

of the molar volume  $V$  for a liquid based on this structure. The minimum  $E$  of  $-24.6$  at  $V=21$  cc, as compared with  $-174$  and  $9.2$  cc respectively for the classical crystals, is in line with the effects (b) and (c), but the agreement with the observed values shown by the point  $\odot$  is poor. Better agreement can be secured by taking  $c=10$ , for which  $a^3=1.39V$ , as shown in Fig. 2. The shift from  $c=12$  to  $c=10$  was advocated by De Boer and Lunbeck,<sup>5</sup> who found that with such a change one can obtain better agreement with observations for the liquid molecular volumes of heavy atoms computed by the Lennard-Jones theory. Figure 3 gives the results for liquid helium based on a face-centered cubic which is only 50 percent populated.  $E$  has a minimum of about  $-1$  calorie at about 80 cc, showing that a coordination number 6 is definitely too low. Although at the observed value of  $V=27.6$ ,  $E_0$  decreases with decreasing  $c$ , the quantum-mechanical effects bring about the opposite trend in the minimal values of  $E$ . Interpolating the minimal values obtained for the three coordination numbers, we

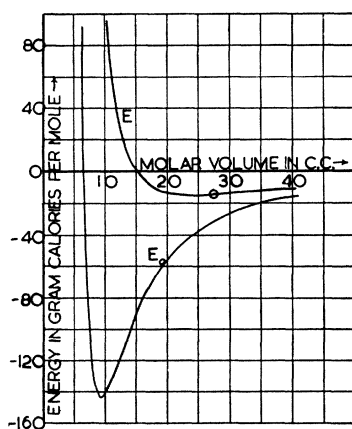


FIG. 2. Computed energy  $E$  of liquid helium as function of the molar volume  $V$ , for the case when the coordination number  $c$  is 10.  $E_0$  is the classical energy of a crystal having a coordination number equal to 10.  $\odot$  is the observed value for liquid helium. At the minimum,  $E = -14.7$ ,  $V = 27.6$ , as against the observed values of  $-14.2$  and  $27.6$ .

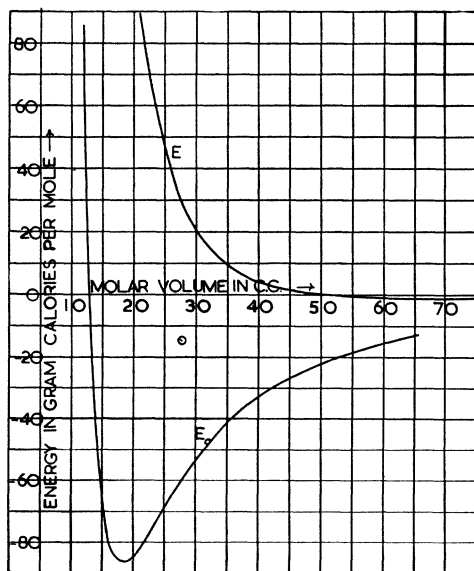


FIG. 3. Computed energy  $E$  of liquid helium as a function of the molar volume  $V$ , based on a model of a face-centered cubic which is only 50 percent populated and has a coordination number 6.  $E_0$  is the classical energy.  $\odot$  is the observed value for liquid helium.

find that the observed values of  $E = -14.2$  and  $V = 27.6$  would be simultaneously achieved at about  $c = 9.5$ .

We have also computed the compressibility  $\chi$  from the curvature of curve  $E$  in Fig. 2 at the minimum:

$$(1/\chi) = \rho(d\rho/d\rho) = V(d^2E/dV^2), \quad (6)$$

and obtained a value of  $9 \times 10^{-3}$  atmos.<sup>-1</sup>. The observations go down only<sup>6</sup> to  $T = 1.25^\circ\text{K}$ , and an external mean pressure of 3 atmos., where  $\chi = 10 \times 10^{-3}$  atmos.<sup>-1</sup>. However, extrapolation to zero external pressure indicates that  $\chi$  may reach a value of  $12 \times 10^{-3}$  atmos.<sup>-1</sup>. Even so, the agreement of this sensitive quantity is better than one of order of magnitude.

Further test of the theory will be afforded when the higher energy levels are determined and applied to the study of the thermodynamics ( $\lambda$ -point) and hydrodynamics of liquid helium. The results presented here suggest a point of attack on the now deadlocked problem of helium, namely to provide a quantum theoretical justification<sup>7</sup> of the scheme underlying the Lennard-Jones theory.

<sup>1</sup> F. Simon, *Nature* **133**, 460, 529 (1934).

<sup>2</sup> J. De Boer, *Physica* **14**, 144 (1948).

<sup>3</sup> F. London, *Proc. Roy. Soc. A*, **153**, 576 (1936).

<sup>4</sup> J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc. A*, **163**, 53 (1937).

<sup>5</sup> J. De Boer and R. J. Lunbeck, *Physica* **14**, 522 (1948).

<sup>6</sup> W. H. Keesom, *Helium* (Elsevier Publishing Company, Amsterdam, 1942), p. 240.

<sup>7</sup> J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940), p. 323.

## A Ferromagnetic Curie Point in $\text{KTaO}_3$ at Very Low Temperatures

J. K. HULM, B. T. MATTHIAS,\* AND E. A. LONG

*Institute for the Study of Metals, University of Chicago, Chicago, Illinois*

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SINCE the ferroelectric Curie points discovered up to the present time all lie at temperatures above the boiling point of liquid nitrogen, and it is generally believed that at a transition point of this type there is a balance between the disordering thermal energy and the lattice dipole interaction energy, the existence of a ferroelectric Curie point at very low temperatures has hitherto seemed rather improbable. Recently, however, we have observed in potassium tantalate,  $\text{KTaO}_3$ , a Curie point at about  $13.2^\circ\text{K}$  characterized by a maximum in dielectric constant of the type shown in Fig. 1 and by the appearance of a ferroelectric hysteresis loop in the polarization-field curve as the temperature is lowered through the critical value.

The unusual dielectric properties of  $\text{KTaO}_3$  at ordinary temperatures have already been reported.<sup>1</sup> The ferroelectric Curie point was then stated to lie in the neighborhood of room temperature, a result which was due to the presence of considerable amounts of sodium in the first crystals. In subsequent measurements (made by J. P. Remeika) on comparatively pure crystals at the Bell Telephone Laboratories, the dielectric constant at liquid nitrogen temperatures was found to follow a Curie-Weiss law with a Curie temperature between  $10^\circ$  and  $20^\circ\text{K}$ .

We therefore studied two  $\text{KTaO}_3$  crystals at temperatures below  $80^\circ\text{K}$ ; one to  $12^\circ\text{K}$  and the other to  $1.3^\circ\text{K}$ . The crystals were of about 1 mm thickness and 2 mm edge, mounted so that the electric field was applied normal to a 100 plane. Temperatures were measured with an accuracy of  $0.1^\circ\text{K}$ , using a helium gas thermometer and a copper-constantan thermocouple.

The dielectric constant,  $\epsilon$ , of both crystals is plotted in Fig. 1. The difference in numerical values, too large to be accounted for by errors of measurement, is thought to be due to differences of internal strain. The temperature dependence of  $\epsilon$  is, however, roughly the same for both crystals and is well represented between  $85^\circ\text{K}$  and  $52^\circ\text{K}$  by the Curie-Weiss law

$$\epsilon = C/(T - \theta) \quad (1)$$

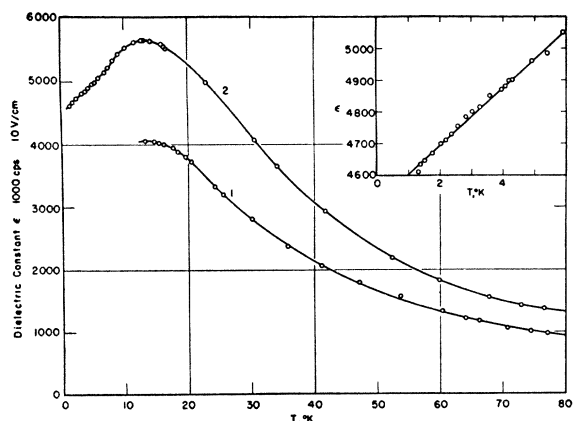


FIG. 1. Dielectric constant of  $\text{KTaO}_3$  at low temperatures.

with  $C = 6.1 \times 10^4$ ,  $\theta = 14.0^\circ\text{K}$ , (No. 1),  $C = 8.3 \times 10^4$ ,  $\theta = 14.6^\circ\text{K}$ , (No. 2). Below  $52^\circ\text{K}$ ,  $\epsilon$  was smaller than is predicted by Eq. (1), and passed through a maximum at  $13.2^\circ\text{K}$ . At liquid helium temperature  $\epsilon$  showed an almost linear decrease which continued down to  $1.3^\circ\text{K}$ , as shown in the inset of Fig. 1. Below  $13^\circ\text{K}$  the polarization-field curve exhibited a small reversible spontaneous polarization superimposed upon a high induced polarization; at the maximum field strength of the present experiment, 5000 volts/cm, the crystal was far from saturated, so that a reliable value of the spontaneous moment was not obtained.

The relatively good agreement between  $\theta$  and the temperature of the maximum of  $\epsilon$  demonstrates once again the validity of using the Curie-Weiss law to estimate the position of a ferroelectric Curie point. Smolenskii<sup>2</sup> has recently concluded from an application of this law to the dielectric constants above room temperature of calcium, strontium, and cadmium titanate that the last two substances have ferroelectric Curie points at  $10^\circ$  and  $50^\circ\text{K}$ , respectively. However, as yet unpublished measurements by Hulm ( $\text{SrTiO}_3$ ) and Matthias ( $\text{CdTiO}_3$ ) to  $80^\circ\text{K}$  gave negative values of  $\theta$ , while further measurements by Hulm on  $\text{SrTiO}_3$  showed that this substance is not ferroelectric above  $1.3^\circ\text{K}$ .

The absence of spontaneous polarization from the above mentioned titanates evidently indicates that the  $\text{Ti-O}_6$  octahedra are much more sensitive to a change of lattice constant or structure than are other similar octahedra, such as  $\text{Nb-O}_6$  and  $\text{Ta-O}_6$ , which give ferroelectric behavior in a number of different compounds and structures.<sup>1,3</sup>

\* On leave of absence from Bell Telephone Laboratories, Murray Hill, New Jersey.

<sup>1</sup> B. T. Matthias, Phys. Rev. **75**, 1771 (1949).

<sup>2</sup> G. A. Smolenskii, Doklady Akad. Nauk S.S.S.R. **70**, 405 (1950).

<sup>3</sup> B. T. Matthias and J. P. Remeika, Phys. Rev. **76**, 1886 (1949).

## A New Long-Lived Krypton Activity

JOHN H. REYNOLDS

Argonne National Laboratory, Chicago, Illinois

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IN the course of a study of branching in the neutron induced activities of bromine,<sup>1</sup> I had cause to examine the isotopic constitution of the krypton distilled from a sample of sodium bromide which had been subjected to prolonged and intense neutron radiation. From this krypton all other elements except argon and xenon had been removed chemically and a slight amount of pure atmospheric krypton had been added for purposes of standardization. The gas was found to consist principally of the isotopes  $\text{Kr}^{80}$  and  $\text{Kr}^{82}$  from the reactions  $\text{Br}^{79} + n \rightarrow \text{Br}^{80} \rightarrow \text{Kr}^{80}$

and  $\text{Br}^{81} + n \rightarrow \text{Br}^{82} \rightarrow \text{Kr}^{82}$ . In addition, a small ion peak was observed at mass 81 which, after the usual tests common to mass spectrometric technique, proved to be due to  $\text{Kr}^{81}$  and not due to an impurity element or to a rare krypton compound ion such as  $\text{KrH}^+$ . The formation of  $\text{Kr}^{81}$  is attributed to the second-order reaction  $\text{Kr}^{80} + n \rightarrow \text{Kr}^{81}$ . The value of the percentage abundance of  $\text{Kr}^{81}$  at the time of measurement was sufficient in itself to place a lower limit on the half-life of this nuclide of 30 days, using a value of 200 barns for the maximum neutron absorption cross section of  $\text{Kr}^{80}$ . 200 barns safely exceeds a preliminary value for this cross section due to Thode.<sup>2</sup>

An aliquot of this gas was introduced to the interior of an argon-ethanol filled Geiger tube. By manipulating a Toepler pump and reading a manometer, it was possible to study the counting rate as a function of the total gas pressure in the counter tube. This quantity, corrected for background, gave a linear plot which intersected the origin when extrapolated to zero pressure, showing clearly the presence of a radioactive gas in the counting system.

A larger sample of the gas was then used to fill a Pyrex cell, equipped with a 1.8 mg mica window, which could be installed within the shield of a conventional end window counting arrangement. An aluminum absorption curve of the radiations from the cell, taken with an argon-ethanol filled mica window counter, showed the presence of soft beta-particles. Although the beta-particle counting rate corrected for geometry amounted to only six percent of the total radiation as counted internally, the effect was large enough to mask the absorption characteristics of soft  $\gamma$ -rays in the insensitive end window arrangement.

It seemed probable that this beta-particle component was due to long-lived  $\text{A}^{89}$  formed by second-order neutron absorption on  $\text{Cl}^{37}$  impurity in the  $\text{NaBr}$ . In accordance with this hypothesis, the gas sample was treated by diluting it heavily with pure argon and pumping it briefly from a charcoal trap at dry ice temperature. Prior pumping tests with artificially prepared argon-krypton mixtures showed that under these conditions 99.8 percent of the argon is removed, while only 60 percent of the krypton (and negligible xenon) is lost. The Pyrex cell was refilled with the purified krypton and used to obtain the aluminum absorption curve shown in Fig. 1. A xenon-ethanol filled end window counter

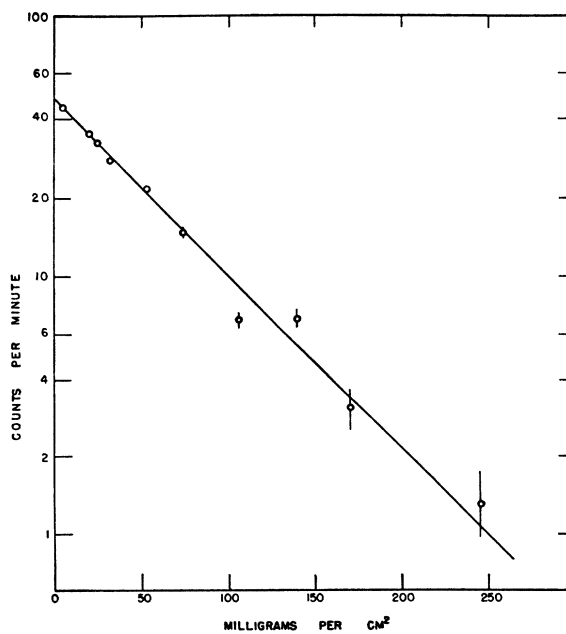


FIG. 1. Absorption in aluminum of radiations from purified krypton distilled from neutron-irradiated  $\text{NaBr}$ .