LATTICE CONSTANTS OF SEPARATED ISOTOPES OF LITHIUM

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
Edward James Covington
1956

LATTICE CONSTANTS OF SEPARATED
ISOTOPES OF LITHIUM

By

Edward James Covington

A THESIS

Submitted to the College of Science and Arts
Michigan State University of Agriculture and
Applied Science in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE

Department of Physics

1956

ABSTRACT

The lattice constants of the separated isotopes lithium - 6 and lithium - 7 are determined at room temperature with a 114.6-mm Phillips camera on a Norelco x-ray diffraction unit. Essentially single crystals are worked with by melting the specimens and allowing them to solidify slowly. Films are measured on an optical linear comparator and the extrapolation method of Nelson and Riley used. No consistent differences in lattice constants between lithium - 6, lithium - 7, and natural lithium were observed, and it is concluded that within one part in one thousand the lattice constants are the same.

ACKNOWLEDGMENT

To Professor D. J. Montgomery I express my appreciation for the suggestion of the problem and for his guidance during the entire work.

Thanks are extended to Dr. George Beard of the Physics Department who did much to get the preliminary apparatus in working condition.

I am grateful to Professor C. D. Hause of the Physics Department for making available some of the measuring equipment in the spectroscopy and the optics laboratories. Dr. J. C. Lee, formerly of the Physics Department, made it possible to obtain samples of separated isotopes on his All-College Research Grant, and I wish to express my gratitude to him and to the All-College Research Committee.

I wish to thank Dean Thomas H. Osgood, Dean of the School for Advanced Graduate Study, for his interest in the work, and for his support during its inception when he was head of the Physics Department.

Through the courtesy of Dr. Carl Brubaker of the Chemistry Department, I was able to use the x-ray unit in Kedzie Laboratory and also to obtain some capillary tubes.

Special acknowledgment is due Dr. A. E. Erickson and Dr. M. Mortland of the Soil Science Department for the use of the diffraction unit and film-developing facilities in that department.

Mr. Theodore L. Brown and Professor Max T. Rogers of the Chemistry Department kindly supplied us with samples of purified natural lithium. Dr. P. S. Baker, in charge of special materials, separation development, and isotope utilization for the Stable Isotope Research and Production

Division of the Oak Ridge National Laboratory, has contributed most generously of his facilities and experience to aid us in procuring samples of the separated isotopes. I am grateful to him and to the Atomic Energy Commission for their assistance.

TABLE OF CONTENTS

I. INTRODUCTION

The determination of the lattice constants of the lithium isotopes is directed towards testing and extending present theories in solid state physics. The constants can also be used in determining the ideal densities of the metals. The lithium isotopes six and seven were chosen in view of their large relative mass difference (14%) and their availability in reasonably large amounts. Moreover, lithium has a simple crystal structure (body-centered cubic) which makes the diffraction film interpretation easy, and a simple electronic structure, which facilitates theoretical analysis. For most purposes in solid state physics, the difference in lattice constants is of greater interest than the precise absolute value themselves. The problem is thus simplified, since accurate absolute determination of lattice constants requires highly-developed techniques and very precise control over the experimental variables.

II. X-RAY DIFFRACTION

X-rays are electromagnetic radiations which lie between the ultraviolet and gamma rays in the electromagnetic spectrum. The x-ray region itself is ordinarily taken to lie between 0.02 and 100 A. The rays used for diffraction work lie between 0.5 and 2.5A. Like visible light they show themselves as having a dual nature, that is, they can behave like waves or like particles. X-rays differ from visible light in that they have a shorter wavelength and a larger photon energy. It is because the wavelength of the x-rays is of the order of magnitude of the unit cell dimension that diffraction patterns occur, a crystalline material acting much like a grating.

When the x-ray photon impinges on matter and approaches an electron, the electron begins to vibrate owing to the periodically changing electric field of the x-ray waves. When the electron accelerates, it is itself a source of waves of the same wavelength. These waves radiate from the electron, and we may then consider that the photon has been deviated from the direction of the primary radiation. This process is known as "coherent" scattering; it has taken place without a change in wavelength.

When a plane wave of x-rays then meets a row of equally-spaced atoms, all atoms act as sources of scattered waves. All the electrons in an atom act as wave sources, but the nucleus, because it has a mass much greater than that of the electron, is not involved in the scattering phenomena. It is the constructive combination of all the waves which results in the diffraction phenomena. The number of new waves sent out depends on the number of electrons present, and thus the intensity will be roughly proportional to the atomic number.

III. POWDER CAMERA METHOD

The method of investigation of a polycrystalline metal is about the same as for a powder. A source of nearly monochromatic x-rays is led into a cylindrical camera where it is allowed to hit a cylindrical sample, suspended and rotating at the center of the cylinder. The diffracted rays then strike a photographic film which is placed on the inside of the cylinder. As shown in Fig. 1, the diffracted rays leave the specimen in the form of a cone of semi-apex angle 2θ, where θ is the angle between the incident ray and the reflecting plane. By Bragg's equation we have then that $n\lambda = 2d\sin\theta$,

where n = order of reflection

λ = wavelength of incident radiation

d = interplanar spacing

θ = incident angle.

Now for a cubic crystal the interplanar spacing d, is related to the lattice constant a_0 by the relation

$$d_{hkl} = \frac{a_0}{\sqrt{h^2+k^2+l^2}}$$

where h, k, l are the Miller indices. For a body-centered lattice the final relation is

$$a_0 = \frac{n\lambda\sqrt{h^2+k^2+l^2}}{2\sin\theta},$$

where the form factor is such that the reflection vanishes unless the sum $h+k+l$ is even. The cone of rays leaves the crystal and intersects the cylindrical film along the generatrix of the cone and cylinder. The angle 2θ is determined by measuring the distance between symmetric reflections along the film axis. Now if the reflections do not lie on

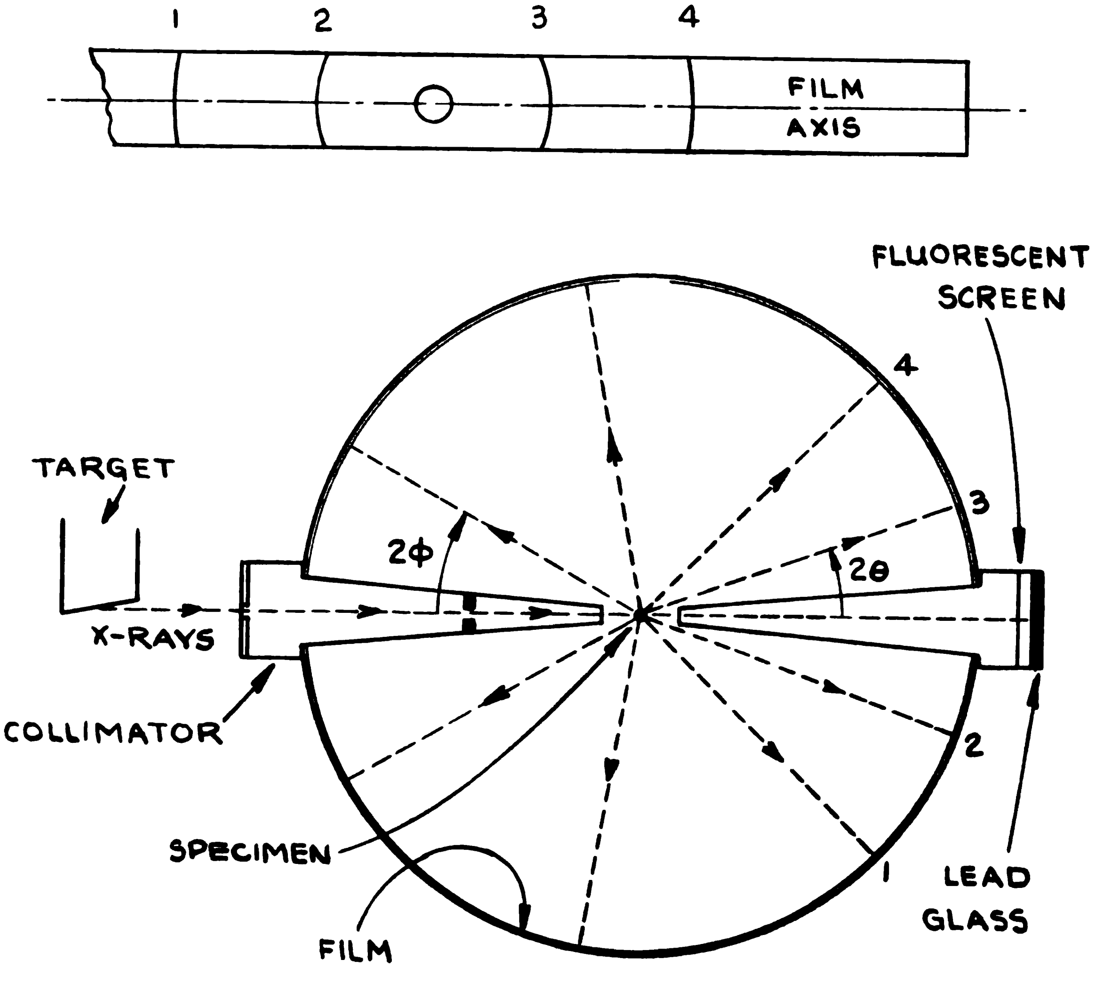

Fig. 1. Schematic diagram of x-ray powder camera.

the axis, the angle θ must be found by a different means. In Fig. 2, it is seen that

$$\cos 2\theta = \cos\beta \cos\alpha \, . \tag{1}$$

Now

$$\beta = \frac{x}{\pi} \text{ radians,} \tag{2}$$

$$\tan\alpha = \frac{y}{\pi} . \tag{3}$$

Substituting (2) and (3) into (1),

$$\cos 2\theta = \cos\left(\frac{x}{\pi}\right)\cos\left(\tan^{-1}\frac{y}{\pi}\right) . \tag{4}$$

Hence

$$\theta = \frac{1}{2}\cos^{-1}\left[\cos\left(\frac{x}{\pi}\right)\cos\left(\tan^{-1}\frac{y}{\pi}\right)\right] . \tag{5}$$

Now

$$n\lambda = 2d\sin\theta ,$$

$$\therefore d = \frac{n\lambda}{2\sin\theta} \, . \tag{6}$$

Substituting θ from (5) into (6),

$$d = \frac{n\lambda}{2\sin\left[\frac{1}{2}\cos^{-1}\left\{\cos\left(\frac{x}{\pi}\right)\cos\left(\tan^{-1}\frac{y}{\pi}\right)\right\}\right]} \, .$$

Since

$$d = \frac{a_0}{\sqrt{h^2+k^2+l^2}} \, ,$$

$$a_0 = \frac{n\lambda\sqrt{h^2+k^2+l^2}}{2\sin\left[\frac{1}{2}\cos^{-1}\left\{\cos\left(\frac{x}{\pi}\right)\cos\left(\tan^{-1}\frac{y}{\pi}\right)\right\}\right]} \, . \tag{7}$$

This expression for a_0 must be used for any reflections which do not lie on the film axis.

When the film is measured it is really θ which is to be determined by measuring linear distances. To find the change δd as a result of a change $\delta\theta$, we differentiate Bragg's law:

$$d\sin\theta = \frac{n\lambda}{2}$$

$$d\cos\theta\,\delta\theta + \sin\theta\,\delta d = 0$$

$$\frac{\delta d}{d} + \cot\theta\,\delta\theta = 0$$

$$\therefore \frac{\delta d}{d} = -\cot\theta\,\delta\theta ,$$

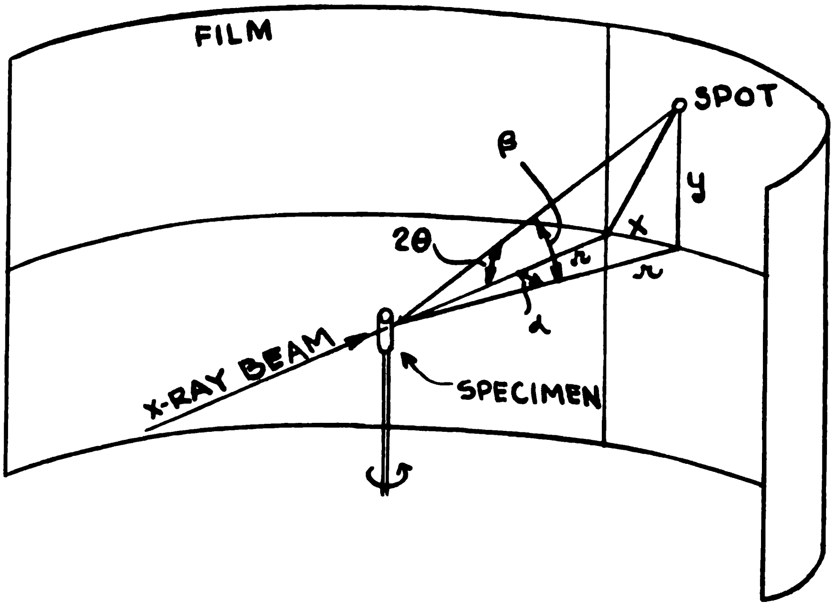

Fig. 2. Determination of 2θ from spots not lying on the film axis.

or,

$$\frac{\delta a_o}{a_o} = -\cot\theta\,\delta\theta$$

for the cubic lattice. From this expression it is clear that the precision measurements are obtained for large values of Θ.

For precision determinations employing the powder camera there are a number of sources of error. These are:

(1) effective camera radius uncertainty
(2) film shrinkage
(3) eccentricity of the specimen
(4) absorption
(5) vertical divergence of the beam .

A detailed discussion of each of these is given in Klug and Alexander(6)and need not be elaborated here. Under a later section on "Film Interpretation" each factor will be considered when appropriate.

IV. EXPERIMENTAL PROCEDURES

Procurement of Samples

Prior to the development of production-type mass spectrographs at the Oak Ridge National Laboratory and other installations of this kind, it was not possible to obtain bulk quantities of highly enriched stable isotopes other than those of hydrogen. In early 1946 ORNL started a program for the enrichment of all naturally-occurring stable isotopes, and by the end of that year had begun shipment of samples. At present stable isotopes of the majority of elements are available for sale or, in some cases, for loan. Among the elements not supplied are those with only one naturally-occurring stable isotope; the majority of radioactive elements; the inert gases; certain of the rare earths; and a few others.

The investigation of the lattice constants of separated isotopes was one part of a broader program on the use of the isotopic mass as a probe for study of the solid state. For the general study a metal was desired. Lithium, with the natural isotopes Li-6 and Li-7 in reasonable abundance ratio (Li-6, 7.52%; Li-7, 92.48%), and the large relative mass difference $(\text{Li-7} - \text{Li-6})/\frac{1}{2}(\text{Li-7} + \text{Li-6}) = 14.\%$, was an obvious choice. Examination of the ORNL Catalog showed that both isotopes were available in very high enrichments, and in adequate amounts.

From the standpoint of theory, lithium is attractive in that it has a rather simple structure, both atomic and crystalline. It is an alkali, and crystallizes in the body-centered cubic form at all but the lowest temperatures. From the standpoint of experiment, on the other hand, lithium offers difficulties in its handling because of its high chemical reactivity. Nonetheless, it was decided that the advantages of high relative mass difference, ready availability, and simplicity of structure outweighed the disadvantages of experimental difficulties.

When the present work was begun in 1955, electromagnetically-separated isotopes were available for distribution only on loan as approved by the U. S. Atomic Energy Commission. Requests for loan were made to the AEC by using Form AEC-100.* The requested amount of lithium-6, the rarer isotope, was 500 milligrams; that of lithium-7, the more common isotope, 1000 mg. With samples of this size the loan fee was $50 per sample. For preparation of the lithium in the elemental form, a special service charge of $60 per sample was made. The total charge was thus $220, which was met by an All-College Research Grant, Physics and Astronomy No. 453, initially given to Dr. J. C. Lee for the academic year 1954 - 1955. The samples were shipped from Oak Ridge National Laboratory on 19 May 1955. The analyses, as furnished by ORNL were as follows:

<u>Li-6</u> <u>Lot No. FY745(bd)</u> <u>530 mg</u>

Isotopic Analysis (mass number and atomic percent): 6, 95.7; 7, 4.3.

Spectrographic Analysis (element and weight percent, precision ± 100%):

Al	0.03	Fe	0.5	Na	0.1
Ba	< 0.05	K	0.03	Ni	0.3
Ca	0.2	Mg	0.02	Pb	0.06
Cr	0.1	Mn	0.02	Sn	0.01
Cu	0.05	Mo	0.1		

---

* The procedure in effect after 13 April 1956 is quite different. Loans of isotopes may be obtained only under unusual conditions, and under a complicated set of rules. Purchases may be made simply, by submitting two completed Forms AEC-391 with the purchase order to the supplier, Dr. C. P. Keim, Director, Stable Isotopes, Research and Production Division, Oak Ridge National Laboratory, Post Office Box Y, Oak Ridge, Tennessee.

Li-7 Lot No. FI668(j) - not redistilled 1000 mg

Isotopic Analysis (mass number and atomic percent): 6, 0.2± 0.1; 7, 99.8± 0.1.

Spectrographic Analysis (element and weight percent, precision+100%):

Al	< 0.01 T	K	< 0.04	Pb	0.15
Ba	0.25	Mg	0.5	Sn	< 0.01
Ca	0.1	Mn	< 0.01 T	Sr	1.0
Cr	< 0.01 T	Mo	< 0.01	V	< 0.01
Cu	0.15	Na	0.5	Zn	< 0.5 T
Fe	0.1	Ni	0.01	(T - trace)	

Unfortunately the concentration of impurities was considered to be too high to allow meaningful results to be obtained. The impurities appear to be introduced during the thermochemical reduction of LiCl to Li by means of metallic Ba, in stainless steel containers. Dr. P. S. Baker, who supervised the preparation of the lithium, suggested that vacuum distillation would be the best method of purifying the metallic lithium, and agreed to have his organization perform the distillation, at a nominal service charge of $50 per sample. The material was accordingly returned for purification about 22 July 1955, without any measurements having been made on them.

The redistilled material was shipped from ORNL on 3 November 1955, in approximately double the amounts initially requested, following the suggestion of Dr. Baker that it would be advantageous to have additional material to make up for the attrition during processing if we were to attempt further distillation. The new samples had the following analysis:

Li-6 Lot No. SS5(a) - redistilled 1045 mg

Isotopic Analysis (mass number and atomic percent): 6, 96.1±0.1; 7, 3.9±0.1.

Spectrographic Analysis (element and weight percent, precision±50%):

Ag	T	Fe	0.5	Ni	< 0.01 T
Al	< 0.01 T	K	< 0.02 T	Pb	< 0.02 T
Ba	< 0.02 T	Mg	0.02	Si	< 0.05
Ca	0.05	Mn	< 0.01	Sn	< 0.01
Cr	< 0.01 T	Mo	< 0.01	Sr	< 0.01
Cu	0.01	Na	0.03	V	< 0.02

Li-7 Lot No. 668 (j) - redistilled 1028 mg + 1000 mg

Isotopic Analysis (mass number and atomic percent): 6, 0.2 ± 0.1; 99.8 ± 0.1.

Spectrographic Analysis (element and weight percent, precision ± 50%):

Ag	T	Fe	0.3	Ni	0.02
Al	0.02	K	0.02	Pb	0.01
Ba	0.01	Mg	0.02	Si	< 0.05T
Ca	0.2	Mn	< 0.01	Sn	< 0.01
Cr	< 0.01T	Mo	< 0.01	Sr	< 0.01
Cu	0.01	Na	0.02	V	< 0.01

With both isotope samples, the iron appears in very great amount (Li-6, Fe = 0.5%; Li-7, Fe = 0.3%). It is believed that these high amounts can be largely discounted, in view of the sampling procedure which involved cutting the material with a steel knife. The only other impurity in high concentration is calcium in the lithium-7 (0.2%). The source is unknown.

In the vacuum distillation, the hardest element to remove is strontium, because of the similarity of its vapor pressure curve to that of lithium. It is gratifying to note that it appears only in very slight amount.

The natural lithium was produced by the Lithium Corporation of America, Minneapolis. It is their low-sodium grade, in the form of 3/8-inch diameter rods with the following specifications:

Na	0.005 %
K	0.01
Ca	0.02
N	0.06
Fe	0.001.

Mr. Ted Brown and Professor Max T. Rogers, of the Chemistry Department of Michigan State University, kindly furnished the natural lithium and the information on its specifications.

Preparation of Specimens

All the lithium samples were kept immersed in oil. Nevertheless, they became coated with a dark layer, which was probably lithium nitride to the greatest extent. The coating can be scraped off and the clean metal obtained, provided that the fresh surface is protected by covering it with a nonreactive substance.

Initially the lithium was extruded from a steel die in such a way that paraffin oil or petrolatum (vaseline) coated the 0.2-mm dia.wire. The short lenths of wire were then sealed in capillary tubes of wall thickness 0.01 mm. It was necessary to seal the lithium since it reacts readily with air to form lithium nitride (Li_3N), lithium oxide (Li_2O), lithium hydroxide ($LiOH$), and lithium carbonate (Li_2CO_3). Specimens were then exposed after annealing at 100°C for one hour, or a long time at room temperature. A few specimens would give sharp reflections while others would not. This was judged to be due to large grains in unfavorable orientations.

Specimens were then prepared in the same manner as above, but in place of annealing they were immersed in oil and brought up to 186°C. All the melted specimens gave sharp reflections, but breakage of tubes in this way was quite considerable. Care must be taken when melting the specimens to position them so that they solidify again in a cylindrical form. Many specimens tended to resemble a twisted ribbon upon solidification. Large grains were obtained in this way, and spots rather than continuous lines resulted on the film.

Exposures and Developing

A 114.6-mm diameter camera was used on a Phillips diffraction unit for all exposures. Copper radiation was used since this has a wavelength for highest angle diffraction of cubic materials of the lattice constant involved(12). All x-radiation of a particular wavelength is accompanied by a continuous spectrum of wavelengths which tends to fog the entire film. The characteristic radiation itself is composed of K_α and K_β. The intensity of K_β is comparable to K_α and the reflections tend to overlap, so it is desirable to eliminate the K_β wavelength. This is accomplished by making use of the element which exhibits strong absorption just to the short-wavelength side of the K_α line of copper ($Z = 29$). Thus a filter of nickel ($Z = 28$) was used for all the exposures.

The specimens were rotated during the exposures, which were for about 22 hours at 35 kv and 20 ma. A Brown 24-hour temperature recorder, reading to a Fahrenheit degree, was set next to the unit.

Kodak No-screen x-ray film was used and developing was done in a Spectrographic developer. Recommended developing and fixing times were followed.

Film Interpretation

It is now necessary to consider the sources of error in the powder camera method listed previously. The 114.6-mm dia.camera employs the asymmetric (Straumanis) method of film position as shown in Fig. 3. The camera dimensions are such that 1 mm distance on the film axis

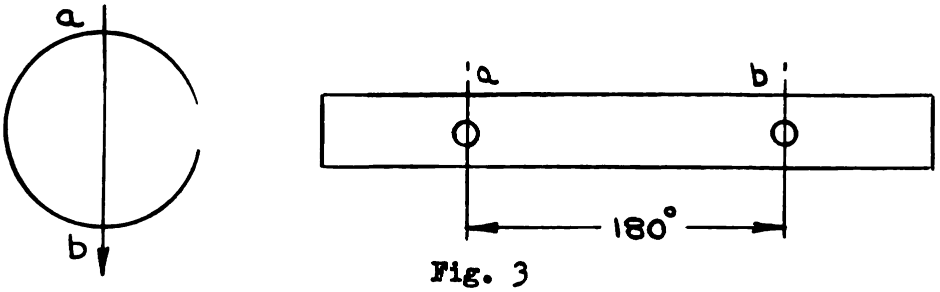

Fig. 3

is equivalent to an angle of 1°. This film position consequently enables one to correct for uniform shrinkage without the use of fiducial marks.

The eccentricity of the sample is reduced to the vanishing point, it is believed, by means of a precise centering arrangement.

It has been seen that high Bragg angles tend to give the most precise measurements. Therefore only those reflections above 60° were used. It is important to get at least one reflection above 80°.

Since lithium ($Z=3$) has low absorbing power and the lines in the back-reflection area were used, the absorption factor is not large. Further reduction of this source of error is obtained by making the specimen diameter small.

The factor of vertical divergence of the beam can be ignored since the slit was small.

All films were measured on a Gaertner linear optical comparator which could be read to 0.001 mm. The necessary accuracy for the measurements was 0.01 mm.

As previously mentioned the specimens were melted before exposure. Large crystalline regions were formed which gave rise to symmetrical spots on the film instead of continuous rings. A typical film is shown in Fig. 4. Fig. 5 shows the effect that a 0.6-mm dia. specimen has on the size of the reflections. Under magnification the diffuse spots disappear into the grainy emulsion of the film. Because of this, the spots were pin pricked under low magnification to obtain well-defined measuring points.

With slow cooling of the lithium during specimen preparation, preferred orientation of the grains was present and subsequently would alter the intensity of some reflections. Since at high angles the intensity is less, in many cases a reflection would be completely absent.

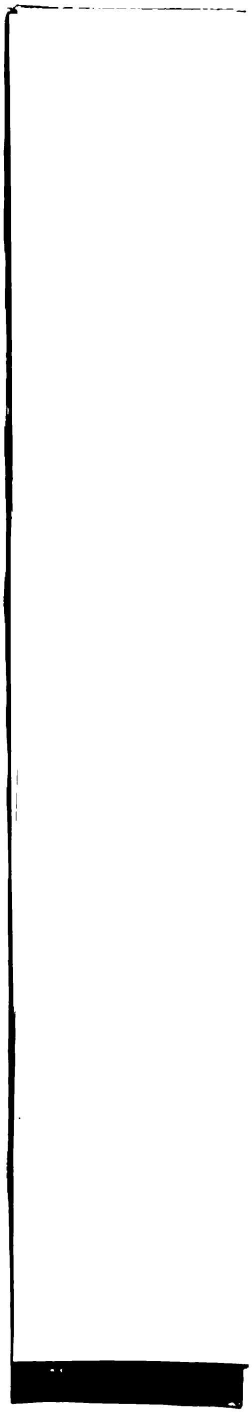

Fig. 4. Typical film taken with a 0.2-mm dia. specimen.

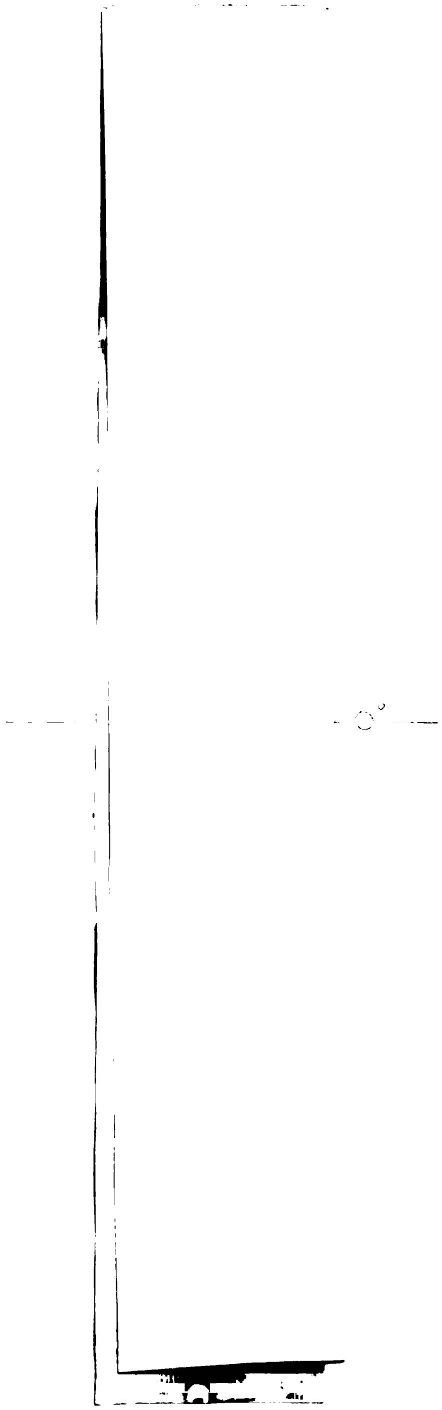

Fig. 5. Film showing effect of a 0.6 mm dia. specimen on spot size.

When the films are measured and lattice constants determined, it is necessary to use an extrapolation function of some kind, since the lattice values will decrease for smaller values of θ. Optimum results are obtained if certain conditions are fulfilled. If a thin specimen is used, the absorbing power is small and the slope of a plot of lattice constants versus an extrapolation function will be minimized. A reflection at least $> 80^\circ$ will fix the one end of the plot with a high degree of accuracy. A linear relationship which holds for low angles would also be desirable.

When the eccentricity error is negligible, it has been found that the lattice constants versus $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$(13) is linear between $\theta = 30^\circ$ to 90°. This linearity to $\theta = 30^\circ$ would seem important for crystals of high symmetry since the number of reflections for $\theta > 60^\circ$ are few. In these determinations however, it seemed that these low angle reflections should be given such little weight that only values where $\theta > 60^\circ$ were employed.

On the following pages data from a typical film are shown. The specimen was the lithium-6 isotope, from a lot obtained for a different purpose.* The first measurements were to determine the film shrinkage. (See Fig. 6).

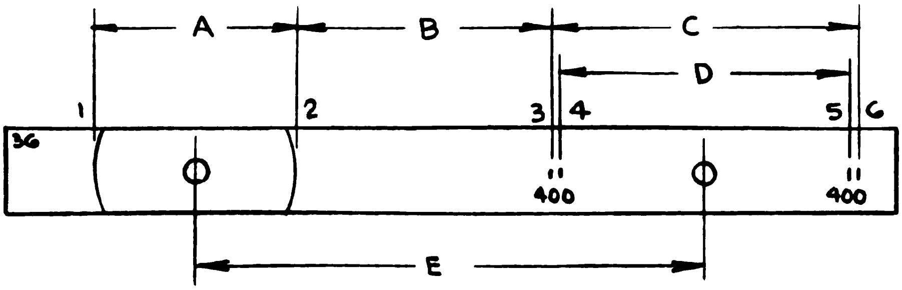

Fig. 6.

---

* Lot SS5(b). Li-6, 99.3 ± 0.2%; Li-7, 0.7 ± 0.2%.
Chief Impurities: Ca, 0.25%; Fe, 0.05%; Zn, < 0.25%.

	Spot 1	Spot 2	Spot 3
(1)	5.1954 mm	51.0290 mm	150.7350 mm
(2)	5.1955	51.0284	150.7338
(3)	5.1910	51.0308	150.7336
(4)	5.1946	51.0270	150.7353
(5)	5.1955	51.0268	150.7326
	mean = 5.1944	mean = 51.0284	mean = 150.7341

Because the maximum range on the comparator was 200 mm it was necessary to reposition the film to take the rest of the measurements.

	Spot 3	Spot 4	Spot 5	Spot 6
(1)	6.5280	7.0452	120.4648	120.9800
(2)	6.5365	7.0432	120.4661	120.9780
(3)	6.5305	7.0475	120.4698	120.9779
(4)	6.5355	7.0453	120.4641	120.9770
(5)	6.5290	7.0422	120.4656	120.9793
	mean=6.5299	mean=7.0447	mean=120.4661	mean=120.9784

Thus we see that

$$A=51.0284-5.1944=45.8340$$

$$B=150.7341-51.0284=99.7057$$

$$C=120.9784-6.5299=114.4485$$

$$D=120.4661-7.0447=113.4214.$$

Now

$$E=\tfrac{1}{2}(A+C)+B$$

$$=\tfrac{1}{2}(160.2825)+99.7057$$

$$=80.1412+99.7057$$

$$E=179.85 \text{ mm}.$$

Hence the film has shrunk 0.15 mm. All measured linear distances must then be multiplied by 180.00/179.85 to correct for the film shrinkage during development.

Since the (400) reflection was used in this determination, we shall work with these values first. As seen in Fig. 6, the (400) reflections happen to fall on the film axis. Thus, correcting for shrinkage:

$$C = \frac{(180.00)\ (114.4485)}{179.85} = (1.0008)\ (114.45)$$

$$C = 114.54 \text{ mm}$$

$$D = (1.0008)\ (113.42)$$

$$D = 113.51 \text{ mm}.$$

The α_1 wavelength is shorter than α_2; consequently the linear distances of the reflections for α_1 are larger. Thus we let

$$4\phi_1 = 114.54,$$

$$4\phi_2 = 113.51,$$

where $4\phi = 360^\circ - 4\theta$;

$$4\theta_1 = 360.00 - 114.54 \qquad 4\theta_2 = 360.00 - 113.51$$

$$= 245.46 \qquad = 246.49$$

$$\theta_1 = 61.365^\circ \qquad \theta_2 = 61.62^\circ$$

$$\sin\theta_1 = 0.877690 \qquad \sin\theta_2 = 0.879815.$$

The expression for a_0 in this instance is

$$a_0 = \frac{n\lambda\sqrt{h^2+k^2+l^2}}{2\sin\theta}.$$

For the (400) reflection, $\sqrt{h^2+k^2+l^2} = 4.00000$;

$$\text{Cu } K_{\alpha_1} = 1.54050\text{A}$$

$$\text{Cu } K_{\alpha_2} = 1.54433\text{A}\ .$$

Thus we now get

θ_1:

$$a_o = \frac{(1.54050)\ (4.00000)}{2(.877690)}$$

$a_o = 3.5104A$ Cu K_{α_1}, (400)

θ_2:

$$a_o = \frac{(1.54433)\ (4.00000)}{2(.879815)}$$

$a_o = 3.5106A$ Cu K_{α_2}, (400).

The measurements of the (411, 330) reflection are now considered.

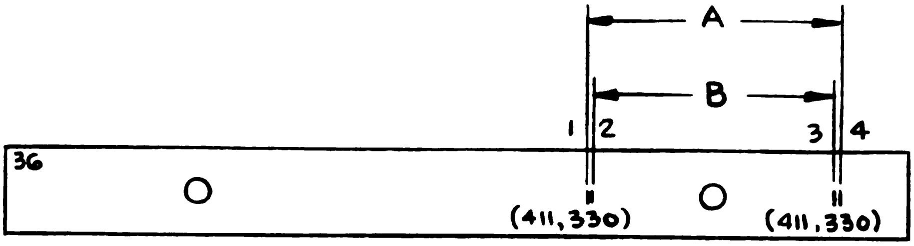

Fig. 7.

	Spot 1	Spot 2	Spot 3	Spot 4
(1)	63.3483	64.0162	148.2478	148.8977
(2)	63.3445	64.0143	148.2461	148.8950
(3)	63.3461	64.0145	148.2448	128.8962
(4)	63.3449	64.0135	148.2440	148.8950
(5)	63.3463	64.0162	148.2439	148.8985
	mean = 63.3460	mean=64.0149	mean=148.2453	mean=148.8965

Following the same procedure as above, we get

$a_o = 3.5100$ A Cu K_{α_1} (411, 330)

$a_o = 3.5109$ A Cu K_{α_2} (411, 330).

The (420) reflection for this film did not lie on the film axis, so this calculation is more lengthy. Consider Fig. 8.

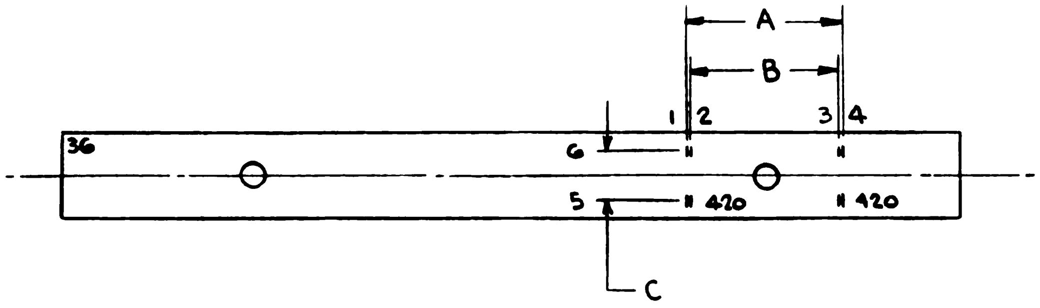

Fig. 8.

	Spot 1	Spot 2	Spot 3	Spot 4
(1)	48.6491	50.0866	91.3950	92.8412
(2)	48.6500	50.0851	91.3933	92.8408
(3)	48.6465	50.0861	91.3943	92.8400
(4)	48.6512	50.0890	91.3968	92.8432
(5)	48.6482	50.0866	91.3975	92.8402
	mean=48.6490	mean=50.0867	mean=91.3954	mean=92.8411

	Spot 5	Spot 6
(1)	90.2448	95.0012
(2)	90.2453	95.0015
(3)	90.2445	95.0007
	mean=90.2449	mean=95.0011

Correcting for film shrinkage we get,

$$A = 44.22 \text{ mm}$$

$$B = 41.34 \text{ mm}$$

$$C = 4.76 \text{ mm.}$$

Referring to Fig. 2, we can let $A = 2x_1$, $B = 2x_2$, and $C = 2y$, where again the subscript "1" is reserved for the α_1 wavelength. Thus, $x_1 = 22.11$, $x_2 = 20.67$, and $y = 2.38$.

From equation (7) we can now find ϕ_1 and ϕ_2.

$$\phi_1 = \tfrac{1}{2}\cos^{-1}\left[\cos\left(\frac{22.11}{57.30}\right)\cos\left(\tan^{-1}\frac{2.380}{57.30}\right)\right]$$

$$= \tfrac{1}{2}\cos^{-1}\left[\cos(.3859)\cos(\tan^{-1}(.0415))\right]$$

$$= \tfrac{1}{2}\cos^{-1}\left[(.926460)\cos(.0415)\right]$$

$$= \tfrac{1}{2}\cos^{-1}\left[(.926460)\ (.999139)\right]$$

$$= \tfrac{1}{2}\cos^{-1}(.925662)$$

$$= \tfrac{1}{2}\cdot(.3880)$$

$$\phi_1 = .1940 \text{ radians}$$

$$\theta_1 = (1.5708 - .1940) \text{ radians}$$

$$= 1.3768 \text{ radians}$$

$$= (1.3768)\ (57.296)^\circ$$

$$\theta_1 = 78.885^\circ.$$

Similarly, we find that $\phi_2 = .1815$ radians and $\theta_2 = 79.60^\circ$.

The values of a_0 are found to be

$$a_0 = 3.5105 \quad \text{Cu } K_{\alpha_1}(420)$$

$$a_0 = 3.5109 \quad \text{Cu } K_{\alpha_2}(420).$$

The results are summarized in Table I. All values of the extrapolation function were obtained from Nelson and Riley. On the extrapolation curve (Fig. 9) the line of best fit was determined by the method of

Table I.

θ	a_0	h,k,l	$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$
61.365	3.5104	400	0.238
61.62	3.5106	400	0.234
68.595	3.5100	411,330	0.127
68.925	3.5109	411,330	0.123
78.885	3.5105	420	0.32
79.60	3.5109	420	0.28

least squares. After the extrapolated value was found it was necessary to correct for thermal expansion. For lithium, a change of 1°C during the exposure amounts to a linear expansion of 0.00016A at room temperature.

V. RESULTS AND DISCUSSION

While the analysis for the lithium-6 isotope given previously is that for sample 5(a), only results for sample 5(b) (the analysis of which is on page 16) will be given. Measurements were first taken using the 5(b) sample since more of this sample was obtainable. Unfortunately time did not permit measurements to be taken using sample 5(a). However, the analyses do show how distillation reduced the amount of impurities in the metal.

Analysis of the experimental data gives the following results for the lattice constants of the samples of lithium-6 (sample 5-b) and lithium-7 (sample 668j), corrected to 20° C, but not corrected for impurities:

Li-6	3.5112 A
Li-7	3.5097 A.

The results for lithium-7 have the greatest reliability, since they were obtained from several films. The results for lithium-6 were obtained from several films, but showed the highest scatter for values obtained from different reflections. Since the isotopic concentration of natural lithium is 92.5 percent Li-7, and that of our sample of lithium-7 is 99.8 percent Li-7, we believe that our value for this isotope is our best estimate for the absolute value for natural lithium.

From the analyses furnished by the suppliers of the samples, it is possible to correct the lattice constants to those for the pure material, if a generalized Vegard's Law is accepted. This law says that the lattice constant of a binary mixture forming a solid solution is a linear function of the molecular fractions of the components. For the small amount of impurities present (less than 0.25 per cent) it is likely that a solid solution is formed. What is less likely is that the law is obeyed; almost all binary alloys violate it to some degree or other, and there are several serious exceptions, namely, copper-manganese and silver-gold. In these cases minima in lattice constant as a function of composition exist. Nonetheless, we have no better guide, and in all probability the generalized Vegard's Law leads to an upper limit of error. Moreover, the corrections are found to be smaller than the other uncertainties. The new values, obtained from the amounts of impurities and from their lattice constants, and taking into account experimental errors, are:

Li-6 3.5107 ± .0010
Li-7 3.5092 ± .0007

One film of the natural lithium sample was measured. The value of a_o obtained for this sample, corrected to 20°C but not corrected for impurities, was 3.5111A. Correcting for impurities a_o is found to be 3.5110A. This result shall be discounted since only one film was measured.

We are now able to calculate the density for lithium-7. For the body-centered cubic structure there are two atoms per cell. If we multiply this number by the mass of each atom, the mass of a unit cell is obtained. The mass of each atom is given by M/N, where M is the atomic weight of lithium-7 and N is Avogadro's number. Since the mass can be written as $a_o^3\rho$, we have

$$2\frac{M}{N} = a_o^3\rho$$

$$\therefore \rho = \frac{2M}{Na_o^3}$$

where ρ is the density.

Now $M = 7.0180$
$N = 6.0247 \times 10^{23}$

$$\rho = \frac{2(7.0180)}{(6.0247\times10^{23})(3.5092\times10^{-8})^{3}}$$

$$\therefore \quad \rho = 0.5391\ \text{gm}\,\text{cm}^{-3}.$$

The predicted value for the density of lithium-7, using the experimentally obtained value for a_0, is .5391 gm cm.$^{-3}$

To gain an idea of the validity of the absolute value of the constants, we cite the results of the other modern determinations for natural lithium:

Aruja and Perlitz (10)	1940	3.5090 A
Lonsdale and Hume-Rothery (11)	1945	3.5094 A
Pearson (14)	1954	3.5087 A
(Present investigator Li-7	1956	3.5092 A)

The samples of Aruja and Perlitz were commercial lithium, of unknown purity; moreover, their extrapolation procedure has been criticized by Lonsdale and Hume-Rothery, and we believe that their value is too low. On the other hand, the samples of Lonsdale and Hume-Rothery may have contained sodium, according to Pearson, and are too high. But Pearson's data upon direct examination, appear to lead to a slightly higher value than he cites; perhaps 3.5090 A. Pearson's samples, however, are by far the purest used. In any event, the agreement is well within the experimental uncertainties of the various investigators.

At the present stage of investigation, we can conclude the following: The lattice constant for lithium-6 appears to be higher than lithium-7 fractionally by 4×10^{-4}, but the experimental uncertainty is such that they may be identical. Lithium-6 is not more than 10×10^{-4} larger than lithium-7, while lithium-7 is not more than 0.5×10^{-4} larger than lithium-6.

So far as theory is concerned, there is no adequate model to describe the effect under investigation. Theory on the basis of an Einstein or Debye model predicts that lithium-6 is larger fractionally by about 3×10^{-4}; Grüneisen - Mie theory predicts 4×10^{-4}. The precision of our measurements is not better than 5×10^{-4}. Hence no inconsistency has been shown.

Similar results have been obtained for Li^6F^{19} and Li^7F^{19} by Thewlis(15). The greater scattering power of this crystal makes high precision more readily obtainable, and Thewlis reports that the compound with the lighter isotope has a larger lattice constant by the fractional difference 2×10^{-4}, whereas London (referred to by Thewlis, loc. cit.) has calculated the value 3.3×10^{-4}.

VI. SUGGESTIONS FOR FUTURE WORK

Impurities must be reduced to be sure that the absolute values are precise. With lithium it appears that only repeated vacuum distillation in a metal still will produce a sample of adequate purity. The effects of nonuniform film shrinkage could be eliminated by using a camera with a set of fiducial marks. The temperature must be known and it should be held constant. If the temperature varies a few degrees the fourth place in the lattice constant is affected. Even a few tenths of a degree variation will affect the fifth place. It was found that two films taken with the sample would vary in their reflections; that is, the spots would be smeared out and more diffuse. This was probably caused by a large temperature variation. It is also true that the higher the temperature, the weaker the diffracted intensities. It would seem desirable then to work at low temperatures. Thus, for high angles the decrease in intensity is minimized by decreasing the thermal agitation in the lattice.

Since there are so few reflections in the high angle region, possibility of not using the filter was investigated. If this could be done the exposure time would be reduced as well as getting more reflections to work with. It was found however, that the general fogging was much more intense and the reflections were barely distinguishable.

While the control of the temperature during exposures is necessary, the control of the temperature and humidity during film measurements is also important. The light source should be fluorescent so that heat is not a disturbing factor. The film base will also suffer dimensional variations with the humidity.

A serious difficulty can arise in the case of the x-ray film. To increase the sensitivity of the film, both sides have a layer of silver bromide. This is characteristic of the Kodak "No-Screen" x-ray film. These images will be superimposed when the x-rays are normal to the film, that is, for reflections along the "equatorial axis". However, when the reflections are off axis, such as we have in some cases, the center is shifted slightly. It would be desirable then to use a film with a single layer of emulsion.

The absorption of x-rays increases with grain size in the emulsion, so if the films are measured with a magnification which is too great, the weak lines are lost in the background. If the lines are sharp enough, one might consider the possibility of using a microphotometer. Also, since the intensities of α_1 to α_2 is about 2: 1, it is probable that measurements using α_1 should be more accurate.

Finally isotopes of elements other than lithium are available in quantities large enough for lattice constant determination. Many of them are less inclement to the experimenter than lithium, because of their lower chemical reactivity and their higher scattering power.

BIBLIOGRAPHY

Book references:

1. Charles S. Barrett, *Structure of Metals*, (Mc Graw-Hill Book Company, Inc., New York, 1952).
2. M. J. Buerger, *X-ray Crystallography*, (John Wiley and Sons, Inc., New York, 1942).
3. George L. Clark, *Applied X-rays*, (Mc Graw-Hill Book Company, Inc., New York, 1955).
4. Andre Guinier, *X-ray Crystallographic Technology*, (Hilger and Watts Ltd., London, 1952).
5. Clifford A. Hampel, *Rare Metals Handbook*, (Reinhold Publishing Corporation, New York, 1954).
6. H. P. Klug and L. E. Alexander, *X-ray Diffraction Procedures*, (John Wiley and Sons, Inc., New York, 1954).
7. H. S. Peiser, H. P. Rooksby, and A. J. C. Wilson, *X-ray Diffraction by Polycrystalline Materials*, (The Institute of Physics, London, 1955).
8. Stable Isotopes Research and Production Division, *Inventory of Electromagnetically-Enriched Isotopes*, (Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1950; revised February, 1955).
9. Stable Isotopes Research and Production Division, *Inventory and Price List of Electromagnetically-Enriched and Other Stable Isotopes*, (Oak Ridge National Laboratory, Oak Ridge, Tennessee, April 1956).

Journal references:

10. E. Aruja and H. Perlitz, Phil. Mag. **30**, 55 (1940).
11. K. Lonsdale and W. Hume-Rothery, Phil. Mag. **36** (7), 799 (1945).
12. L. Muldawer and R. Feder, Rev. Sci. Instru. **26** (9), 827 (1955).
13. J. B. Nelson and D. P. Riley, Proc. Phys. Soc. (London) **57**, 160 (1945).
14. W. B. Pearson, Can. J. Phys. **32**, 708 (1954).
15. J. Thewlis, Acta Cryst. 8, **36** (1955).