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The electrical resistivity of lithium-6

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The electrical resistivities of lithium-6 and lithium of natural isotopic composition have been studied between 4 °K and room temperature. In addition, their absolute resistivities have been carefully compared at room temperature. These measurements show that the effect of ionic mass on electrical resistivity agrees with simple theoretical predictions, namely, that the properties of the conduction electrons in lithium do not depend on the mass of the ions, and that the characteristic lattice frequencies for the two pure isotopes are in the inverse ratio of the square roots of their ionic masses. A comparison with the specific heat results of Martin (1959, 1960), where the simple theory is found not to hold, indicates the possibility that anharmonic effects are present which affect the specific heat but not the electrical resistivity.

1. Introduction

Many of the physical properties of a metal depend on the mass of its atoms, and the effect on these properties of changing the atomic mass is of considerable interest. Lithium is a very suitable material for studying such effects, as the mass ratio of its two stable isotopes is large ($\simeq 7/6$) so that differences in the behaviour of the metal isotopes should also be fairly large. In addition to this, the two isotopes are commercially available in metallic form with isotopic enrichments of greater than 99 % and with only very small amounts of chemical impurity.

The first experiments on the isotopes of metallic lithium were those of Montgomery and his collaborators; in particular Snyder & Montgomery (1958) published a note on the relative resistance of the two isotopes down to 77 °K (see also Leffler & Montgomery 1960). More recently Martin (1959, 1960), in this laboratory, has made a detailed study of the specific heats of natural lithium and of ^{6}Li. Snyder & Montgomery concluded from their measurements that the broad features of the temperature dependence of resistance of the two isotopes were in accordance with the Bloch–Grüneisen theory of electrical resistivity although they found considerable deviations in detail from this theory (cf. the figure in their paper). In our paper we present results on both the *absolute* resistivities of the isotopes and on their temperature dependence, and we show that they are consistent with a more general theory.

2. Theoretical considerations

According to the Bloch–Grüneisen relation, the ideal resistivity of a metal may be expressed as follows

$$\rho_i = \frac{KT}{M\theta_R^2} f(T/\theta_R) \tag{1}$$

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(see, for example, Ziman 1960, p. 364). M is here the ionic mass and K and θ_R are terms which are independent of temperature but which are in general dependent on volume: K is a measure of the electron-lattice interaction, and θ_R is a characteristic lattice temperature. f is a well known, tabulated function (see, for example, Wilson 1953, p. 337). The theoretical limitations of the Bloch–Grüneisen theory are now widely recognized, and although it is known that it does represent the experimental data surprisingly well, at least for the monovalent metals, there are discrepancies in detail. For our present purposes, however, the actual function f is immaterial, provided only that it is the same for the two isotopes. We shall therefore take f to be such an arbitrary function and we shall first discuss what this generalized form of equation (1) implies for the resistivity of the two lithium isotopes. We shall then show that a more general and more soundly based expression for the resistivity of a metal leads to the same conclusions.

We know that the two metal isotopes of lithium have closely the same molar volume (Covington & Montgomery 1957) and if we therefore assume that the electron properties of the metal are independent of the ionic mass, we can expect that the restoring forces on the ions, when they are displaced from their equilibrium positions in the lattice, will be the same in both isotopes. Consequently the normal modes of vibration in the two lattices should differ only on account of the mass difference of the ions. Thus the characteristic frequencies (ν_{i1} and ν_{i2}) and the characteristic temperatures (θ_1 and θ_2) of the two lattices should be related by the equations

$$M_1 \nu_{i1}^2 = M_2 \nu_{i2}^2, \quad M_1 \theta_1^2 = M_2 \theta_2^2,$$

where M_1 and M_2 are the masses of the ions in the two lattices. In the present instance, therefore, we expect that

$$\theta_R^{(6)}/\theta_R^{(7)} = (\tfrac{7}{6})^{\frac{1}{2}} = 1{\cdot}080.*$$

If we now compare the ideal resistivities of the two isotopes at corresponding temperatures T_1 and T_2 such that $T_1/\theta_1 = T_2/\theta_2$ we shall expect to find, according to equation (1), that

$$\frac{\rho_1(T_1)}{\rho_2(T_2)} = \frac{K_1 T_1}{K_2 T_2} = \frac{K_1 \theta_1}{K_2 \theta_2}$$

and if we also assume that $K_1 = K_2$ we find that for the lithium isotopes

$$\frac{\rho^{(6)}(T_1)}{\rho^{(7)}(T_2)} = \frac{\theta^{(6)}}{\theta^{(7)}} = 1{\cdot}080.$$

(Here T_1/T_2 is equal to 1·080.) This, therefore, is a prediction based on equation (1) which can be tested experimentally.

It is now illuminating to consider a more general equation for the electrical resistivity of a metal (Ziman 1960, equation 9·5·14) which does not depend '...upon the shape of the Fermi surface, whether it touches the zone boundaries, the form of

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* Strictly the ratio of the masses is 7·018/6·017. The square root of this ratio is the same as that quoted.

the matrix element of the scattering, nor whether we are dealing with N-processes or U-processes' (Ziman, p. 365).* This equation is of the form:

$$\rho_i = K'F/MT. \tag{2}$$

$K' = 1/\kappa^2 S^2$ (where κ is the Fermi radius and S the area of the Fermi surface), M is the ionic mass and F a complicated double integral over the Fermi surface which is also a function of temperature. (All the universal and mathematical constants involved have been taken into the function F.) Inspection of the function F, which depends mainly on the geometry in k-space of possible scattering processes, shows that it depends on temperature only through terms of the form $h\nu_i/kT$ where ν_i is the frequency of the ith normal mode of the lattice. If we now assume that the Fermi surfaces of the two lithium isotopes are the same and that $\nu_i^{(6)}/\nu_i^{(7)} = \sqrt{\frac{7}{6}}$ and if we then compare the resistivities of the two isotopes at temperatures $T^{(6)}$ and $T^{(7)}$ having this same ratio, i.e. $T^{(6)}/T^{(7)} = \sqrt{\frac{7}{6}}$, the integral F will have the same value for both ^{6}Li and ^{7}Li. Moreover, if the Fermi surfaces of the two isotopes are the same, $K'^{(6)} = K'^{(7)}$, so that:

$$\frac{\rho_i^{(6)}}{\rho_i^{(7)}} = \frac{M^{(7)}T^{(7)}}{M^{(6)}T^{(6)}} = 1{\cdot}080$$

Thus the more general relation expressed in equation (2) leads to the same result as the simplified expression in equation (1).

We can put this result in a different way if we wish to think in terms of a characteristic temperature of the lattice. Equation (2) may be rewritten as

$$\rho_i = \frac{K'}{MT} F\left(\frac{T}{\theta'_R}\right), \tag{2a}$$

where $k\theta'_R = h(\nu_i)_{\text{av.}}$; $(\nu_i)_{\text{av.}}$ is an appropriate average over the frequency spectrum, depending in part on the shape of the particular Fermi surface considered. (2a) may then be rewritten as

$$\rho_i = \frac{K'T}{M\theta'^2_R} F_1\left(\frac{T}{\theta'_R}\right), \tag{2b}$$

where $F_1 = (\theta'_R/T)^2 F$. This now has the form of equation (1) although K' has a different significance from K in equation (1) and F_1 is no longer a universal function but depends on the electron properties of the metal considered. (In particular, however, one would expect that F_1 should be the same for isotopes of equal molar volume.)

We can test this more general form of equation (1) in three ways. First, we can find out if the two isotopes do have the same form of the function F_1; secondly we can test whether or not the relation $\theta'^{(6)}/\theta'^{(7)} = 1{\cdot}080$ holds; and thirdly we can find out if $K'_6 = K'_7$. These measurements provide three different but related tests of whether or not the electronic properties of lithium depend on the ionic mass. The first two tests depend only on the temperature dependence of resistivity; the third, however, depends on a knowledge of the *absolute* resistivities of the two isotopes.

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* The equation does, however, assume that the lattice vibrations are harmonic and that the phonon distribution is in thermal equilibrium.

In these experiments, because pure ^{7}Li is very expensive, we have in fact made measurements on ^{6}Li and on *natural* lithium. Natural lithium contains 92·5 at. % ^{7}Li and 7·5 at. % ^{6}Li, so that it can provide nearly as good a test of the theory as can the use of pure ^{7}Li. As we shall discuss later, the use of natural lithium changes slightly the values to be used in the numerical comparison of experiment with theory.

3. EXPERIMENTAL METHODS AND RESULTS

3·1. *Absolute resistivity measurements*

3·1·1. *Bare rod measurements*

The specimens to be measured were extruded into medicinal paraffin (Stanolax) in the form of cylindrical rods about 5 mm in diameter and of lengths between 10 and 25 cm. The current and potential electrodes were of platinum; they were held normal to the axis of the rods by nylon bushes and protruded about 1 mm into the lithium metal. The potential electrodes (the innermost pair of the four) were separated by about 1 cm from the current electrodes. The resistance of the rods was measured by the potentiometer method, the rods being immersed in Stanolax at a known temperature.

The dimensions of the rods were measured with a travelling microscope. The measurements were made with the rods immersed in Stanolax and it was found important to use proper illumination of the specimens to secure accurate results. Comparisons were made between the diameter of the rods as measured by the microscope and as measured directly by a micrometer; similar comparisons were made on steel rods as a check on the method of illumination.

To make comparison between the resistivity of ^{6}Li and natural lithium, two groups of specimens were measured by means of the same procedure and equipment for each specimen. Each group consisted of two natural lithium specimens and one of ^{6}Li. Details of the samples used are given in table 1, and the results are given in table 2. By far the largest source of error was in the measurement of the diameter of the rod. We have reduced this uncertainty by using a more precise technique which is described below.

3·1·2. *Glass-tube measurements*

For these measurements, the lithium was extruded through a die of 0·19 in. diameter into thick-walled glass tubes which had an inside diameter of 0·18 in. The glass tubing was of precision-bore Pyrex; the tolerance on the inside diameter specified by the manufacturer was ± 0·0005 in. The extrusion was made at room temperature and after extrusion the lithium which filled the glass tubing was visually inspected for filling deficiencies; it was then kept immersed in dry Stanolax for several days at room temperature. If there was a gap between the lithium and the glass wall which was filled either by Stanolax or air, that part of the lithium surface became dark grey because of oxidation. The parts of the specimen tube which showed such obvious faults were cut off. Next the tubing was ground at both ends and electrodes were pushed into the lithium from these ends. The potential electrodes consisted of 0·8 mm piano wires pushed about 8 mm into the specimen along its axis. These wires were insulated except at the very tip and so defined accurately the effective length of the specimen. This length was measured by means of a precision vernier calliper. The resistance measurements were made as described above. The inside diameter of the tubing was subsequently measured by cutting the tubes at various points. This showed that the diameter was very uniform and that its mean value was 0·18037 ± 0·00004 in.

TABLE 1. DETAILS OF LITHIUM SAMPLES

material	source	isotopic composition	residual resistance ratio, $\rho(4{\cdot}2\,°\mathrm{K}) / \rho(273\,°\mathrm{K})$	principal impurities (at. %)
natural lithium batch 1	Lithium Corporation of America	92·7 ± 0·1 % ^{7}Li, 7·3 % ^{6}Li	$3{\cdot}1 \times 10^{-3}$	Al 0·003, Ca 0·01, Na 0·005, K 0·002, Fe 0·001, Cu 0·0004, Mg 0·04, N 0·02
natural lithium batch 2	Lithium Corporation of America	not analyzed; assumed to be natural lithium	$1{\cdot}3 \times 10^{-3}$	Na 0·013, K 0·005, Cu 0·0006, Mg 0·017
^{6}Li batches 1 and 2	Oak Ridge National Laboratory	99·3 ± 0·2 % ^{6}Li, 0·7 ± 0·1 % ^{7}Li	$2{\cdot}5 \times 10^{-3}$	Al trace,* Ca 0·25, Na 0·02, Fe 0·05, Cu 0·02, Mg 0·01, Sr 0·01, Cr F trace, Ba 0·01

* Supplier's analysis of a typical batch.

TABLE 2. THE ABSOLUTE RESISTIVITIES OF NATURAL LITHIUM AND ^{6}Li

	resistivity (μΩ cm)		
	bare rod method	glass tube method	
	22 °C	22 °C	65 °C
natural lithium	9·54 ± 0·15	9·35 ± 0·05	11·00 ± 0·10
^{6}Li	9·36 ± 0·15	9·22 ± 0·05	10·90 ± 0·10
ratio $\dfrac{\rho^{(\mathrm{nat.})*}}{\rho^{(6)}}$	1·019 ± 0·01	1·014 ± 0·005	1·009 ± 0·01
ratio $\dfrac{\rho^{(6)}(1{\cdot}074T)}{\rho^{(\mathrm{nat.})}(T)}$	$1{\cdot}07_1$	$1{\cdot}07_5$	$1{\cdot}07_9$

* These values were obtained from a comparison of specimens prepared in similar ways. For this reason the error in the ratio does not include the uncertainty in the specimen diameter, and the limits of error are therefore less than the errors in the determination of the absolute resistivities.

The results of these measurements are summarized in table 2 together with the estimated experimental errors. The error due to incomplete filling is rather difficult to estimate. Since the lithium is extruded into the glass under considerable force and through a die whose diameter is slightly greater than that of the glass tube the filling should be complete. In order to increase the certainty of this, some of the measurements were made at 65 °C, at which temperature the metal will have expanded relative to the glass. For other reasons, however, the measurements at 65 °C, although consistent with those at room temperature, were rather less accurate. As we noticed above, any large filling errors were revealed by contamination of the lithium surface; we have roughly estimated the sensitivity of this method of detection and conclude that it should detect a cavity corresponding to 0·1 % of the radius of the rod. In fact measurements made on specimens showing slight surface imperfections were in good agreement with each other and with the results of more perfect specimens.

Measurements were made on three lithium samples, two of natural lithium and one of ^{6}Li. No significant difference was found between the results for the two batches of natural lithium. The resistance measurements were made at two temperatures for each specimen (22 and 65 °C). A comparison of the results of the two methods shows that they agree well for the value of the ratio of the resistivities at 22 °C, but that the absolute values of resistivity given by the glass tube method are about $1\frac{1}{2}$ % lower than those obtained from bare rods. Although this lies within our estimated experimental errors, it appears that there may be a systematic difference between the results of the two methods; for our present purposes however, we are only concerned with the *ratio* of the resistivities and on this both methods agree.

3·2. *The temperature dependence of the electrical resistivity*

The experimental method has already been fully described by Dugdale & Gugan (1960). In brief the specimens and thermometers were enclosed together with exchange gas in an isolated copper container whose temperature could be held constant by means of an adiabatic shield surrounding it. The thermometers used were a calibrated platinum resistance thermometer for the range from ~ 15 to 350 °K and a carbon resistance thermometer for the range 2 to 20 °K.

The specimens were extruded, bare wires of about 0·5 mm in diameter and about 100 cm in length. Oxidation of the specimens occurs slowly at temperatures above about 260 °K and a small correction for this was made from the resulting time dependence of resistance. The details of the materials from which the specimens were made are given in table 1 and the results of the resistivity-temperature measurements are given in table 3. Direct comparisons of the resistivity of ^{6}Li and natural lithium were also made by mounting a specimen of each together in the cryostat and measuring them under the same conditions.

3·3. *The martensitic transformation*

At low temperatures a phase transformation of the martensitic type occurs in lithium (see, for example, Barrett 1947; Barrett & Trautz 1948; Dugdale & Gugan 1961). In this transformation lithium changes its structure from body-centred cubic, stable at high temperatures, to a close-packed structure stable at low temperatures. The spontaneous transformation begins when a lithium specimen is first cooled below about 75 °K and at the lowest temperatures about one-half of the specimen has changed phase[*] (Barrett & Trautz 1948). On subsequently warming the specimen, reversion to the body-centred form begins at about 90 °K but is not complete until a temperature of about 160 °K is reached.

TABLE 3. THE IDEAL RESISTIVITY OF NATURAL LITHIUM AND ^{6}Li AS A FUNCTION OF TEMPERATURE[*]

T	natural lithium		^{6}Li	
(°K)	ρ_i ($\mu\Omega$ cm)	θ_R (°K)	ρ_i ($\mu\Omega$ cm)	θ_R (°K)
320	10·28 ± 0·01	—	10·17 ± 0·01	—
310	9·90	—	9·79	—
300	9·51	—	9·40	—
290	9·134	412 ± 25	9·02	449 ± 50
280	8·754	408	8·635	444
270	8·375 ± 0·001	407	8·248 ± 0·001	423
260	7·994	398	7·867	418
250	7·613	391	7·484	421
240	7·232	392 ± 10	7·099	419 ± 10
230	6·853	389	6·715	415
220	6·471	394	6·327	417
210	6·088 ± 0·001	397	5·935 ± 0·001	417
200	5·704	392	5·542	426
190	5·311	385 ± 5	5·143	429 ± 5
180	4·911	389	4·740	430
170	4·511	396	4·338	422
160	4·113	397	3·936	421
150	3·708 ± 0·001	397	3·533 ± 0·001	419
140	3·303	397 ± 5	3·134	423 ± 5
130	2·898	396	2·730	421
120	2·497	395	2·330	421
110	2·101	395	1·940	418
100	1·714	390	1·562	408
90	1·342	378	1·210	394
80	0·995 ± 0·005	369 ± 5	0·888 ± 0·005	377 ± 5

[*] These results are taken from the average of measurements on at least three specimens of each isotopic composition. The ideal resistivity was calculated on the assumption of Matthiesen's rule and was normalized to agree with the absolute resistivity determinations at high temperatures (table 2). The estimated errors refer to the *relative* and not to the *absolute* values of resistivity.

The θ_R values are calculated according to the Bloch–Grüneisen theory of electrical resistance by the method of logarithmic derivatives (cf. Kelly & MacDonald 1953).

If the amount of phase transformation were the same, and if the distribution of the two phases were similar for the two isotopes, one would expect the isotope effect in the two-phase mixtures to be the same as for the pure high-temperature phase. It would be interesting to be able to test this, but unfortunately there are rather large deviations from Matthiessen's rule in the temperature range below

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[*] More recent work by Hull & Rosenberg (1960) shows that at 4 °K about 90 % of a typical specimen is transformed.

80 °K (cf. Dugdale & Gugan 1961) and these make a precise test difficult. These departures also affect the comparison of the ideal resistivities in the single-phase region but by choosing specimens of almost the same residual resistivity we believe that the maximum uncertainty due to this (at 80 °K) will be less than $\frac{1}{2}$ %.

In studying the isotope effect in the two-phase region we were careful to reduce as much as possible any differences in the transformation in the different specimens. Our experiments on natural lithium had already shown that changes in the resistance of lithium due to the transformation were all quite small (less than 1 %) and that the actual values were very sensitive to the physical and chemical state of the specimen, e.g. grain size, state of cold work, impurity, etc. In the present measurements we therefore adopted the following procedure. For each set of measurements we prepared two specimens from the same ingot using the same procedure for each. These were then mounted together in the cryostat, electrically in series, so that the resistance of both could be measured at each temperature. By comparing the measured resistance of the two specimens it was possible to see if there were any comparatively large random variations in the resistive behaviour which occurred in spite of preparing the specimens by similar procedures. In fact it turned out that this was not so. We were thus able to compare in the same way specimens of ^{6}Li and of natural lithium (prepared from ingots of similar purity) with a reasonable assurance that we were indeed measuring differences due to the

TABLE 4. THE RATIO OF THE IDEAL RESISTIVITIES OF NATURAL LITHIUM AND ^{6}Li AT A GIVEN TEMPERATURE AND THE RATIO OF THE TEMPERATURES AT WHICH THEIR RESISTIVITIES ARE EQUAL*

b.c.c. phase		
T (°K)	$\rho_i^{(6)}/\rho_i^{(\text{nat.})}$†	$T^{(6)}/T^{(\text{nat.})}$
295·0	0·9861 ± 0·0002	1·012 ± 0·002
272·7	0·9843	1·013
258·2	0·9825	1·014
239·5	0·9814	1·015
215·0	0·9750 ± 0·0001	1·019 ± 0·001
200·2	0·9719	1·021
179·8	0·9656	1·023
160·0	0·9573	1·028
151·3	0·9531	1·028
140·3	0·9467 ± 0·0001	1·031 ± 0·001
129·5	0·9393	1·032
119·9	0·9320	1·036
108·2	0·9205	1·039
100·0	0·9113	1·040
86·4	0·8940	1·04$_5$
80·0	0·8838 ± 0·0005	1·04$_7$ ± 0·005

* Corrections for the change in dimensions of the specimens due to thermal contraction have been made by assuming that the shape factors of the specimens were in a constant ratio at corresponding temperatures. Strictly speaking, these and subsequent comparisons should be made for specimens at constant density. Since this correction is small in lithium and proportionately almost the same for the two isotopes it has not been made.

† These measurements were made with both specimens mounted in a cryostat in series.

difference in isotopic composition of the two specimens. In the experiments of interest here we first cooled the specimens to 4 °K thereby transforming them as completely as possible to the low-temparature phase. Provided they were not warmed above 90 °K the phase composition remained unchanged and it was in this state that the resistivity measurements were made. The results obtained from this comparison are included in table 5.

TABLE 5. THE RATIO OF THE IDEAL RESISTIVITIES OF ^{6}Li AND NATURAL LITHIUM AT CORRESPONDING TEMPERATURES*

b.c.c. phase		the two-phase region†	
T (°K)	$\dfrac{\rho_i^{(6)}(1{\cdot}074T)}{\rho_i^{(\mathrm{nat.})}(T)}$	T (°K)	$\dfrac{\rho_i^{(6)}(1{\cdot}074T)}{\rho_i^{(\mathrm{nat.})}(T)}$
295·0	1·075 ± 0·002‡	80·0	$1{\cdot}07_2$
272·7	1·075	75·5	$1{\cdot}07_4$
258·2	1·074	70·0	$1{\cdot}07_3$
239·5	1·076	65·0	$1{\cdot}07_7$
215·0	1·074 ± 0·001	59·5	$1{\cdot}06_7$
200·2	1·073	55·4	$1{\cdot}06_5$
179·8	1·073	50·4	$1{\cdot}07_1$
160·0	1·073	46·7	$1{\cdot}07_1$
151·3	1·074	43·2	$1{\cdot}07_1$
140·3	1·072 ± 0·001	40·0	$1{\cdot}06_9$
129·5	1·074	37·0	$1{\cdot}06_2$
119·9	1·075	34·3	$1{\cdot}04_9$
108·2	1·073	31·7	$1{\cdot}04_9$
100·0	1·072	27·0	$1{\cdot}05_5$
86·4	1·071	25·0	$1{\cdot}07_2$
80·0	1·069 ± 0·005	—	—
average value	1·074 ± 0·001 (r.m.s.)	(T > 37 °K)	$1{\cdot}07_1$

* See first footnote of table 4.

† These measurements were made with successively *increasing* temperature (i.e. for constant phase composition). See text.

‡ These error limits do not include the error in the ratio of the absolute resistivities (cf. table 2).

4. DISCUSSION

4·1. *A reduced equation of state for electrical resistivity*

Before comparing our results directly with the predictions of equation (1) let us first consider the more general question of whether the curve of resistivity against temperature for ^{6}Li can be reduced to that for natural lithium by some suitable scaling. In order to show that no simple scaling of the *temperature* alone or of the *resistivity* alone suffices to reduce one curve to the other, we have calculated as a function of temperature the ratio of the resistivities at a given temperature ($\rho^{(6)}/\rho^{(\mathrm{nat.})}$), and the ratio of the temperatures ($T^{(6)}/T^{(\mathrm{nat.})}$) at which the resistivities are equal. It is seen (table 4) that neither of these ratios remains constant. It is, however, possible to reduce one curve to the other by scaling both ρ_i and T. Our experimental accuracy is sufficient to show that to obtain a constant value for the ratio of the resistivities they must be compared at temperatures whose ratio lies between 1·07 and 1·08. The best value is found to be close to 1·074 (cf. table 5) and this gives therefore the ratio of the reduced temperatures for ^{6}Li and natural lithium. Moreover, the value of the ratio of the resistivities, when so compared, then turns out to be the same, namely, $1{\cdot}07_4 \pm 0{\cdot}005$. This follows from our measurements of the *absolute* resistivity. We can therefore conclude from our experiments that the resistivities of the two isotopes depend on temperature through a function of the following kind:

$$\rho_i = TF_2(T/\theta), \tag{2c}$$

i.e. our experiments definitely establish the existence of the factor T outside the function $F_2(T/\theta)$. In coming to these conclusions we have used only the results for the single-phase region. We have included in table 5 a similar analysis for specimens in the two-phase region, and one can see immediately that the scatter in the values of the ratio $\rho^{(6)}/\rho^{(\mathrm{nat.})}$ is much greater than in those for the single-phase region. Nevertheless, except for the results below 37 °K, the resistivity ratio is reasonably constant with a mean value of $1{\cdot}07_1$ which is only slightly less than the value in the single-phase region. The discrepancy below 37 °K is probably connected with the deviations from Matthiessen's rule which we have mentioned earlier.

When we come to compare our results more specifically with the predictions of theory we must make allowance for the fact that natural lithium is not entirely composed of ^{7}Li but contains about 7 % of ^{6}Li.* We shall assume for simplicity that, since the concentration of ^{6}Li is small, the characteristic resistive temperature of natural lithium, $\theta_{\mathrm{nat.}}$, is linear in concentration, i.e. that

$$\theta_{\mathrm{nat.}} = x\theta_7 + (1-x)\,\theta_6, \tag{3}$$

where x is the fraction of ^{7}Li ions present in natural lithium metal.†

On this basis and assuming that $\theta_6/\theta_7 = 1{\cdot}080$, we then expect that $\theta_6/\theta_{\mathrm{nat.}}$ should have the value 1·074. We should thus compare the resistivities of natural lithium and ^{6}Li at temperatures differing by a factor of 1·074, i.e. the resistivity of natural lithium is to be taken at temperature T and that of ^{6}Li at $1{\cdot}074T$. According to the discussion of § 2 we would then also expect that the ratio of the resistivities should be 1·074. But as we have seen this is just what we do find within our experimental error of about $\frac{1}{2}$ %. It therefore seems that Ziman's formula does represent correctly the dependence of electrical resistivity on ionic mass.

It will be recalled that in comparing theory with experiment the only additional assumption that we have had to make is that the electronic properties do not depend on the ionic mass. In terms of equation (1) this assumption appears in three forms: (*a*) that the electron-lattice interaction constants K_6 and K_7 are equal, (*b*) that the function f appearing in equation (1) is the same for both isotopes, and (*c*) that the atomic restoring forces for given displacement are the same in the two isotopes. Assumption (*a*) is tested when $\rho_i^{(6)}$ and $\rho_i^{(\mathrm{nat.})}$, the absolute resistivities, are compared: assumptions (*b*) and (*c*) are tested by the comparison of the characteristic temperatures. Since in both comparisons agreement with theory is found we

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* We ignore the small percentage of ^{7}Li in the ^{6}Li samples (0·7 %) since it would not affect the results within our experimental error.

† Some justification for (3) may be obtained from the theory of specific heats (cf. below).

conclude that our assumption is valid. We have independent evidence that this assumption is correct from the measurements by Martin (1961) of the electronic specific heats of the two isotopes.

4·2. *Comparison with specific heat results*

The agreement between our results and the theory outlined in § 2 appears so striking that it is of interest to inquire whether the correspondence between the specific heats of the lithium isotopes is equally simple. These have been measured by Martin (1959, 1960) and a comparison of his results for natural lithium and ^{6}Li is made in table 6. In making this comparison we expect that the specific heat of the lattice at constant volume should be a function of a reduced temperature only. We are thus interested in the *lattice* specific heat at *constant volume* whereas experiment gives us the *total* specific heat at *constant pressure*, C_p. We assume in making the necessary corrections to obtain C_v (lattice) from C_p that: (*a*) the electronic contribution to the specific heat is the same in both isotopes* and (*b*) that for the present purpose the thermal expansion coefficients and compressibilities of the two metal isotopes do not differ significantly. It should be emphasized, however, that even if we have estimated these corrections wrongly no values which could reasonably be assigned to them would seriously alter the conclusions we reach.

TABLE 6. THE RATIO OF THE TEMPERATURES ($T^{(\text{nat.})}$, $T^{(6)}$) AT WHICH C_v (LATTICE) FOR NATURAL LITHIUM EQUALS THAT FOR ^{6}Li (FROM THE RESULTS OF MARTIN 1959, 1960)

C_v (lattice) (cal °C^{-1} mole^{-1})	$T^{(6)}/T^{(\text{nat.})}$
	b.c.c. region
5·30	1·127 ± 0·01
5·10	1·123
4·90	1·126
4·70	1·122
4·50	1·118 ± 0·008
4·30	1·113
4·00	1·105
3·75	1·101 ± 0·005
3·50	1·102
3·25	1·100
3·00	1·099
2·75	1·095 ± 0·004
	two-phase region
1·89	1·089
0·99	1·081
0·60	1·078
(0	1·073 ± 0·001)*

* Extrapolated value.

In comparing the specific heats, we have deduced at a number of points the ratio of the temperatures at which C_v (lattice) has the same value for the two isotopic

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* This has now been verified experimentally by Martin (1961).

compositions. For pure isotopes we should expect, neglecting anharmonic effects, that this ratio would have the constant value $\surd(7/6)$. Since in fact the measurements were not made on pure isotopes we might expect that as with the resistive characteristic temperature, the ratio would be reduced from $\surd(7/6)$ (= 1·080) to 1·074. In table 6, we see that in fact the ratio varies between about 1·08 and 1·13. At 200 °K the discrepancy with simple theory is seen to be about 4 % in θ which at this temperature corresponds to more than 5 times the estimated experimental error.

Let us consider further the theoretical aspects of the specific heat of lithium.* It is known from harmonic lattice theory that, in so far as this harmonic approximation is valid, the temperature dependence of the specific heat of a monatomic solid at comparatively high temperatures ($\gtrsim \theta/3$)† is governed by a single characteristic temperature θ_∞ which depends only on the second moment of the frequency spectrum of the solid. It can be shown that (as in an Einstein model of a solid) the calculation of θ_∞ involves the calculation of the frequencies of vibration of each atom when all the other atoms of the lattice are held in their equilibrium positions. If we assume that the ^{6}Li atoms are randomly distributed through the lattice of predominantly ^{7}Li atoms then any particular atom (either ^{6}Li or ^{7}Li) has on the average the same environment and so experiences the same restoring force when displaced from equilibrium. Thus the Einstein frequency of vibration of an atom is determined purely by the mass of the atom considered. Consequently if ν_6 and ν_7 are the Einstein frequencies of the ^{6}Li and ^{7}Li atoms respectively, $\nu_6^2 \propto \frac{1}{6}$ and $\nu_7^2 \propto \frac{1}{7}$. Moreover, the contribution of ^{6}Li and ^{7}Li atoms to the second moment of the frequency spectrum is just in proportion to their relative abundance. Thus to this approximation the value of the high temperature characteristic temperature for an isotopic mixture containing a fraction x of ^{7}Li atoms is given by

$$\theta_x^2 = x\theta_7^2 + (1-x)\,\theta_6^2,$$

where θ_7 and θ_6 are the temperatures characteristic of the pure isotopes.

Bearing in mind that on this model $(\theta_6/\theta_7)^2 = \frac{7}{6}$ we deduce that $\theta_6/\theta_{\text{nat.}}$ should have the value 1·074 which to four significant figures is exactly what we deduced earlier by assuming θ to be *linear* in x. The theoretical conclusions are therefore effectively unchanged and, as we have seen, there is a significant difference between them and the experimental findings. If therefore we accept the specific heat results it seems that a purely harmonic lattice theory cannot completely explain them.

If we conclude that anharmonic effects must be present to account for the discrepancy we must then ask what would be the effect of anharmonicity on the electrical resistivity. To this question there is at present no theoretical answer since no detailed, realistic study of the effect of anharmonicity on electrical resistivity appears to have been made. From our present experiments we should have to conclude either (*a*) that the experimental agreement with the predictions deduced from equation (2) is fortuitous, or (*b*) that the anharmonic effects do not significantly affect the electrical resistivity.

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* We are greatly indebted to Dr T. H. K. Barron for his explanation of these aspects of harmonic lattice theory (cf. also Domb & Salter 1952).

† For natural lithium, θ_{Debye} is about 380 °K at a temperature of 200 °K.

In considering this second possibility it is perhaps worth bearing in mind the following difference between the lattice contribution to the specific heat and the lattice contributions to electrical resistivity. At high temperatures all the modes of vibration contribute to the specific heat so that anharmonic effects in any of them could influence the specific heat. On the other hand, it is probable that even at high temperatures only *certain* modes of vibration contribute significantly to the electrical resistivity (in the Bloch model, for example, only the longitudinal modes contribute); if these particular modes happened to show quite small anharmonic effects this could explain the effects we observe.

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