

Elastic Modulus of Isotopically-Concentrated Lithium*

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The effect of isotopic mass on elastic properties of solids was studied by measuring the elastic modulus of isotopically-concentrated polycrystalline specimens of metallic lithium at 25°C. The elastic modulus of lithium-6 (96.1% Li⁶, 3.9% Li⁷) was found to be $(7.93 \pm 0.21) \times 10^{10}$ dynes/cm², and that of lithium-7 (7.5% Li⁶, 92.5% Li⁷) $(7.98 \pm 0.33) \times 10^{10}$ dynes/cm². Within the limits of precision of the experiments, the values do not differ. It is concluded that isotopic mass has no effect on static elastic properties other than that arising from the change in lattice constants.

TO examine the effect of isotopic mass on elastic modulus, as well as to obtain data on a material of reasonable theoretical simplicity and of potential technological application in nuclear power, measurements of the elastic modulus of polycrystalline lithium were undertaken on specimens of high concentration of lithium-6 and lithium-7. Extension of the measurements over a wide temperature range would have special value in certain metallurgical problems, notably phase transformations in solids.

For the material of high Li⁷ concentration, natural lithium (7.5% Li⁶, 92.5% Li⁷) was obtained from Lithium Corporation of America, in their "low-sodium

grade." Their analysis gives the impurity content as follows: N, 0.06%; Ca, 0.02%; K, 0.1%; Na, 0.005%; Fe, 0.001%. For the material of high Li-6 concentration, electromagnetically-separated lithium (96.1% Li⁶, 3.9% Li⁷) was obtained from the Isotopes Division, Oak Ridge National Laboratory. Their analysis gives the impurities as follows: Ca, 0.05%; Na, 0.03%; Mg, 0.02%; all others less than 0.02%.

In measuring the elastic modulus of lithium, problems arise from its high chemical reactivity and from the scantiness of the separated isotopes. A simple method, which can be readily adapted to measurements over a wide range of temperature, is the observation of the resonant frequency of transverse vibration of a cantilever beam¹ driven in an alternating electric field.² A sketch of the apparatus is shown in Fig. 1. The beam consisted of a circular wire extruded through a die directly down into a CO₂-filled chamber. The free end of the wire was located between two electrodes, and the clamped end was held by the walls of the dies and the mass of the unextruded material. The length and the diameter of the wire were measured with a traveling microscope, which served also for detection of resonance. The electrodes were fed from the secondary of a step-up transformer excited by a power amplifier driven by an audio-frequency oscillator. For each run a short piece of wire was first extruded, on which measurements of length, diameter, and resonant frequency were made. The wire was then extended and successive sets of measurements were made, up to a total of perhaps five. The lengths ranged from 3 to 10 cm, the diameters from 0.06 to 0.10 cm, and the frequencies from 40 to 400 cycles/sec.

Observation with the microscope showed that the wire deviated somewhat from roundness. As a consequence, the frequency of vibration in the fundamental mode assumed first one and then the other of two different values as the direction of the driving field was rotated about the axis of the wire. The change in frequency could be correlated with the variation in diameter by assuming that the cross section was

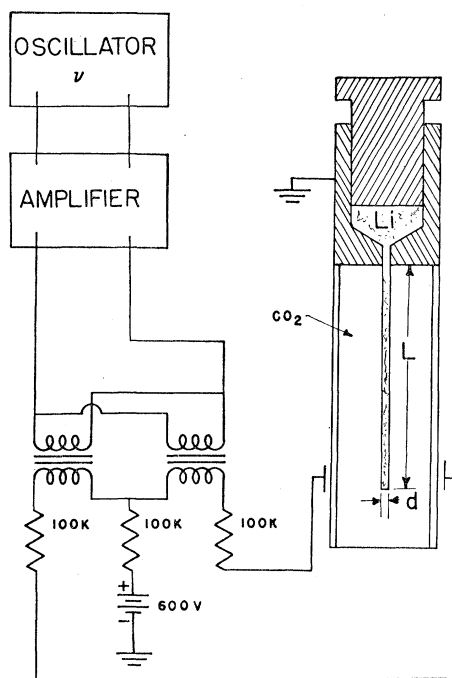


FIG. 1. Schematic diagram of apparatus for vibroscope determination of elastic modulus.

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¹ E. M. Kärholm and B. Schröder, *Textile Research J.* **23**, 208 (1953).

² D. J. Montgomery and W. T. Milloway, *Textile Research J.* **22**, 729 (1952).

elliptical, the wire being forced into vibration in the plane of either the major or the minor axis of the ellipse. Accordingly, the two principal diameters and the two fundamental frequencies were determined for every length of each wire.

As discussed in standard texts,³ the elastic modulus is given by

$$E = 16\pi^2\nu_1^2\rho L^4/s_1^4b^2,$$

where E =elastic modulus (Young's modulus) of material, ν_1 =lowest natural frequency, ρ =density (mass/unit volume) of material, L =length of bar, s_1 =lowest root of characteristic equation = 1.875..., and b =principal semidiameter in plane of vibration. Substitution in this equation gives E in terms of the observed resonant frequencies, the measured lengths and diameters, and the densities reported by Snyder and Montgomery.⁴

Measurements were made on seven wires of high Li⁷ concentration (natural lithium) and on five wires of high Li⁶ concentration (electromagnetically enriched). From one to five lengths were used with each wire, depending on the success of the extrusion. To check the validity of the method, the quantity $\nu/2b$ was plotted against $1/L^2$ for each wire when more than one length was used. No trend away from a straight line through the origin was noted, and it was concluded that the slight deviations from roundness and straightness did not vitiate the method. A composite plot of $\rho^{\frac{1}{2}}\nu/2b$ vs $1/L^2$ for all the wires is shown in Fig. 2. The value of the elastic modulus, as calculated directly from the data, is $7.98 \pm 0.33 \times 10^{10}$ dynes/cm² for natural lithium (92.5% Li⁷), and $7.93 \pm 0.21 \times 10^{10}$ dynes/cm² for electromagnetically-separated lithium (96.1% Li⁶).

DISCUSSION

On current theories of the solid state, the only effect of isotopic mass on elastic modulus would be that resulting from the shift in lattice constant with isotopic composition. The magnitude of this effect can be estimated from the temperature dependence of the lattice constant and of the elastic modulus, if it is assumed that the shift in lattice constant due to change in isotopic composition at constant temperature is equivalent to the shift due to change in temperature at constant isotopic composition. The fractional difference in lattice constant between lithium-6 and lithium-7 has been found by Covington and Montgomery⁵ to be about 400×10^{-6} . The temperature coefficient of linear

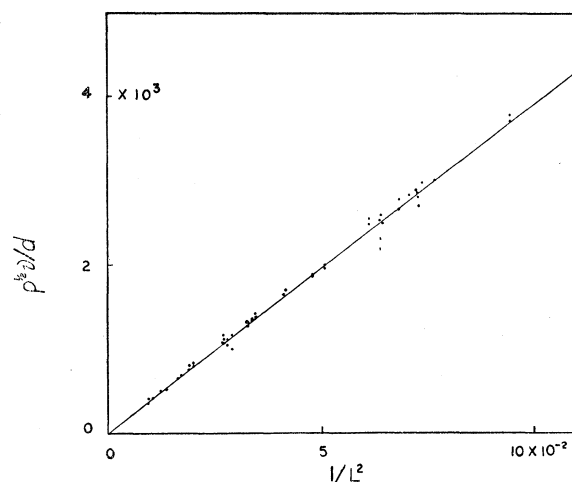


FIG. 2. Composite plot for vibroscope determination of elastic modulus for isotopically-concentrated lithium. The data for seven wires of natural lithium ("Li⁷") and for five wires of electromagnetically-enriched lithium ("Li⁶") are included. Ordinate: $(\text{density})^{1/2}(\text{resonant frequency})/(\text{diameter in plane of vibration})$. Abscissa: $1/(\text{length})^2$. All quantities are in cgs units.

expansion for natural lithium as reported by Bernini and Cantoni⁶ is about $50 \times 10^{-6}/\text{C-deg}$. Hence the change in isotopic composition between lithium-6 and lithium-7 is equivalent to a change in temperature for natural lithium of say 8 C-deg. The temperature coefficient of elastic modulus for lithium does not appear to have been measured; for most metals this coefficient is the range $200\text{--}500 \times 10^{-6}/\text{C-deg}$, and for lithium it is likely to be at the high end. Under these assumptions the fractional difference in elastic modulus between lithium isotopes would be about 4×10^{-3} , the lighter isotope having the lower elastic modulus. The experimental results happen to give the fractional difference as 6×10^{-3} , in the same direction; the closeness is of course fortuitous. In view of the inexactitude of the measurements and the small number of replications, it can be concluded only that the effect of isotopic mass on the elastic modulus of lithium at room temperature is very small.

The value given above, about 8.0×10^{10} dynes/cm², is in serious disagreement with what is apparently the only previously reported value, namely that of 4.9×10^{10} dynes/cm² found by Bridgman⁷ in experiments on static bending under oil at room temperature. Other authors have measured the stiffnesses c_{11} , c_{44} , and c_{12} on single or polycrystals at low temperatures. It is possible to estimate the elastic modulus for polycrystalline material at room temperatures by first averaging in some way over the microscopic crystals, and then extrapolating the result to higher temperatures. In this way Bender⁸ reported a value of 11.5×10^{10} dynes/cm² at 90°K, which would probably be de-

³ P. M. Morse, *Vibration and Sound* (McGraw-Hill Book Company, Inc., New York, 1948), second edition, Chap. 4; Lord Rayleigh, *The Theory of Sound* (Macmillan and Company, Ltd., 1894), second edition, Vol. 1; reprinted by Macmillan and Company, Ltd., 1926, 1929; reprinted by Dover Publications, New York, 1945.

⁴ D. D. Snyder and D. J. Montgomery, *J. Chem. Phys.* **27**, 1033 (1957).

⁵ E. J. Covington and D. J. Montgomery, *J. Chem. Phys.* **27**, 1030 (1957).

⁶ A. Bernini and C. Cantoni, *Nuovo cimento* **8**, 241 (1914).

⁷ P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **57**, 41 (1922).

⁸ O. Bender, *Ann. Physik* **34**, 359 (1939).

creased by about 20% at room temperature to give a value of 9.2×10^{10} dynes/cm². Nash and Smith⁹ by ultrasonic techniques determined the single-crystal stiffnesses of natural lithium at 78°K. From their values the elastic modulus for a polycrystalline aggregate can be calculated to be 18×10^{10} dynes/cm² by Voigt's analysis, and 7×10^{10} dynes/cm² by Reuss's analysis (see Hearmon¹⁰ or Huntington¹¹ for a description of

these analyses). At room temperature these two values would decrease to perhaps 15×10^{10} and 5.5×10^{10} dynes/cm², respectively, to bracket the values cited above for the present work (8.0×10^{10}) and for Bender's work (9.2×10^{10}).

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⁹ H. C. Nash and C. S. Smith, *Bull. Am. Phys. Soc.* **3**, 123 (1958).

¹⁰ R. F. S. Hearmon, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 323.

¹¹ H. B. Huntington, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 213.

F-Center Growth Curves*

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It is shown that the increase in the density of *F* centers in KCl due to x-ray irradiation can be described kinetically by considering two independent groups of negative ion vacancies. One group is composed of vacancies in the lattice before irradiation, while the other is composed of vacancies generated during the irradiation. It is concluded from the difference in the electron capture cross sections for the two groups of vacancies and the intensity dependence of the rate of generation of new vacancies that the vacancies are generated at dislocations by a multiple ionization process.

AN investigation has been made of the growth curves of *F* centers in KCl at room temperature. It appears that the experimental data can be very well fitted by a theoretical curve based on the assumption that the vacancies involved in the rapid growth (initial portion) and those involved in the slow growth (later portion) may be treated independently and have different rate constants for the capture of electrons. The vacancies associated with the rapid growth are assumed to be in the lattice before irradiation, while the vacancies associated with the slow growth are assumed to be generated during the irradiation. In general we have

$$\begin{aligned} df_i/dt &= b(n - f_i), & df_o/dt &= c(at - f_o), \\ f_i &= f_o = 0 \text{ at } t=0, \end{aligned} \quad (1)$$

where f_i and f_o are the densities of *F* centers produced from initially present and from freshly generated vacancies, respectively; b and c are the corresponding rate parameters for the capture of electrons; n is the initial density of vacancies; and a is the rate constant for the generation of new vacancies. This leads to

$$f = f_i + f_o = n(1 - e^{-bt}) + at - (a/c)(1 - e^{-ct}). \quad (2)$$

The form of f is not changed if a bleaching term $-af$, which is important only at low intensities, is included in each of Eqs. (1).

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A set of KCl Harshaw crystals was irradiated simultaneously with 140 kev, 5 ma x-rays through not less than $\frac{1}{16}$ in. of Al to insure body coloration. The radiation flux was controlled within the limits of 1 to 100 by focal spot to sample distance. All growth curves showed a tendency to saturation for very high irradiations but only the portions given in Fig. 1 were taken into account. Using an IBM 650 computer the data were then fitted to Eq. (2) by the least squares method and the fit of the calculated curve to experimental points is very good as shown in Fig. 1 and is within 2%. The parameters a , b , c , and n were thus obtained as a function of x-ray intensity. The most notable result is an apparently quadratic dependence of the parameter a on the x-ray intensity, which suggests a two-step process for the generation of new vacancies. The value of n is essentially constant with intensity and of the order of 10^{16} per cc as expected. The parameter b is of the order of 2–3 hr⁻¹, increases with irradiation intensity, and is 10 to 20 times greater than c .

The striking difference between the two rate parameters b and c indicates that the two groups of negative ion vacancies differ considerably in their physical environments. If new vacancies are found in the vicinity of dislocations and the old vacancies are randomly distributed, several qualitative reasons can be proposed to account for the fact that b is much bigger than c . The basic assumption that the two groups