures, since the resistance due to thermal motion falls off rapidly with temperature.

The temperature-dependent part of the electrical resistivity may be approached as follows. Consider the behavior of free electrons in a perfect lattice (thermal motion absent). Consider independently the motion of ions about their lattice sites. Superpose these two models, let them interact weakly, and determine transition probabilities; from them find the scattering term in the Boltzmann equation. With the use of appropriate statistics an expression for electrical conductivity is obtained.

Let us consider this problem in more detail. To treat the lattice vibrations, take a collective model. For the crystal write a Hamiltonian which ignores electron coordinates, considering only the atomic cores. The electrons are light particles and presumably accommodate very quickly to the nuclear motion. This "adiabatic principle" enables the electronic states to be treated as a unique function of the nuclear coordinates at any instant. To a first approximation this system may be analyzed into a set of independent normal vibrational modes, each equivalent to a simple harmonic oscillator. The energy is given by

$$E = \sum_{\mathbf{q}} \left(n_{\mathbf{q}} + \frac{1}{2} \right) \hbar \omega_{\mathbf{q}}$$

the eigen states corresponding to traveling waves characterized by a wave vector $\mathbf{q}$. Because one is dealing with lattice waves and not with a continuum dispersion exists; moreover the allowed values of $\mathbf{q}$ are discrete and finite. The maximum value of $\mathbf{q}$ corresponds to a wave length of twice the lattice spacing. Larger $\mathbf{q}$'s correspond to nothing new physically. The transport of energy in one of the states turns out to be proportional to the group velocity of the waves, in the same way as in classical field theories. A quantum of lattice vibration may thus be defined as a phonon--in analogy with the photon--which travels through

the lattice with the group velocity of that mode. In a sense phonons may be considered as particles, and they then satisfy Bose-Einstein statistics. Two transverse modes and one longitudinal mode are associated with each $\underline{q}$ vector. If there is more than one particle per unit cell, additional branches may arise in the dispersion curve, a feature of no interest for the present work.

We can define $g(\omega)d\omega$ as the number of modes with frequencies between ω and $\omega+d\omega$. A good low temperature approximation is for $g(\omega) \sim \omega$. The values of $\underline{q}$ are distributed with uniform density in reciprocal space, and the number with wave constants lying in the interval $\underline{q}$ and $\underline{q} + d\underline{q}$ would be proportional to $q^2 dq$ in a continuum. Then

$$q(\omega) \propto \omega^2$$

It is convenient to define a new parameter θ such that $k\theta$ is the maximum allowed energy of a phonon.

For the electrons, let us consider in particular a monovalent metal, and concern ourselves only with conduction electrons. For a single atom it is assumed that the entire mass is associated with the nucleus and that the inner closed shells of the electrons form a rigid halo about the nucleus, the valence electrons moving independently in the field of the core. When all the atoms are brought together to form a metallic solid, the valence electrons move in the field of all the ions combined, together with a smeared-out field due to all the other valence electrons. The wave functions for such a system are not localized, but spread out throughout the crystal field. The group of valence electrons as a whole forms a pool from which the energy states for a crystal as a whole may be filled.

At this stage of the argument assume that the lattice is perfect, that is, the ions are at rest in their equilibrium positions. The Hamiltonian for such a system contains a kinetic-energy term for the

electron, a potential-energy term for the ion-electron interaction, and another potential-energy term for the electron-electron interaction. From the mathematical point of view the resulting Schroedinger equation is hopelessly complicated. The simplest thing to try is to neglect all but the kinetic-energy term in the Hamiltonian. Then

$$E(k) = \hbar^2 k^2 / 2m$$

where $k = 2\pi/\lambda$ is the magnitude of the wave vector. The wave function is a simple product function of plane waves not containing a spin function and not antisymmetrized in the coordinates of the electrons. A function incorporating these features, such as that given by a Slater determinant would be too hard to work with. A simple product function is tractable, and is kept realistic by the stipulation that not more than two of the single electron functions may be identical. This case amounts to discussing free electrons and is essentially the Sommerfeld presentation. The surfaces of constant energy in $\underline{k}$ space are spheres. This model serves as a general guide to the behavior of electrons in metals, but to get any details of electron behavior, notably band structure, the next term in the Hamiltonian must be taken into account. Considering the potential term to act as a small perturbation on the free electrons, one finds that there are values of $\underline{k}$ for which there may be discontinuities in the energy. That is, gaps exist in the quasi-continuous energy spectrum, and the energy is no longer proportional to k^2 . The regions of allowed energy separated by energy gaps are called energy bands. The surfaces in $\underline{k}$ space mapped out by these surfaces of energy discontinuity form the boundaries of the Brillouin zones of the reciprocal space. Surfaces of constant energy in $\underline{k}$ space tend to be spheres for small values of $\underline{k}$, but those surfaces which cross zone boundaries must cross them at right angles, and hence must be drastically distorted from spherical shape.

The electronic states considered so far have been stationary states, appropriate to equilibrium conditions. We are interested in transport problems wherein a steady state--rather than an equilibrium state--is attained under the influence of external driving forces of some kind. For this purpose wave packets must be constructed from the simple plane waves, the motion of which then corresponds to a particle motion. In a dispersive medium wave packets travel with the group velocity, given by

$$\underline{v}_k = \frac{1}{\hbar} \frac{\partial E}{\partial \underline{k}} \quad .$$

The dynamics of such a wave packet may be quite different from that of free classical particles. From now on we think of this wave packet in the solid as an electron and associate with it the crystal "momentum" $\hbar \underline{k}$. The velocity will approach zero at a zone boundary since $\partial E / \partial \underline{k}$ goes to zero then. In general $\underline{k}$ and $\underline{v}_k$ are not parallel, as seen below. The electric current associated with an electron in state $\underline{k}$ is $e \underline{v}_k$. A consequence of a theorem due to Wannier (14) is that $\hbar \dot{\underline{k}} = e \underline{E}$ for a single non-overlapping band. This equation of motion says that the electron is accelerated until it reaches the Bragg wavelength, at which time it is reflected by the lattice, to be accelerated again.

The acceleration of the electron is given by

$$\dot{\underline{v}}_k = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial \underline{k} \partial \underline{k}} \cdot \underline{F}$$

where $\underline{F}$ is an external force, and the factor just preceding it is an inverse mass tensor. This quantity may become negative and may then be interpreted as a positive hole. A consequence of electrons obeying Fermi-Dirac statistics is that, practically speaking, only the electrons lying in a "thermal layer" of the order of kT about the Fermi surface can have their states altered. Thus the shape and area of the Fermi surface are determining.

Everything said so far has assumed that the phonons and electrons are entirely independent. That is, excitations of one are entirely independent of those of the other. With these simplified models no transport properties can be predicted. To go further one no longer neglects the anharmonicity of the lattice forces generating the phonons, the coulomb-forces between electrons, or the complicated forces which act on electrons due to thermal distortion of the lattice. Real crystals contain also imperfections in the lattice due to vacancies, dislocations, impurity sites, grain boundaries, and so on. The effect of these properties is treated by including in the Hamiltonian terms which allow for weak interactions between them, usually in the form of perturbations of the harmonic independent-particle states, the perturbations causing exchange of energy between the states. The effect of the perturbing term in the Hamiltonian is to give the system initially in the state $|i\rangle$, of energy E_i , a probability of finding the system in a state $|f\rangle$, of energy E_f after a time t . The time derivative of this probability is called the transition probability. For the case of electron-phonon interactions, one conceives of an electron in a particular eigenstate and a lattice vibration described by its eigenstate. The phonon represents a lattice disturbance in which some of the atoms are moved out of their ideal lattice sites. An electron is affected by this disturbance and is liable to be scattered out of its eigenstate.

As shown by a direct calculation of the matrix elements, the general condition for scattering is that the total wave vector cannot be changed except by a reciprocal lattice vector, i. e.

$$\underline{q} = \underline{k} - \underline{k}' - \underline{g}$$

where $\underline{g}$ is a reciprocal lattice vector. When $\underline{g} = \underline{0}$ the process is called a normal process. When $\underline{g} \neq \underline{0}$ the process is called an Umklapp process.

To take into account the other electrons, the adiabatic approximation or Born-Oppenheimer approximation is adopted, wherein the motion of the ions is assumed to be so slow compared with that of the electrons that the electron configuration is always the equilibrium configuration for the particular positions of the ions at that instant. This assumption enables the eigenfunctions for the total Hamiltonian to be broken up into a product of two functions, one containing the nuclear coordinates only, the other containing electronic coordinates as variables with the nuclear coordinates entering merely as parameters. The adiabatic principle allows us to think of the electronic state of the system as being almost independent of the lattice vibrational state of the system. Each makes an independent contribution to the total energy. This separation of energies is the most valuable contribution of the principle.

The small cross term previously neglected in the Hamiltonian is what gives such properties as electrical resistivity. The matrix element calculated from this cross term does not vanish, and corresponds to events in which both electronic and vibrational configurations are altered, as in electrical resistance. The matrix element refers to a process in which a phonon is absorbed or emitted, and an electron is scattered. Examination of this matrix element shows that in the scattering process energy must be conserved, i.e.

$$E_{k'} = E_k + \hbar \omega_q$$

The change in the phonon energy is usually very small, and it is sometimes permissible to consider that the electron is scattered into a state of essentially the same energy.

In evaluating the integrals in the expression for transition probability, the assumption of a Debye frequency spectrum is almost the

only reasonable one to adopt and still be able to calculate. It turns out that the electron-lattice interaction is mainly due to longitudinal phonons.

The scattering term of the Boltzmann equation is now known in principle. The final result for the ideal electrical conductivity, known as the Bloch-Grueneisen equation is

$$\sigma_1 = \left[4 A \left(\frac{T}{\theta} \right)^5 J_5 \left(\frac{\theta}{T} \right) \right]^{-1} \quad (1)$$

where A is approximately constant, J_5 is a Debye integral, and θ is a parameter for the electrical resistivity analogous to the Debye temperature in the theory of specific heats. Define

$$J_5(x) \equiv \int_0^x \frac{z^5 dz}{(e^z - 1)(1 - e^{-z})}$$

No mention has been made of the term in the Hamiltonian for the interaction of the conduction electrons. The question arises whether electron-electron scattering contributes to electrical resistance. As before one may speak of normal and Umklapp scattering processes. Normal processes correspond to the interchange of momentum between the conduction electrons and do not contribute to resistance. Umklapp processes do contribute a term which is proportional to T^2 at low temperatures. For a monovalent metal this contribution is very small, and while it is expected that this T^2 term should dominate the resistance at very low temperatures this has never been observed.

The static imperfections of most interest here are isolated point imperfections such as chemical impurities, vacancies, and interstitials. To a first approximation the contributions of these to electrical resistance are independent of each other, of temperature, and of the temperature dependent contributions, because the scattering mechanisms are assumed to be independent. Calculations (Sondheimer, 1950) (15) and experiment support this assumption. The additive

aspect of the separate contributions to the resistivity was determined experimentally by Matthiessen (1862) (16) and is known as the Matthiessen rule. Thus for the total resistivity

$$\rho = \rho_{\text{lattice vibrations}} + \rho_{\text{electron-electron}} + \rho_{\text{impurities}} + \dots$$

The adequacy of the functional form of equation (1) has been extensively investigated for natural lithium in the papers of Kelly and MacDonald (17). Results of this investigation will be discussed later. The isotopic mass dependence of the parameter θ in equation (1) should be examined now to test the soundness of the underlying structure of the theory. According to the Bloch formula, the conductivity at any temperature T (after normalization through division by the conductivity at some standard T_0) should be a universal function of T/θ . How well this prediction is verified will be treated in the Discussion of Results.

To study the effects of isotopic composition, we make use of some work of Pirene (7) on the change of frequency distribution when isotopic impurities are introduced randomly in the lattice. His fundamental treatment for monatomic crystals shows that to first-order terms in $\delta M/M$, where M is the average atomic mass, and δM is the deviation from it for a given isotope, the frequency spectrum is modified in proportion to the mass excess. (Actually Pirene shows that the harmonic mean is a better choice than the arithmetic mean, a parameter proposed earlier by Prigogine (6) in a perturbation treatment.) For $\delta M/M$ less than say $1/5$ the difference between the two means is insignificant, and it is impossible to decide between the two representations in typical experiments.

SAMPLES

A. Procurement and Analysis

Stable isotopes of lithium having high chemical purity and high isotopic enrichment have been made available by Oak Ridge National Laboratory. All of the lithium samples used in this experiment were made from Li-6 (99.3% Li-6; 0.7% Li-7), Li-7 (0.01% Li-6; 99.99% Li-7), and natural lithium (7.52% Li-6; 92.48% Li-7).

The natural lithium was obtained from Lithium Corporation of America, Minneapolis, as their low-sodium grade lithium, in rods of 3/8-inch diameter. The chemical specifications were the following:

Na	0.005%
K	0.01
Ca	0.02
N	0.06
Fe	0.001

The highly-enriched isotopes were distilled at Oak Ridge National Laboratory to remove as much of the chemical impurity as possible.

The spectroscopic analyses before distillation are as follows:

Lot No. SS5(b)

Isotopic Analysis (atomic percent):

Li-6, $99.3 \pm 0.2\%$; Li-7, $0.7 \pm 0.1\%$

Spectrographic Analysis (element and weight percent, presumed precision $\pm 100\%$):

Al	.01T	Fe	.05	Pb	.01
Ba	.01	K	.01	Sn	.01
Be	.001	Mg	.01	Sr	.01
Ca	.25	Mn	.01	V	.01
Cr	.01T	Na	.02	Zn	.25
Cu	.02	Ni	.01		

Lot No. SS7(b)

Isotopic Analysis (atomic percent):

Li-6, $0.01 \pm 0.01\%$; Li-7, $99.99 \pm 0.01\%$

Spectrographic Analysis (element and weight percent, presumed precision $\pm 100\%$):

Al	.05	K	.01	Rb	.01
Ba	.02	Mg	.01T	Si	.05
Ca	.02	Mn	.02	Sn	.05
Cr	.05	Mo	.05	Sr	.2
Cu	.01T	Na	.01	V	.02
Fe	.05	Ni	.05		

No chemical analysis was made after distillation. A comparison with analyses before and after distillation on other lithium isotopes (Lot No. SS5(a)) indicates that a substantial decrease in impurities occurs in those elements which are present in amounts greater than .01 atomic percent. (An exception is found in the case of strontium, presumably because the vapor pressure curves for strontium and lithium are very nearly identical.) It is therefore assumed that the material actually used contained impurities in amounts less than these of the above analyses.

B. Preparation

The samples consisted of wires of lithium about one millimeter in diameter. They were extruded from a steel die in a dry-box containing a carbon dioxide atmosphere. The samples remained in this atmosphere within the dry-box during installation into the measuring apparatus until the sample chamber was evacuated. This procedure was necessary because of the chemical reactivity of lithium with the nitrogen, oxygen, and water vapor in the air.

"Alloys" of the isotopes were prepared by melting weighed amounts of the pure isotopes in mineral oil previously degassed by long

heating above 100°C . After thorough mixing, the molten material was drawn into a rod suitable for insertion in the steel die, and the samples of wire were extruded. Under the assumption of uniform mixing, the isotopic concentrations of the samples used are as follows:

<u>Sample No.</u>	<u>Li-6</u>	<u>Li-7</u>
10-5	99.3 $\pm .2\%$	0.7 $\pm .2\%$
10-6	0.01 $\pm .01$	99.99 $\pm .01$
15-5	99.3 $\pm .2$	0.7 $\pm .2$
15-6	7.5	92.5
17-5	.01 $\pm .01$	99.99 $\pm .01$
17-6	7.5	92.5
18-5	99.3 $\pm .2$	0.7 $\pm .2$
18-6	.01 $\pm .01$	99.99 $\pm .01$
20-5	25 ± 1	75 ± 1
20-6	25 ± 1	75 ± 1
21-5	50 ± 1	50 ± 1
21-6	75 ± 1	25 ± 1

APPARATUS

A. Measurement of Resistance

The resistance was measured potentiometrically. In this laboratory previous measurements down to liquid-air temperatures were made with a Rubicon Standard Kelvin Bridge. For measurements down to liquid-helium temperatures however, this method is no longer practical, because the design of the bridge demands that one of the current leads to the unknown sample have very small electrical resistance and therefore correspondingly large heat conductance. The large heat leak thereby introduced into the cryostat hinders cooling and renders the achievement of thermal equilibrium impossible. Moreover, even when the Kelvin bridge is in balance a small current flow in the potential leads from the sample. Hence these leads cannot be of arbitrarily small diameter. The potentiometric method, on the other hand, allows use of both current and potential leads of small diameter, and accurate results may be obtained with small currents. The choice for the optimum lead sizes was made according to the suggestions of McFee (18).

Figures 1, 2, and 3 are photographs of the experimental setup. Figure 4 is a schematic diagram of the system. A potential of about 6 volts was supplied to the external circuit by a lead-acid storage battery. A decade resistance box controlled the current. A reversing switch was placed across the battery. The current, whose value was kept at about .036 ampere for most of the measurements, was determined by noting the potential drop across a ten-ohm standard resistor. This drop was measured by a Leeds and Northrup K-3 Potentiometer used in conjunction with a high-sensitivity d-c galvanometer (7×10^{-8} v/mm).

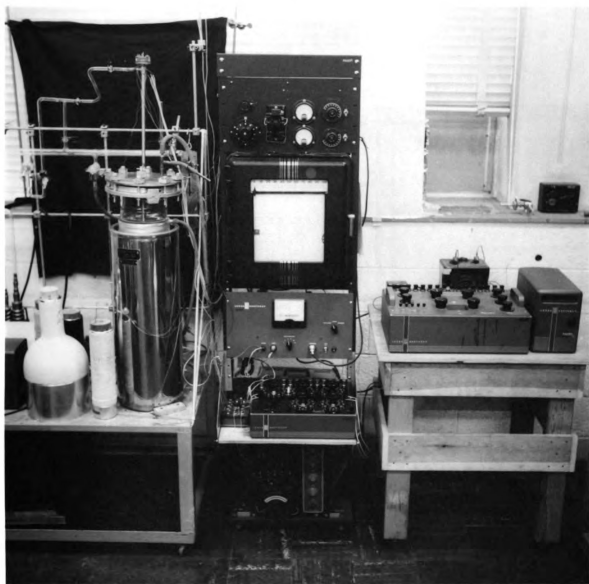


Figure 1. Over-all view of apparatus. To the left of center is the metal Dewar. From its mouth projects the top of the glass Dewar covered by the brass top plate. In the center at the top is the control and switching panel. Below it is the Speedomax recorder whose input consists of the output from the d-c microvolt amplifier just beneath it. The Mueller bridge is placed on a shelf in front of the amplifier. At the bottom are the storage batteries and current-control circuit. On the table to the right is the K-3 potentiometer with its galvanometer.

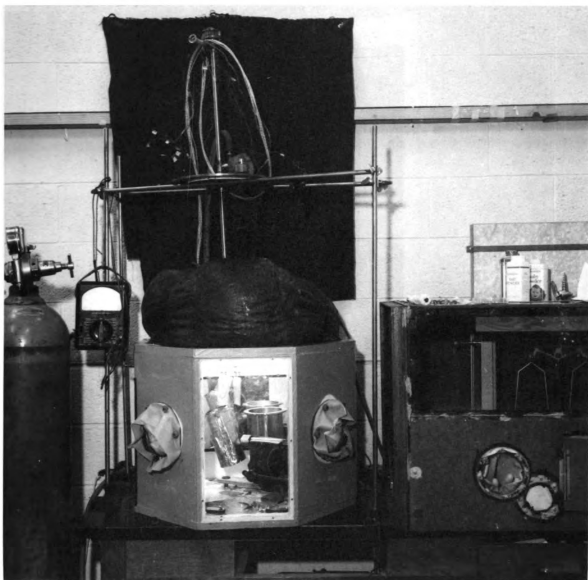


Figure 2. View of internal parts of apparatus positioned in dry box and ready for sample placement. At the top of the picture is the conduit through the center of brass top plate. The conduit projects through the balloon buoyed up by carbon dioxide from the cylinder to the left. Within the dry box may be seen in the foreground a vise holding the extrusion apparatus, and at its end the aluminum radiation shield. Behind the vise is the brass tank.

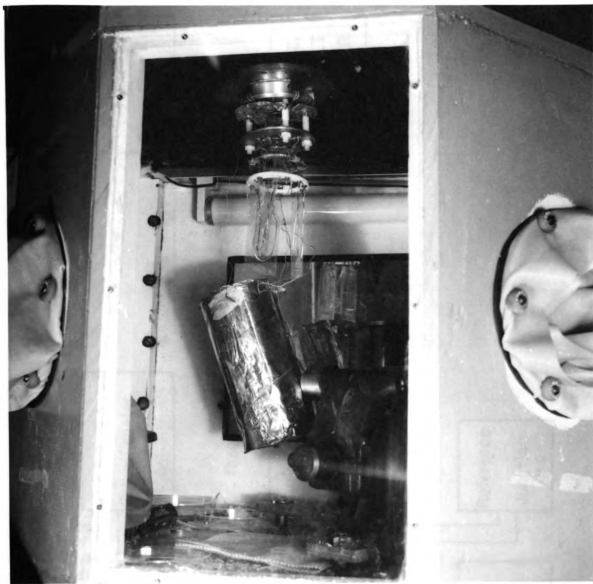


Figure 3. Close-up view of the interior of the dry box. At the top is the brass plate holding the aluminum doughnut with openings through which the leads have been wrapped. Three Teflon stand-off insulators carry an aluminum plate, which in turn supports the temperature-equalizing ring around which the leads are wrapped several times. Beneath it is the Teflon sample holder with the lithium samples (covered by polyethylene envelopes) looping down from it. The aluminum radiation shield hangs in the middle of picture, just in front of the extrusion apparatus.

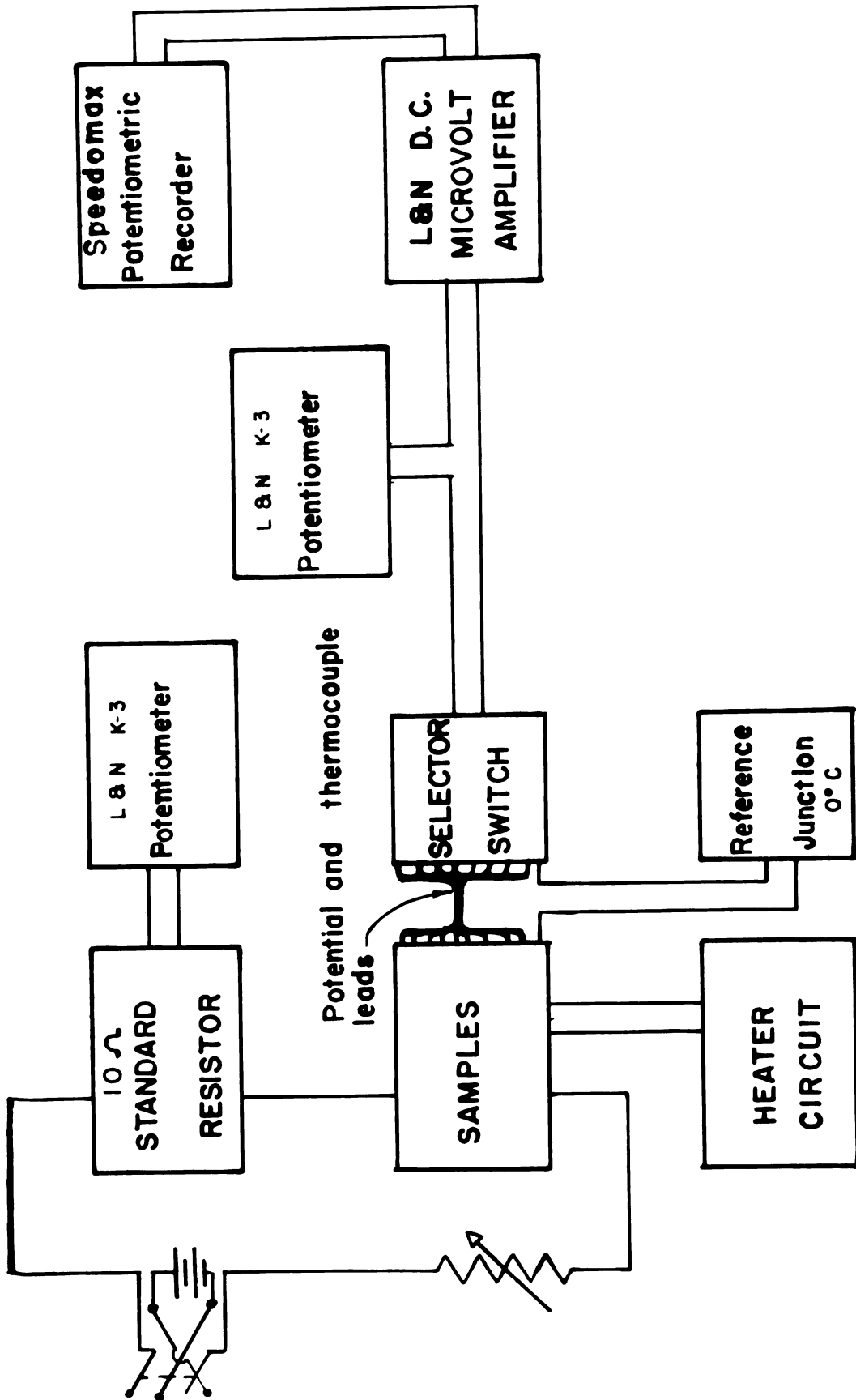


Figure 4. Block diagram for external circuit.

A precision of about 0.01% was attainable in the current measurement. The potential drop across the lithium samples was measured with the same arrangement.

B. Measurement of Temperature

The temperature of the sample in any given resistance measurement should be known to within 1°K or better. Two copper-constantan thermocouples were employed (constantan, Leeds and Northrup thermocouple wire, 30-gauge wire; copper, Leeds and Northrup thermocouple wire, 30-gauge, matched for copper-constantan thermocouples.) One thermocouple, at the top of the sample container, gave the temperature in the neighborhood of the samples. The other thermocouple was wound around a dummy sample and gave the temperature of the lithium. If the readings of these two thermocouples were nearly the same, it was assumed that the temperature gradients in the lithium wires themselves were quite small. In addition, a differential thermocouple detected thermal gradients within the sample container. Manually-controlled heaters helped eliminate these thermal gradients and thus ensured uniform temperature in the container surrounding the samples.

The thermocouple junctions were made with high-melting silver solder. The reference junction was cemented to a piece of glass tubing and immersed in an ice bath, where it was surrounded with crushed ice made from distilled water. The temperature of the reference junction was determined by a calibrated platinum resistance thermometer immersed in the junction bath and in juxtaposition with the thermocouple junction. The output from the thermocouples was fed into a Leeds and Northrup d-c microvolt amplifier. A portion of this signal was backed off with a potentiometer, and the net emf. was fed into a Leeds and Northrup Speed-o-Max self-balancing recording potentiometer.

Calibration points for the thermocouple were obtained in order to determine the deviation from the copper-constantan thermocouple tables. A certified platinum resistance thermometer was used as the standard at all temperatures except 4.2°K , the boiling point of helium at atmospheric pressure. For the standardization the thermocouple was wrapped around and cemented to the platinum resistance thermometer. To get temperatures below that of liquid air, the platinum resistance thermometer and the thermocouple were mounted on the end of a piece of glass tubing and inserted into a liquid-helium Dewar flask at varying levels above the surface of the liquid.

C. Cryostat and Sample Holder

The measurements of resistance were made in a cryostat shown schematically in Figure 5. The sample holder, shown enlarged in Figures 6 and 7, consisted of a flat ring of Teflon. Samples of lithium wire were suspended at both ends of this ring, and were held in place by copper bolts placed in the plate and serving as current contacts. Care was taken not to deform the wire except at the bolt itself. Similar copper bolts placed near the current contacts served as the base from which the potential contacts were made. Springs were made from brass spring wire in a hair-pin shape. A sharp point was put on one end of the wire, and the other end was bent into a small circle in the plane of the hairpin. The springs were fastened in place by copper bolts with copper nuts, and acted as spring-loaded potential contacts. Figure 7 shows this construction in detail. Current and potential leads were connected to the copper bolts with copper nuts. The sample holder was suspended by its lead wires from a flat aluminum ring around which all the current, potential, and thermocouple leads were fastened. This ring, which served as a heat exchanger, was in turn, suspended from the top plate

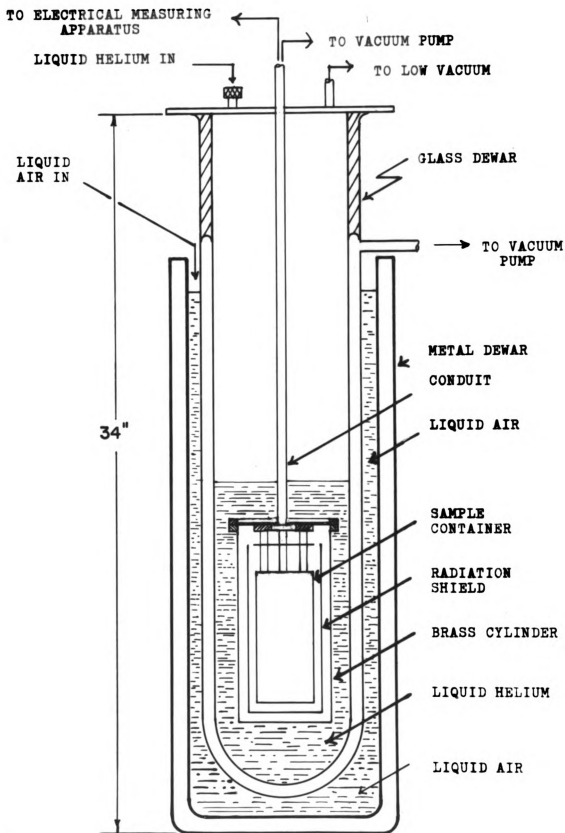


Figure 5. Cross-sectional view of cryostat assembly.

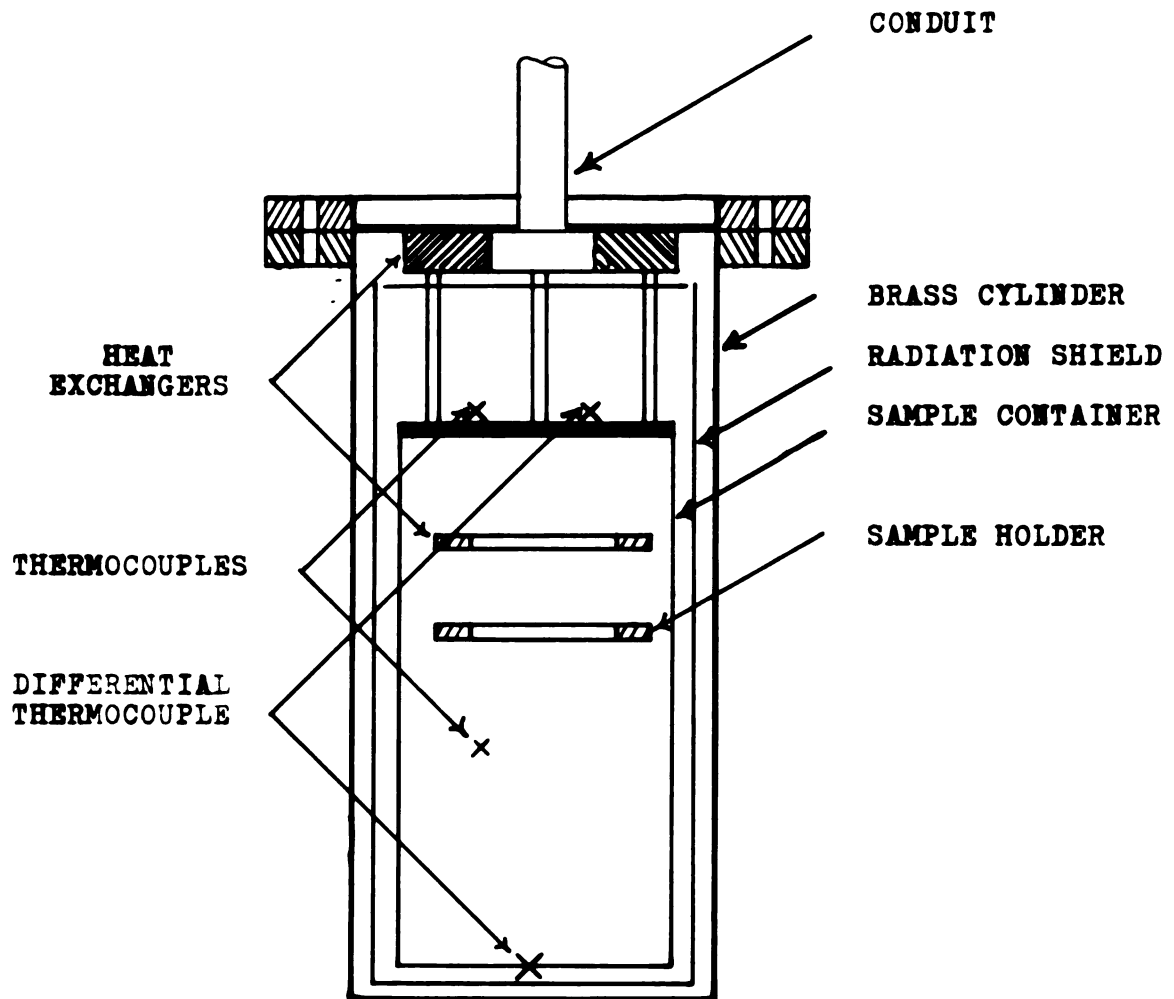


Figure 6. Detail of measuring chamber. The locations of the thermocouples are indicated by x's. To avoid confusion, the leads have been omitted.

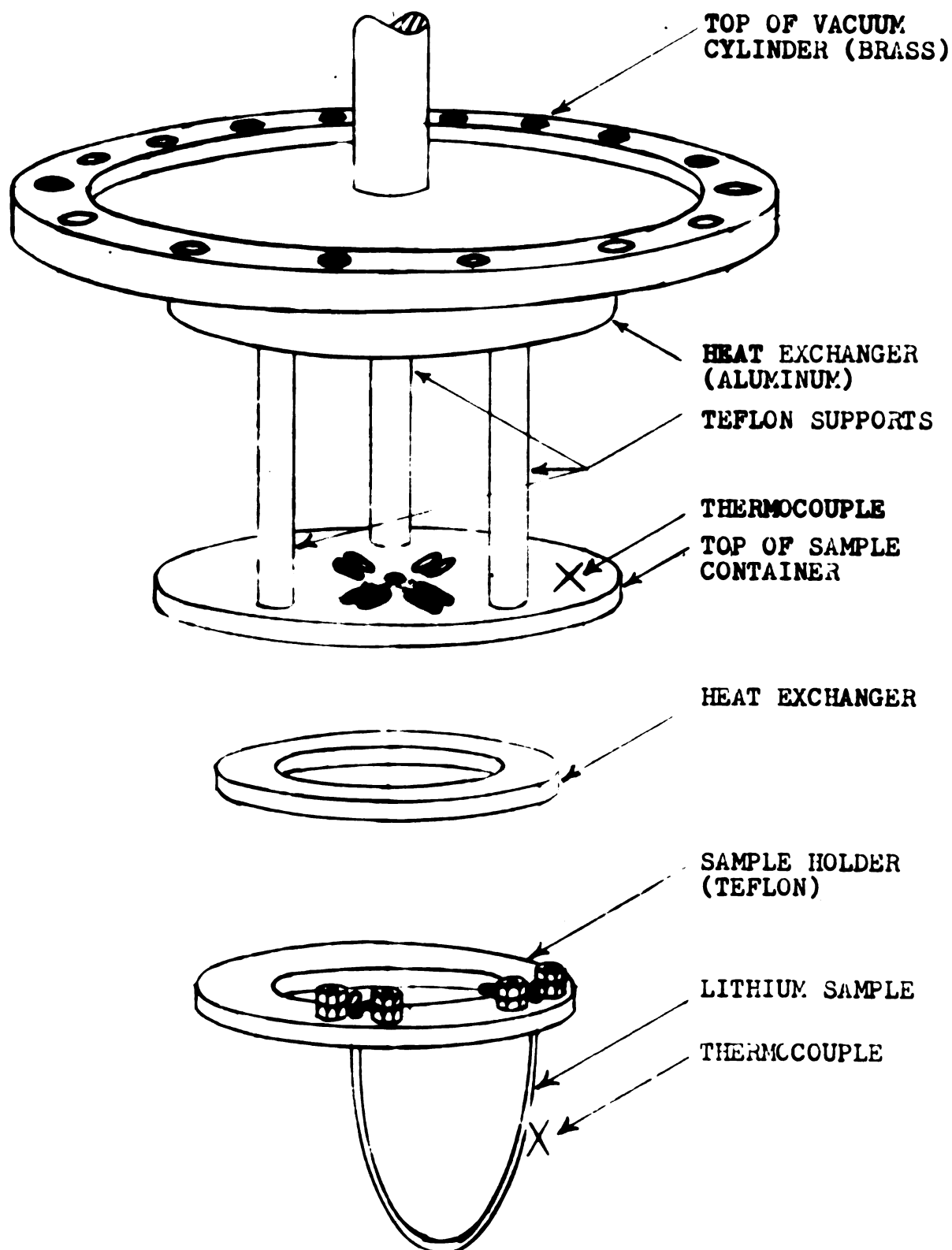


Figure 7. Detail of sample holder. To avoid confusion the leads are not shown.

of the sample container. The sample container was an aluminum cylinder surrounding the sample holder and samples. The sides and bottom of this cylinder were made from aluminum foil of double thickness, and the top plate was made from 1/8-inch aluminum plate.

A radiation shield of aluminum foil surrounded this cylinder. The assembly was enclosed in a brass cylinder with side thickness of about 1/24 inch, a bottom plate about 1/8 inch thick, and a top plate consisting of an outer brass ring soldered to a 1/16-inch brass disc. This ring is 1/8 inch thick, with outer diameter 5 inches and inner diameter about 4 inches. A similar ring is soldered to the top of the cylinder. Matching holes were drilled in both rings, so that a vacuum seal could be formed between the top plate and the rest of the cylinder by a lead fuse-wire gasket. A stainless-steel tube, 1/2 inch outside diameter, and about 2 1/2 feet long, was soldered inside a 1/2 inch hole in the middle of the top plate. This tube served both for evacuation of the cylinder and for taking the electrical leads out of the cryostat. The leads were sealed at the top of the stainless-steel tube by imbedding in a disc of cast plastic 1/2 inch thick and 2 inches in diameter (Liquid Casting Plastic, Castolite Casting Company, Woodstock, Illinois). A vacuum seal could then be obtained between the plastic and a small plate soldered to the stainless-steel tube.

The assembly was placed in a cylindrical glass Dewar flask of height 24 inches and inside diameter 6 inches. The topmost five inches of the Dewar consisted of glass pipe with a ground collar at the top. This flat surface permitted a 3/8-inch brass plate to be clamped over the top of the plate, to allow partial evacuation of this Dewar. The glass Dewar itself was placed in a stainless-steel Dewar, as shown in Figure 5. When measurements were being made below liquid-air temperature, this outer Dewar permitted precooling samples, and served as a radiation shield.

D. The External Circuit

The electrical leads consisted of seven Teflon-covered No. 27 copper wires for the current leads to the six samples, seven Formvar-covered No. 30 copper wires for potential leads to them, three Teflon-covered No. 27 wires for two heaters, and the six thermocouple wires mentioned earlier.

The leads enter the assembly through the plastic disc, descend through the stainless-steel tube, and wind four times around an aluminum torus serving as a heat exchanger. The torus is placed in good thermal contact with the underside of the brass plate to which the tube is silver soldered (that is, the top plate of the vacuum chamber). The leads are fastened to the torus with insulating varnish. They then descend to the top plate of the aluminum cylinder surrounding the sample holder, where they are wrapped several times around spokes in the aluminum plate and secured with varnish. The leads go next to the copper bolts on the sample holder where they are secured with copper nuts. Thermal emf's are minimized by making the circuit almost entirely of copper.

After leaving the cryostat, the potential leads and the thermocouple wires go to a twelve-point thermal-free switch. The current leads to to a rotary switch which connects each sample in turn with the external circuit. The differential thermocouple wires go directly to a galvanometer. Each heater circuit contains an ammeter, a 1000-ohm potential divider, and a Heath-kit Battery Eliminator as a power supply.

EXPERIMENTAL PROCEDURE

Alloys of the isotopes were prepared by melting weighed quantities of the high-purity lithium isotopes in mineral oil. Before the lithium was melted it was cleaned of all reaction products by scraping the surface with a steel knife blade to remove the oxide and nitride coating. Cleaning, as well as weighing, was done in a dry box with a dry carbon-dioxide atmosphere. The two chunks of lithium were pressed together before melting and stayed together during melting, to form a single globule of molten metal floating in the oil. During the melting the surface of the melted lithium did not stay shiny. Apparently a surface reaction had taken place to form a very thin surface layer. This layer actually served as a protective surface, and was pliable enough that mixing by mechanical deformation could be carried out. The globule was kneaded by means of a stainless steel rod for several minutes to insure a homogeneous mixture. From this globule some of the metal was drawn up into a glass tube coated with hot oil, and immediately extruded into a beaker of cooler oil.

In preparation for extruding the lithium wires, the surface of the alloy was again cleaned with a knife in the carbon-dioxide atmosphere. The extruding device consisted of a steel barrel with a plunger threaded to advance along threads tapped in the barrel. The plunger forced the lithium through a 1-mm circular hole in a steel die screwed into the end of the barrel.

The samples were extruded and placed in the sample holder while kept in the dry box. Then the brass chamber and stainless-steel tube, complete with all of the apparatus inside it, were placed in the dry box. The samples were extruded from the die by placing it in a vise and turning

the plunger with a wrench. Care was taken during the mounting not to deform the wires in any way except where the wire was attached to the current junctions. After the sample holder had been loaded, the potential contacts were made, the sample container and radiation shield were put in place, and the brass cylinder was assembled with the lead gasket in place. The double-Dewar apparatus containing the brass cylinder was then evacuated, in order to prevent any surface reaction due to slight amounts of impurities in the dry-box atmosphere, or to slow reaction with the carbon dioxide.

At temperatures below 80°K the apparatus was pre-cooled to liquid-air temperature by introducing helium gas inside the glass Dewar and into its vacuum jacket. The transfer tube from the helium liquefier was put into place, the helium-gas return to the liquefier was connected, and the vacuum jacket of the glass Dewar was then pumped out. Liquid helium was then brought in from a Collins helium liquefier. Six to eight liters introduced into the glass Dewar lowered the temperature to about 4.2°K . The brass cylinder was evacuated, and the heaters were adjusted manually so as to approach thermal equilibrium, as indicated by the differential thermocouple. In several trial runs it was found that adjustment of the heaters did not significantly affect the measurements. Hence for most of the measurements between 4.2°K and liquid-air temperature, natural warming, due to the normal leak of heat into the sample container, was sufficiently gradual that near thermal equilibrium was almost always achieved. The consistency of the experimental results, as well as the agreement with the work of Kelly and MacDonald (17) lends confidence to this assumption. Above 80°K , essentially the same procedure was followed, with liquid air replacing liquid helium as the cooling medium.

As mentioned earlier, the thermocouple reference-junction temperatures were monitored with a platinum resistance thermometer.

Periodic checks were made on the reference-junction temperature. Simultaneous readings of temperature and resistance were not possible, but nearly continuous readings for temperature and resistance could be obtained by sampling the two specimens and the two thermocouples in order. The breaks in the curves on the recorder chart were then filled in.

RESULTS

The direct experimental results for the resistance consist of voltage readings which are translated into resistance values. Since the dimensions of the specimens are not known precisely, the actual values of resistance are of little interest. Instead we consider the ratio of these resistances to that at some reference temperature, T_0 , taken as 293.1°K . Moreover since we are concerned primarily with the phonon-electron interaction, we need to subtract the temperature-independent residual resistance due to chemical impurities and other imperfections. At 4.2°K the temperature-dependent part of the total resistance is negligibly small. We compute then the ratio of net resistance $R(T)$ at temperature T , defined as the total resistance $R'(T) - R'(4.2^\circ)$, divided by the net resistance $R(T_0)$ at reference temperature T_0 . The behavior of this normalized net resistance is shown schematically in Figure 8 for isotopically-pure Li-6 and Li-7. The numerical values will be given later.

Residual Resistances

The actual values of the residual resistance give an excellent indication of the chemical purity of the material. At room temperature our samples had resistances of about 20 milohms, decreasing to about 30 microhms at liquid helium temperature, to give a ratio of about one or two parts per thousand. These values are summarized in Table 1. The results give confidence that possible failure of Matthiessen's rule cannot affect the conclusions very much since the residual resistances are small and of uniform magnitude for all samples. The values agree very well with those found by Snyder and by Dugdale et al.

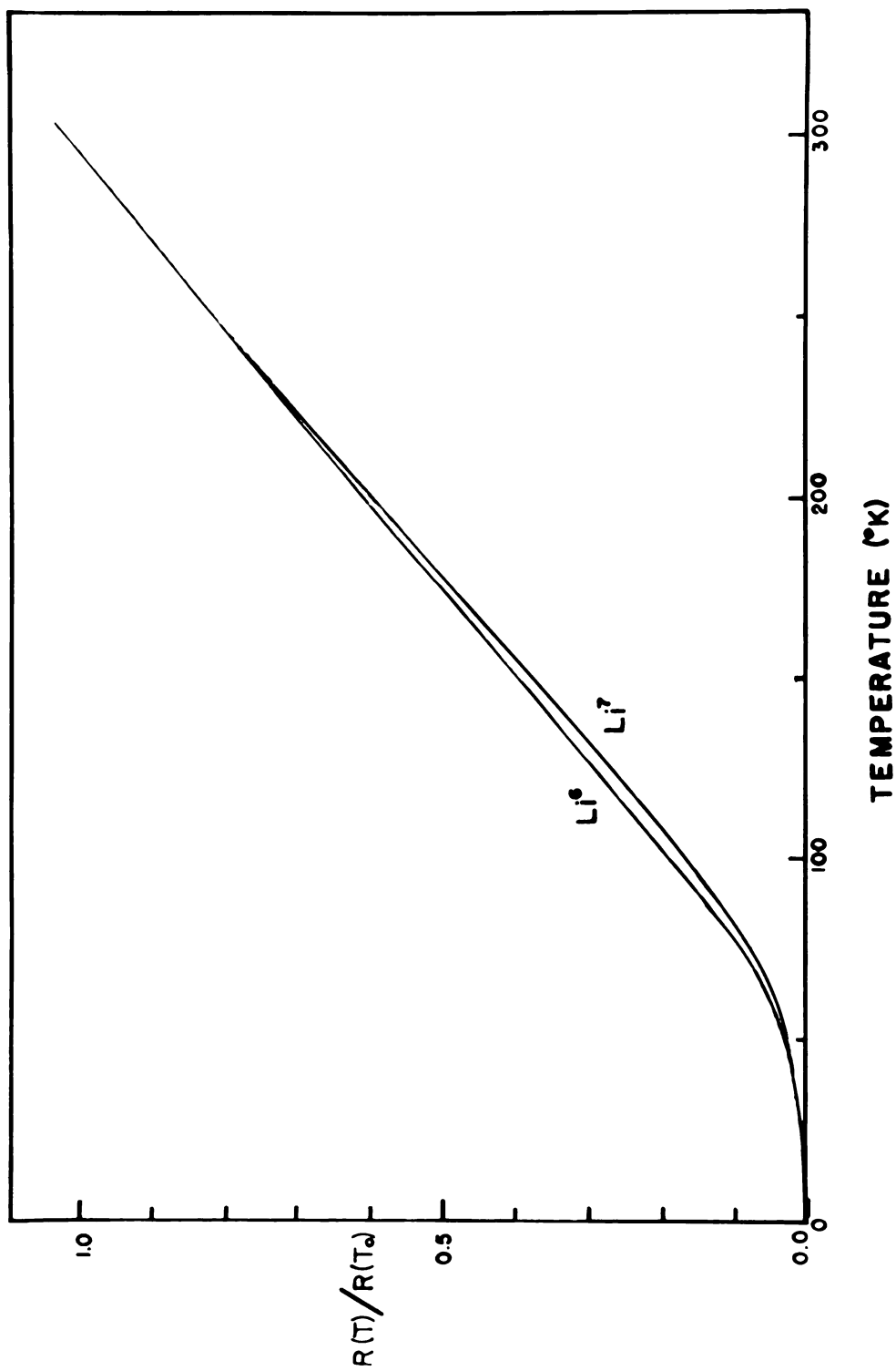


Figure 8. Representation of the normalized net resistance for lithium-6 and lithium-7 as a function of temperature.

Table 1. Residual and Normalizing Resistances for Lithium Specimens

Material	Sample Number	Total Resistance at 4.2°K R'(4.2)	Total Resistance at 293.1°K R'(293.1)	$\frac{R'(4.2)}{R'(293.1)}$
"Li-6" (99.3%)	10-5	.0412 m Ω	23.63 m Ω	1.74×10^{-3}
"Li-7" (99.99%)	10-6	.0350	23.44	1.49
"Li-6"	15-5	.0416	23.82	1.75
Li-Nat. (92.5% Li-7)	15-6	.0280	24.20	1.16
Li-Nat.	17-5	.0233	23.29	1.00
"Li-7"	17-6	.0318	23.68	1.34
"Li-6"	18-5	.0385	23.90	1.61
"Li-7"	18-6	.0206	16.37	1.26
25% "Li-6" 75% "Li-7"	20-5	.0355	15.94	2.23
25% "Li-6" 75% "Li-7"	20-6	.0345	15.03	2.30
50% "Li-6" 50% "Li-7"	21-5	.0350	19.44	1.80
75% "Li-6" 25% "Li-7"	21-6	.0378	21.70	1.74

For the isotopically-pure samples the residual resistivity is somewhat higher than that of the natural lithium. This result is not surprising in view of the techniques which must be used for preparation of the separated isotopes in metallic form. Only small quantities of starting material are available, and the distillation technique is special. For the isotopic alloys the residual resistivities are only a little higher than those for the separated isotopes. This increase is to be expected, for the manipulations involved in their preparation can only introduce additional impurities. Nonetheless the smallness of the increase is gratifying, and lends confidence to the assumption that no spurious effects have been introduced.

Effect of Temperature

The effect of temperature on the normalized net resistance of lithium metal of varying isotopic composition is presented in Tables 2, 3, 4, 5, 6, and 7. Graphical presentation of this body of data in full is not feasible. To give an idea of the reproducibility of the data, Figure 9 shows a section of the data for lithium-6 and lithium-7 between the temperatures 60°K and 80°K . The reproducibility from one sample to another of the same material is usually better than one part per thousand.

Comparison with Other Workers

The present results, which are considerably more precise than those of Snyder, are not in contradiction with his. Our values agree well with those of Dugdale et al., who claim somewhat greater precision than we do. To give an idea of the agreement, Figure 10 shows results of calculation from a portion of the data, with the ratio of resistivities for lithium-6 and lithium-natural plotted as a function of temperature for our work and for that of Dugdale et al. Since the dimensional data for our samples are not available we do not have direct knowledge of the

Table 2. Normalized Net Resistances, Run No. 10

Sample Number 5, Li ⁶ ; Sample Number 6, Li ⁷					
No. 5	No. 6	Temp.	No. 5	No. 6	Temp.
.00000	.00000	4.2	.04680	.05363	63.0
.000017	.000013	8.8	.04680	.05363	63.1
.000046	.000043	11.3	.05958	.06839	68.1
.00005	.00005	12.2	.05958	.06839	68.1
.000085	.000085	12.7	.07050	.08025	71.8
.00013	.00017	14.1	.07050	.08025	71.9
.00086	.00093	20.6	.08138	.09168	75.2
.00086	.00093	20.6	.08138	.09168	75.3
.0012	.0017	22.9	.08625	.09787	76.8
.00163	.00176	24.1	.08625	.09787	76.9
.00234	.00258	27.0	.3143	.3304	133.2
.00362	.00402	30.4	.3701	.3856	145.7
.00431	.00483	31.9	.3990	.4142	152.3
.00431	.00483	31.9	.4195	.4350	157.0
.00512	.00580	33.4	.4643	.4786	167.0
.00630	.00712	35.4	.6428	.6535	207.9
.00724	.00823	37.0	.7541	.7633	233.8
.00944	.01088	39.7	.8003	.8108	245.2
.01198	.01378	42.3	.8567	.8672	258.7
.01198	.01378	42.3	.9005	.9129	269.2
.01587	.01830	45.7	.9433	.9590	279.4
.01587	.01830	45.7	.9805	.9982	288.4
.02069	.02409	49.4	.9816	.9828	288.7
.02069	.02409	49.6	1.0000	1.0000	293.15
.02818	.03310	54.2	1.0014	1.0015	293.5
.02818	.03310	54.2	1.0285	1.0263	299.9

Table 3. Normalized Net Resistances, Run No. 15

Sample Number 5, Li ^{Nat} ; Sample Number 6, Li ⁶					
No. 5	No. 6	Temp.	No. 5	No. 6	Temp.
.0000	.0000	4.2	.2523	.2361	115.6
.00004	.00004	11.0	.3090	.2949	128.7
.00014	.00014	14.2	.3451	.3318	136.8
.00036	.00036	17.2	.3664	.3530	141.6
.00098	.00094	20.7	.4095	.3965	151.7
.00127	.00122	21.8	.4304	.4171	156.6
.00182	.00174	24.3	.4457	.4325	160.1
.00179	.00174	24.6	.4471	.4345	160.1
.00221	.00213	26.0	.4744	.4630	166.5
.00289	.00277	28.0	.5145	.5030	176.2
.00326	.00303	29.1	.5256	.5147	178.2
.00379	.00348	30.1	.5521	.5416	184.4
.00464	.00428	31.9	.5661	.5567	187.8
.00531	.00477	32.9	.5767	.5663	190.5
.00672	.00603	35.1	.5835	.5739	191.8
.00917	.00812	38.5	.6091	.6003	197.9
.01254	.01100	41.7	.6413	.6322	205.8
.01477	.01295	43.5	.6430	.6356	205.9
.01798	.01550	45.9	.6459	.6381	206.5
.02198	.01898	48.5	.6483	.6406	207.1
.02561	.02235	50.7	.7298	.7238	226.8
.03486	.03027	55.3	.7426	.7372	229.6
.04387	.03759	59.0	.7554	.7494	233.1
.05231	.04442	62.4	.7876	.7821	241.1
.06310	.05542	66.4	.8264	.8224	250.4
.06909	.06079	68.6	.8264	.8228	250.5
.07640	.06767	71.0	.8719	.8690	261.8
.08417	.07464	73.3	.8913	.8883	266.4
.08876	.07884	74.8	.9860	.9857	289.8
.09645	.08631	77.0	.9909	.9908	291.2
.10690	.09622	80.0	.9921	.9916	291.5
.1315	.1203	86.7	.9959	.9958	292.5
.1784	.1653	98.5	1.0000	1.0000	293.15
.2357	.2214	111.8	1.0054	1.0059	294.44
.2355	.2215	111.9			

Table 4. Normalized Net Resistances, Run No. 17

Sample Number 5, Li ^{Nat} ; Sample Number 6, Li ⁷					
No. 5	No. 6	Temp.	No. 5	No. 6	Temp.
0.000073	0.000076	8.8	0.3731	0.3733	139.0
0.000056	0.000076	10.8	0.3982	0.3983	148.8
0.000322	0.000304	14.8	0.4500	0.4506	160.3
0.00128	0.00125	21.9	0.4581	0.4590	162.7
0.00248	0.00247	26.4	0.4848	0.4852	169.0
0.00833	0.00842	37.0	0.4899	0.4907	169.8
0.01114	0.01119	40.0	0.4968	0.4975	171.9
0.01458	0.01465	43.2	0.6028	0.6030	197.6
0.01832	0.01835	45.8	0.6556	0.6558	210.5
0.22117	0.02155	48.0	0.6690	0.6698	211.9
0.03922	0.03926	57.4	0.7316	0.7318	227.9
0.04873	0.04873	61.3	0.8922	0.8936	266.9
0.06123	0.06111	65.6	0.9133	0.9134	271.7
0.07097	0.07128	69.1	0.9506	0.9514	281.2
0.08162	0.08205	72.7	0.9584	0.9590	283.1
0.09004	0.09024	75.0	0.9785	0.9797	288.2
0.09906	0.09916	77.6	0.9742	0.9742	286.9
0.1069	0.1077	79.8	0.9863	0.9869	290.0
0.1663	0.1676	95.6	1.0008	1.0017	293.5
0.2481	0.2483	114.6	1.0030	1.0042	294.3
0.2797	0.2802	121.9	1.0232	1.0245	299.4

Table 5. Normalized Net Resistances, Run No. 18

Sample Number 5, Li ⁶ ; Sample Number 6, Li ⁷					
No. 5	No. 6	Temp.	No. 5	No. 6	Temp.
.000473	.000654	18.4	.08565	.09664	76.9
.000992	.00117	21.7	.0918	.1032	78.7
.00254	.00304	27.9	.09762	.1094	80.4
.00456	.00555	32.7	.2655	.2833	122.5
.00595	.00712	35.1	.2972	.3150	129.8
.00852	.01036	38.9	.3318	.3494	137.9
.01172	.01410	42.4	.3729	.3892	146.7
.01492	.01809	45.3	.4003	.4165	152.8
.01907	.02267	48.8	.4460	.4625	162.9
.02286	.02716	50.9	.4753	.4917	169.35
.02881	.03366	54.9	.5289	.5415	181.4
.03703	.04290	59.0	.5598	.5721	188.8
.04106	.04743	60.6	.5941	.6042	196.7
.04837	.05558	63.8	.6448	.6536	208.6
.05490	.06286	66.3	.8536	.8570	257.8
.06046	.06909	68.4	.9134	.9151	272.2
.06506	.07446	70.2	.9481	.9487	280.5
.07096	.08100	72.2	.9762	.9768	287.4
.08025	.09114	75.2			

Table 6. Normalized Net Resistances, Run No. 20

Sample Number 5, 25% Li⁶, 75% Li⁷; Sample Number 6, 25% Li⁶, 75% Li⁷

No. 5	No. 6	Temp.	No. 5	No. 6	Temp.
.000659	.000625	16.4	.4747	.4740	166.9
.000922	.000858	18.3	.4881	.4876	170.1
.00149	.00150	21.9	.5065	.5059	174.4
.00315	.00327	27.6	.5356	.5323	180.5
.00529	.00536	32.1	.5524	.5506	185.2
.00756	.00767	35.7	.5681	.5675	188.9
.01093	.01092	39.6	.5792	.5782	191.8
.01347	.01347	41.9	.6065	.6054	198.5
.01792	.01796	45.7	.6306	.6296	204.5
.02264	.02271	48.7	.6440	.6423	207.8
.03136	.03137	53.5	.6582	.6568	211.1
.03871	.03852	57.1	.6724	.6710	214.3
.04623	.04631	60.3	.6769	.6760	215.5
.05270	.05281	62.8	.6913	.6906	218.9
.06437	.06454	67.1	.7064	.7052	222.5
.07089	.07106	71.2	.7302	.7285	227.9
.08375	.08343	73.4	.7547	.7545	233.9
.08940	.8922	75.1	.7666	.7665	236.6
.09586	.09594	77.1	.7735	.7738	238.4
.1062	.1062	80.0	.7880	.7871	241.9
.1144	.1142	82.2	.8005	.7997	244.9
.1421	.1420	89.8	.8124	.8117	247.75
.2009	.2013	104.5	.8237	.8230	250.5
.2261	.2263	110.1	.8344	.8337	253.0
.2644	.2649	118.65	.8469	.8463	256.0
.2668	.2666	119.6	.8582	.8570	258.8
.2845	.2845	123.3	.8708	.8696	261.7
.3037	.3032	128.2	.8934	.8916	267.0
.3458	.3449	129.0	.9021	.9009	269.3
.3970	.3971	149.2	.9122	.9108	271.6
.4053	.4054	151.2	.9197	.9188	273.6
.4104	.4107	151.9	.9348	.9348	277.25
.4161	.4259	156.0	.9467	.9468	280.2
.4422	.4419	159.6	.9768	.9767	287.55
.4553	.4548	162.6			

Table 7. Normalized Net Resistances, Run No. 21

Sample Number 5, 50% Li ⁶ , 50% Li ⁷ ; Sample Number 6, 75% Li ⁶ , 25% Li ⁷					
No. 5	No. 6	Temp.	No. 5	No. 6	Temp.
.00024	.00029	15.7	.3824	.3778	146.6
.00053	.00055	17.5	.4002	.3974	150.8
.00151	.00152	22.9	.4180	.4148	154.9
.00225	.00219	25.3	.4422	.4382	160.2
.00335	.00335	28.2	.4565	.4530	163.5
.00407	.00416	30.2	.4814	.4780	169.6
.00558	.00551	32.8	.4928	.4896	172.1
.00740	.00728	35.6	.4983	.4955	173.4
.00979	.00958	38.6	.5130	.5101	176.7
.01214	.01187	40.8	.5190	.5161	178.0
.01506	.01463	43.6	.5301	.5276	180.2
.01848	.01802	46.4	.5522	.5502	185.8
.02295	.02225	48.9	.6008	.5982	197.8
.02709	.02586	51.6	.6148	.6129	201.3
.03404	.03315	55.3	.6269	.6244	204.1
.04211	.04030	59.1	.6349	.6327	206.1
.05100	.04912	62.7	.6560	.6553	211.4
.05928	.05705	65.8	.6700	.6687	214.35
.06640	.06401	68.4	.6785	.6774	216.45
.07237	.06982	70.4	.6921	.6903	219.6
.07979	.07687	72.8	.7056	.7037	222.8
.08571	.08276	74.7	.7186	.7166	225.7
.09413	.09097	77.3	.7312	.7290	228.8
.10005	.09696	78.9	.7432	.7419	231.6
.1058	.1026	80.5	.7548	.7539	234.5
.1324	.1298	88.1	.7663	.7654	237.2
.1457	.1422	91.6	.7844	.7839	241.6
.1617	.1581	95.8	.8230	.8221	250.5
.1801	.1762	100.4	.8390	.8378	254.25
.1978	.1943	104.8	.8516	.8475	256.55
.2185	.2146	109.6	.8796	.8788	264.15
.2396	.2357	114.5	.8887	.8876	266.25
.2572	.2537	118.6	.8982	.8972	268.55
.2859	.2818	124.7	.9283	.9286	276.0
.3228	.3191	130.8	.9423	.9424	279.35
.3359	.3319	136.4	.9669	.9668	285.3
.3474	.3435	139.0	.9809	.9811	288.6
.3483	.3442	139.2			
.3652	.3613	142.9			
.3696	.3662	144.2			

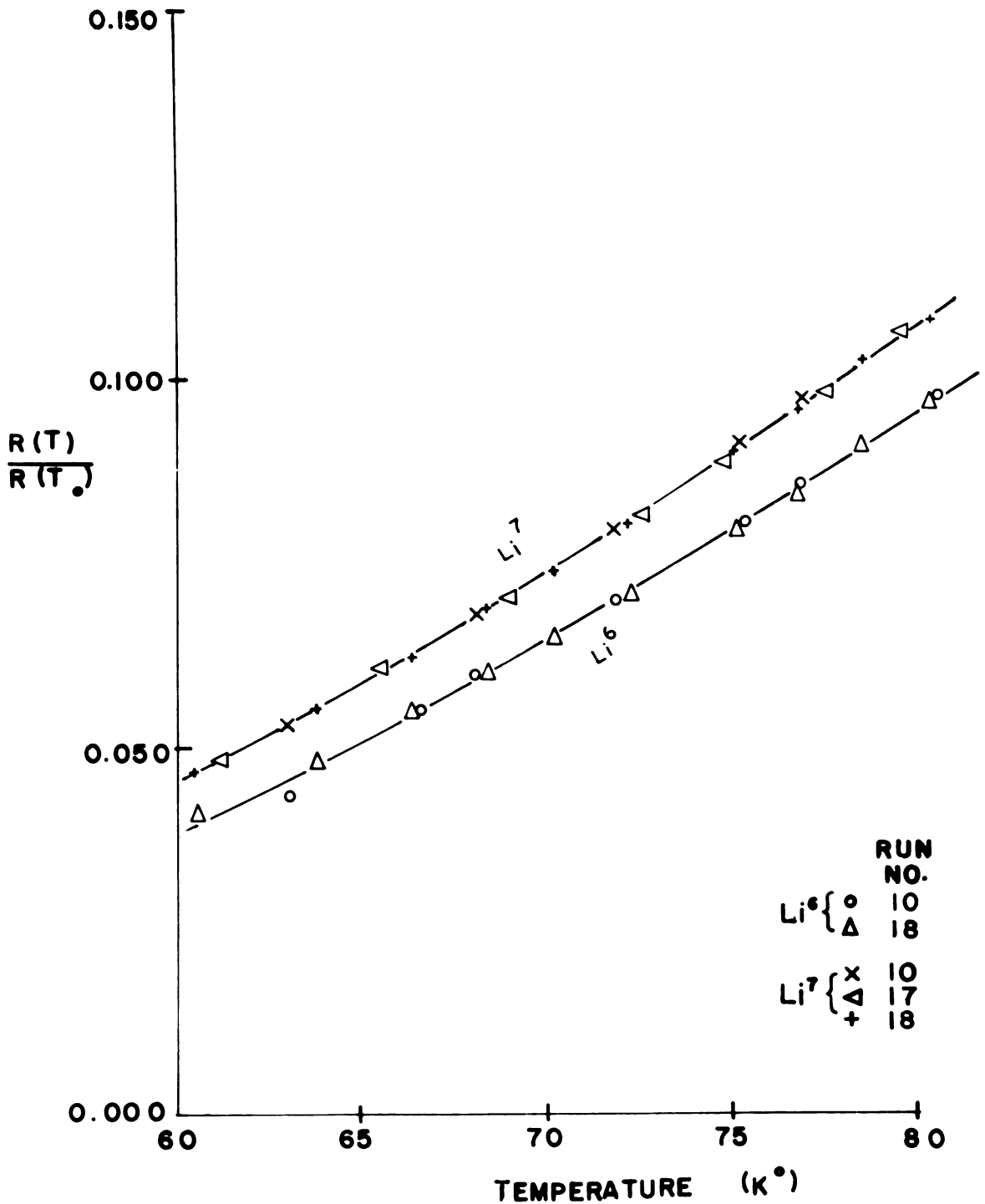


Figure 9. Portion of the data to illustrate sample-to-sample reproducibility, (run-to-run) showing normalized net resistance for lithium-6 and lithium-7 in the temperature range 60°-80° K. The actual resistances are about 1 or 2 milohms, amounting to 5 to 10 percent of the room-temperature resistance.

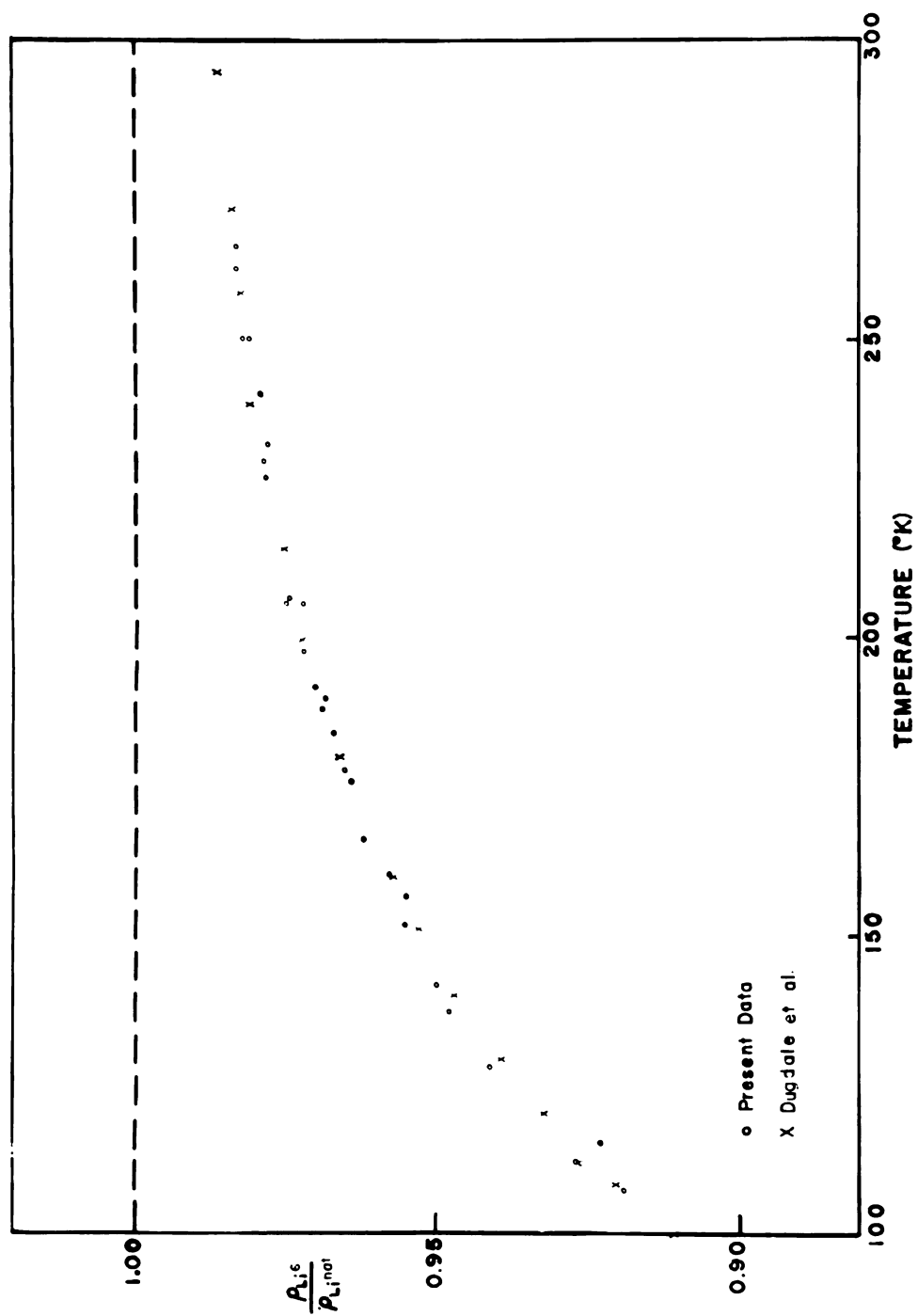


Figure 10. Ratio of resistivity of lithium-6 to that of lithium-natural in the temperature range 100°-300° K. The curves are made to coincide at 295° K.

resistivity of our samples. We have therefore accepted the results of Dugdale et al., and assumed in view of the identical sources and the high purity that our samples have the same value of absolute resistivities at room temperature. A comparison with Dugdale et al. below 80°K is given in Table 8. His data represent a ratio of ideal resistivities

$$\frac{\rho_i^6 (1.074 \text{ T})}{\rho_i^{\text{Nat}} (T)}$$

As will be explained later the constancy of this ratio is a measure in part of the validity of the theory. For comparison our data are made to correspond to his resistivities at 295°K.

Comparison with Theory--Separated Isotopes

The form of the function appearing in the Bloch-Grueneisen formula has been extensively tested for natural lithium by Kelly and MacDonald (17). To compare the theoretical predictions with the experimental results, these workers computed at each temperature T the value of the parameter θ necessary to make the formula fit the measured value of resistance. The departure of θ from constancy is then a measure of the inadequacy of the theoretical expression. Kelly and MacDonald found, as with most other metals, that the departure is considerable, and that the formula can be considered only as a fairly good first approximation. Dugdale et al. (5) have followed the same procedure with the separated isotopes of lithium, with the same result.

Instead of repeating this type of presentation with our data--which are in good agreement with theirs--we prefer a more direct though less sensitive means of showing the nature of the agreement of our results with the theory. Figure 11 shows (in percent) the excess over unity of the ratio of the normalized net resistance of lithium-7 to that

Table 8. Comparison of Data Below 80°K with Dugdale et al.
(See Text for Explanation)

T	Dugdale	Present Data
80.0°K	1.07	1.08
75.5	1.07	1.06
70.0	1.07	1.07
65.0	1.08	1.06
59.5	1.07	1.08
55.4	1.06	1.08
50.4	1.07	1.09
46.7	1.07	1.08
43.2	1.07	1.10
40.0	1.07	1.11
37.0	1.06	1.09
34.3	1.05	1.06
31.7	1.05	1.11
27.0	1.06	1.15
25.0	1.07	1.19

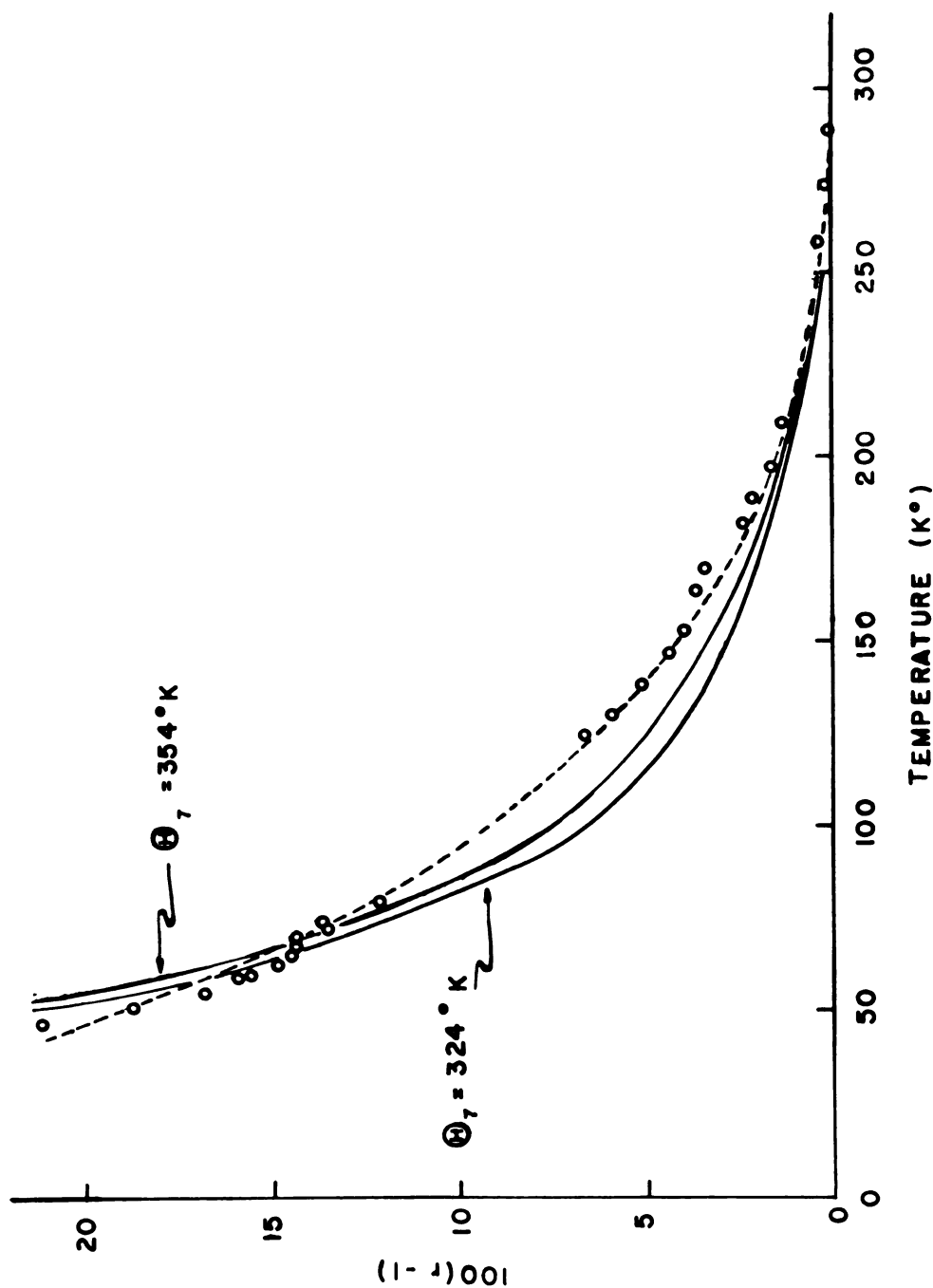


Figure 11. Comparison of the present results with theory. The ordinate is the percent excess over unity of the ratio of the normalized net resistance for lithium-7 to that of lithium-6. The abscissa is absolute temperature. The dashed line is an average curve drawn through the experimental points. The solid lines are curves calculated according to the Bloch-Grueneisen law for two values of the parameter Θ for lithium-7. By definition, the curves pass through zero at $T_0 = 293^\circ \text{K}$.

of lithium-6 at temperatures between 50°K and 300°K . The dashed line represents our experimental data, the solid curves the predictions of the Bloch-Grueneisen formula for two values of the parameter θ for the heavier isotope. It is clear that adjustment of this parameter cannot much improve the agreement over the temperature range shown. At lower temperatures, the theoretical curve continues to rise, but flattens off to approach the vertical axis at about 38 percent. The experimental points begin to scatter badly, since the absolute values are only a few percent of the room temperature values, and differences between small quantities are involved. We believe that the scatter is due to experimental uncertainties inherent in the present method and apparatus, but we cannot rule out possible effects of the martensitic transition, or even of departures from Matthiessen's rule.

With respect to the behavior of the parameters occurring in the Bloch-Grueneisen formula, only the parameter θ will yield much of interest. All the other quantities appearing in the formula (lattice constant, atomic field, and so on) are virtually identical between isotopes of lithium (see, e.g., Covington and Montgomery, 1957) (19). In our own experiments the lack of knowledge of the sample dimensions prevents our verifying these identities; but the work of Dugdale and collaborators however shows indeed that the limiting resistivities of the two isotopes at high temperatures are the same.

So far as the behavior of the parameter θ is concerned, it is easier to describe the results for the isotopic alloys and the pure isotopes simultaneously. Accordingly we postpone this discussion.

Dependence on Isotopic Composition (including pure isotopes)

For the isotopically-pure metals, it is clear from the equations of motion that the lattice-vibration frequency spectrum must be identical between isotopes, after application to the frequency of a scaling factor

proportional to the square root of the isotopic mass. For in the equation of motion the mass of each particle is multiplied by the second derivative with respect to time. Since neither mass¹ nor time appears elsewhere in the equations, the solutions can contain mass and frequency only in the combination mass times frequency squared. A dimensional-analysis argument next suggests that the only way the frequency can enter is through the combination $\hbar\omega/kT$, where the characteristic frequency ω is proportional to the square root of some interatomic force constant divided by the atomic mass. Now, as we have just seen, any frequency appearing in the derivation will have this same dependence on mass. Hence it is strongly indicated that a universal curve with abscissa T/θ , where θ varies inversely as the square root of the atomic mass, will describe the dependence of electrical resistance on temperature. The arguments given in Dugdale et al. (5), based on derivations in Ziman (20), amount to illustrations of this conclusion for specialized models. The Bloch-Grueneisen equation itself is a very specific illustration of this argument.

For the isotopic alloys it appears that the only effect of introducing isotopes is to modify the frequency vibration spectrum. Prigogine (1954) (6) has shown that to first-order perturbation terms the spectrum is modified merely by scaling the frequency in inverse proportion to the square root of the arithmetic mean of the mass; Pirenne (7) has shown that the first order correction in an exact treatment gives a spectrum modified merely by scaling the frequency in inverse proportion to the square root of the harmonic mean. For isotopic alloys of lithium-6 and lithium-7 the difference between the two means is a few parts per

¹The electron orbits are modified a small amount (actually about one part in ten thousand) by the difference in reduced mass for electron-nucleus between isotopes, so that the atomic fields are not exactly identical; but this difference may be ignored in the present work.

thousand at most, and we need not differentiate between them in this treatment. We shall try then to account for the effect of isotopic composition, from 100 percent lithium-6 to 100 percent lithium-7, simply by scaling the temperature in proportion to the square root of the average mass of the isotopic mixture.

We arbitrarily take lithium-natural as the standard. Then the normalized net resistance is adjusted by the scaling factors and divided by that for natural lithium. If the theory is correct this ratio should be unity. The results of this procedure are given in Table 9. Each entry in the table is of the form

$$W_x \frac{R_x(T/y)/R_x(T_0)}{R_{\text{Nat}}(T)/R_{\text{Nat}}(T_0)}$$

where x denotes the isotopic content of the sample, $R_x(T)/R_x(T_0)$ is the net normalized resistance of the sample x , y is defined as $\sqrt{M_x/M_{\text{nat}}}$, and W_x is defined as $1.0000 - (293.1 - 293.1\sqrt{M_x/M_{\text{nat}}}) N$, where N (equal numerically to 0.00407) is the slope of the lithium-natural curve at 293.1°K ; M_x is the average mass of the sample of isotopic composition x . W_x is the scaling factor by which the point $R_x(293.1/y)/R_x(293^\circ\text{K})$ on the R_x curve is made to lie on the R_{nat} curve.

In the range from 290°K to 80°K the disagreement is at most a few parts per thousand. From 80°K to about 30°K the disagreement is a few parts per hundred. Below 30°K the absolute resistances are so small that the effects of any slight absolute errors are greatly magnified, and the numerical comparison becomes meaningless. The last rows in the table reflect the onset of this trend.

The agreement then is to be considered excellent, the variability at low temperatures reflecting simply the difficulties in the experimental work there. It is particularly significant that no strong trend appears in the deviations of the ratios from unity. Thus it would seem that there are no scattering mechanisms unaccounted for.

Table 9. The Data Reduced to a Universal Curve

T (°K)	100% Li-6 0% Li-7	75% Li-6 25% Li-7	50% Li-6 50% Li-7	25% Li-6 75% Li-7	0% Li-6 100% Li-7
290.0	--	--	--	1.001	1.001
280.0	1.001	1.001	1.000	1.006	1.001
270.0	0.999	0.998	0.999	0.998	1.000
260.0	1.001	1.000	0.994	0.999	1.002
250.0	0.999	0.997	1.001	0.997	1.006
240.0	1.000	0.998	0.997	0.996	1.007
230.0	0.996	0.993	0.992	0.993	1.004
220.0	0.998	0.995	0.994	0.993	1.002
210.0	0.997	0.990	0.990	0.988	1.001
200.0	1.010	1.004	1.004	1.003	1.003
190.0	1.000	0.994	0.995	0.996	1.003
180.0	0.997	0.997	0.997	0.999	1.004
170.0	1.002	1.000	0.998	1.001	1.004
160.0	0.998	0.996	0.999	0.997	1.004
150.0	1.000	0.998	0.999	0.999	1.004
140.0	1.000	1.000	0.996	1.007	0.997
130.0	1.004	0.998	1.001	0.996	1.002
120.0	0.997	0.997	1.000	0.995	1.000
110.0	0.992	0.992	0.994	1.000	1.001
100.0	1.009	0.998	0.998	1.009	1.001
90.0	1.003	1.002	1.008	1.004	1.001
80.0	1.008	1.018	1.015	1.009	1.008
70.0	0.988	1.016	1.025	1.022	1.019
60.0	0.988	1.014	1.018	1.005	0.971
50.0	1.029	1.069	1.072	1.048	1.003
40.0	1.012	1.135	1.101	1.042	0.994
30.0	1.088	1.069	1.133	1.208	1.008
20.0	1.355	1.171	1.013	1.290	0.960

Effect of the Martensitic Transition

Although a transformation from one crystal structure to another would be expected to affect the lattice-electron interaction, and thereby the electrical resistivity, we have been unable to locate definitely any such change due to the well-known martensitic transformation of lithium from its normal bcc structure to hcp at low temperatures. In all our measurements the material was first cooled to liquid-helium temperatures, and then kept there for some time before warming. Consequently we were not in position to detect any hysteresis in the transition. Still, we should have noticed any irregularity in the resistance curve when passing through the transition region during warming. We have not yet scrutinized our data specifically to locate this effect, but routine examination has failed to pick it up. It is to be remembered that the resistances actually measured are about 2 milohms, and that changes of only a few percent of this value are to be expected. The slightest error in the measurement of resistance or of temperature, or the introduction of any spurious effect, would render detection of such irregularity very difficult.

As pointed out earlier, the data for temperatures much below 80°K show considerable scatter. Although it is possible to attribute this scatter to the martensitic transition, the absence of systematic trends in this scatter works against this interpretation.

SUMMARY

1. A method was developed for measuring the resistance of small samples of metallic lithium from room temperature (295°K) to liquid helium temperature (4.2°K).

2. Measurements were made on natural lithium, and on essentially isotopically-pure lithium-6 and lithium-7. The low values of the residual resistance, less than 2×10^{-3} times the room temperature resistance, showed that the samples were of high chemical purity. The course of the temperature dependence of resistance was in good agreement with results obtained earlier in work at our laboratory and elsewhere.

3. Measurements were made on isotopic alloys of lithium, prepared in our laboratory from the same batches of separated isotopes used in our other measurements. The low values of the residual resistance, less than 3×10^{-3} times the room temperature resistance, showed that only slight chemical impurity was introduced in the preparation. The course of the temperature dependence of resistance was of the same type as that obtained for the natural lithium and for the separated isotopes.

4. For all the specimens, the course of the temperature dependence showed that the Bloch-Grueneisen formula is a good first approximation to describe the variation of resistance with temperature, but that--as with most metals--the formula fails in its details.

5. For all the specimens, the effect of isotopic mass on the parameter θ appearing in the Bloch-Grueneisen formula could be treated simply by scaling the resistance and the temperature by appropriate factors derived from the theory. A universal curve can thus be used to represent the behavior of lithium of any isotopic composition.

6. From the previous finding it appears that the introduction of isotopes may be explained simply by their effect on the lattice-vibration frequency spectrum, and that no new mechanism of impurity scattering need be invoked when an atom of a given atomic number and atomic mass is replaced by one of the same atomic number but of different atomic mass.

7. The low-temperature martensitic transition in lithium produces little if any irregularity in the dependence of the electrical resistance on temperature.

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