

Variations in the Isotopic Abundances of Neon and Argon Extracted from Radioactive Minerals*

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(Received May 21, 1954)

Large excesses of Ne^{21} , Ne^{22} , and Ar^{38} have been found in uranium and thorium minerals. These abnormal abundances are ascribed to (α, n) and (α, p) reactions in the minerals. It is shown that it is possible that a part of the atmospheric Ne^{21} originated in this way.

I. INTRODUCTION

THE most careful determination of the isotopic abundances of neon and argon was made by Nier.¹ However, his investigation, as well as the earlier ones, was restricted to the analysis of atmospheric neon and argon. In the course of some experiments on spontaneous fission of uranium and thorium,² the neon and the argon from the radioactive minerals pitchblende, euxenite, and monazite were analyzed in a mass spectrometer in order to see if any variations in their isotopic abundances could be found. Gross variations were found which are presumably a consequence of nuclear reactions induced by the natural radioactivity of these minerals. During the course of this work similar variations in the abundance of argon were reported by Fleming and Thode.³

II. EXPERIMENTAL METHODS

The gases occluded within the minerals were released by fusing the mineral with NaOH in vacuum and chemically reactive gases removed by use of the apparatus shown in Fig. 1 as described in a previous paper.² After most of the chemically reactive gases were cleaned up, the helium and the small quantities of neon present were separated from the rest of the inert gases by absorbing the heavier gases on activated charcoal held at -195°C and pumping the helium and neon into the gas separator (Fig. 2) with the Toepler pump. After some further purification the xenon, krypton, and argon were again absorbed on charcoal and sealed off. The gas separator was used to separate neon from helium. It is essentially the same as the gas separator constructed and used by Arrol, Chackett, and Epstein.⁴ Their separator was patterned after one designed by Glückauf⁵ which is used in Paneth's laboratory at Durham. A

similar apparatus was used by Aston⁶ in an attempt to separate the isotopes of neon. The operation of the apparatus has been described by Glückauf.⁵ The separation is effected by the fractional adsorption of neon and helium on activated charcoal. The apparatus consists of a series of four 100-cc Toepler pumps with a dead space between each of them consisting of a U-tube containing 2.5 g of activated charcoal. Fractionation is achieved because this dead space has a larger effective volume for neon than it has for helium causing the efficiency of the pump to be greater for helium.

By use of this apparatus the heavy fraction was depleted in helium by a factor of several thousand with a loss of neon of about 15 percent. The neon is then treated in the final purifier, adsorbed on the neon sample charcoal C_4 , and sealed off.

The gas samples were analyzed in the mass spectrometer described previously.²

The sample tubes containing the gases adsorbed on charcoal were sealed onto the sample system of the mass spectrometer and the gas introduced by the use of conventional glass breakoffs. The argon sample tubes containing about 0.5 g of charcoal were held at -100°C with ethyl alcohol cooled with liquid nitrogen. At this temperature most of the argon was desorbed. The neon sample tubes contained about 10 g of charcoal. The neon was first observed with the charcoals at liquid nitrogen temperature and then another set of data was taken at -100°C , at which temperature all the neon was desorbed.

The gas flowed into the mass spectrometer through an orifice of about 0.001-in. diameter. Since molecular flow was maintained at all times, the measured isotope ratios represented the isotopic composition of the gas in the reservoir behind the orifice. In some cases it was necessary to correct for the change in isotopic composition of the gas in this reservoir with time, since the lighter isotopes flow through the leak more rapidly than the heavier ones, causing the gas remaining in the reservoir behind the leak to become enriched in the heavier isotopes. The mass spectrometer used was equipped with an electron multiplier, and, since the sensitivity of the electron multiplier varied slightly with mass, it was necessary to apply a correction of about two per-

* This work was supported in part by a grant from the National Science Foundation.

† This work was done while the author held a U. S. Atomic Energy Commission predoctoral fellowship at the University of Chicago.

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¹ A. O. Nier, *Phys. Rev.* **79**, 450 (1950).

² George W. Wetherill, *Phys. Rev.* **92**, 907 (1953).

³ W. H. Fleming and H. G. Thode, *Phys. Rev.* **90**, 857 (1953).

⁴ Arrol, Chackett, and Epstein, National Research Council of Canada, declassified document CRC-297.

⁵ E. Glückauf, *Proc. Roy. Soc. (London)* **A185**, 98 (1946).

⁶ F. W. Aston, *Mass Spectra and Isotopes* (Longmans, Green and Company, New York, 1941), p. 33.

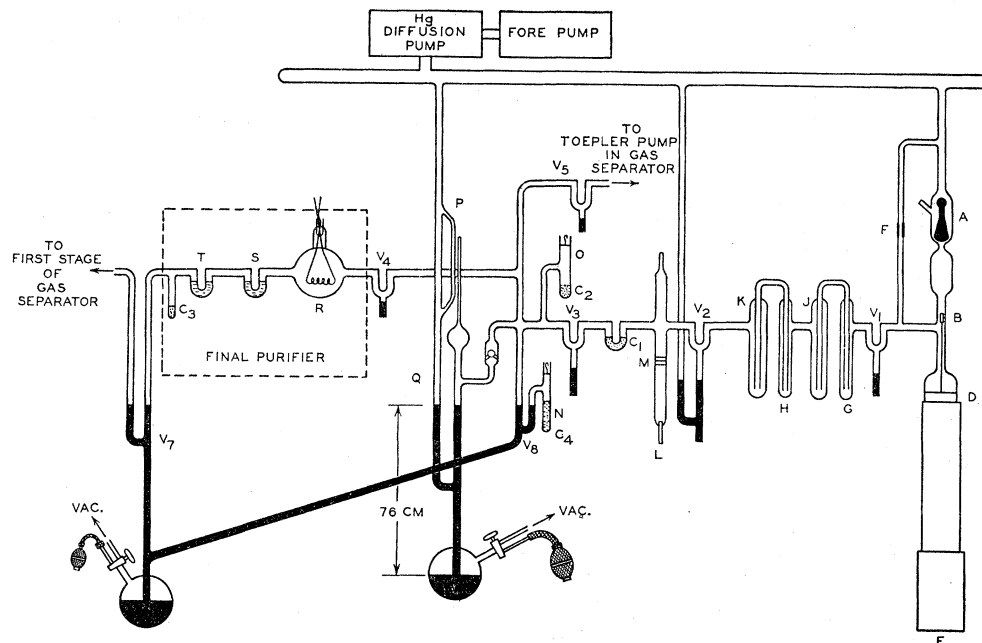


FIG. 1. Apparatus for the extraction of inert gases from minerals. A. Magnetic valve; B. Stirring rod; C₁. Tube containing .5 g of activated charcoal; C₂. Tube containing .5 g of activated charcoal; C₃. Tube containing .5 g of activated charcoal; C₄. Tube containing 10 g of activated charcoal; D. Nickel furnace; E. Electric heater winding; F. Constriction for sealing off; G. Magnesium perchlorate trap; H. Potassium hydroxide trap; L. Calcium vapor furnace; M. Quartz-pyrex graded seal; N. Neon sample tube; O. Argon, krypton, xenon sample tube; P. McCleod gauge; Q. McCleod exhaust; R. Tungsten bulb; S. Copper oxide trap; T. Magnesium perchlorate trap.

cent per mass unit. The discrimination was determined by measuring samples of normal gas and comparing the results with the accepted values of the isotope ratios as given by Bainbridge and Nier.⁷

III. EXPERIMENTAL RESULTS AND DISCUSSION

1. Variations in the Isotopic Abundances of Neon

Mass spectrometric determinations were made of neon extracted from pitchblende, euxenite, and monazite. The isotope ratios as well as estimates of the abso-

lute quantity of the gas contained in the mineral are given in Table I. It is believed that the gas observed here is neon rather than some impurity for the following reasons:

- (1) The electron-accelerating potential in the ion source was adjusted to a value so low that doubly charged interfering ions such as A^{40++} and CO_2^{++} could not be present.
- (2) It was possible to resolve completely the interfering H_2O^{18} peak from the neon peak at mass 20.
- (3) At no time, even when the background of the mass spectrometer was so high that the instrument could not be used to analyze the krypton and xenon samples, was a background peak of any kind observed at mass 21.
- (4) Separate aliquots of the neon were taken from activated charcoal at temperatures of $-195^\circ C$ and $-100^\circ C$; the ratios were the same in both cases.
- (5) During the course of the measurements the pressure in the ion source dropped by a factor of at least four. The isotope ratios did not change.
- (6) The pressure in the source decayed with time as the gas in the reservoir was depleted in every case with the decay constant characteristic of neon.

It should be noted that the Ne^{21} is always anomalously high; in the extreme case of the euxenite the

TABLE I. Isotope ratios and absolute quantities of neon from radioactive minerals.

Sample	Size of sample	Age $\times 10^{-6}$ yr	Per-cent uranium	Per-cent thorium	Isotope ratios		Excess Ne^{21} cc STP/g ^b
					21/20 ^a	22/20 ^a	
Atmospheric ^c					0.00283	0.0970	
Belgian Congo Pitchblende	20.0 g	650 ^d 215 ^e	44.	0	0.00519 ± 0.00017	0.103 ± 0.005	1.36×10^{-7}
Brazilian Monazite	13.8 g	460 ^f	0.2	6	0.402 ± 0.024	0.0954 ± 0.011	8.7×10^{-9}
Madagascar Euxenite	109.6 g	60 ^g ~ 600 ^f	6.0	3.5	1.05 ± 0.09	4.72 ± 0.32	8.0×10^{-9}

^a The errors shown represent the mean deviations of the peak heights.

^b Mass spectrometer calibrated with krypton tracer.

^c See reference 7.

^d Alfred O. Nier, Phys. Rev. 55, 153 (1939).

^e Helium age, as calculated from the quantity of helium obtained from the mineral and the uranium content.

^f Uranium-lead ages. These ages were measured in this laboratory.

^g K. T. Bainbridge and A. O. Nier, Preliminary Report No. 9, Nuclear Science Series, National Research Council (unpublished).

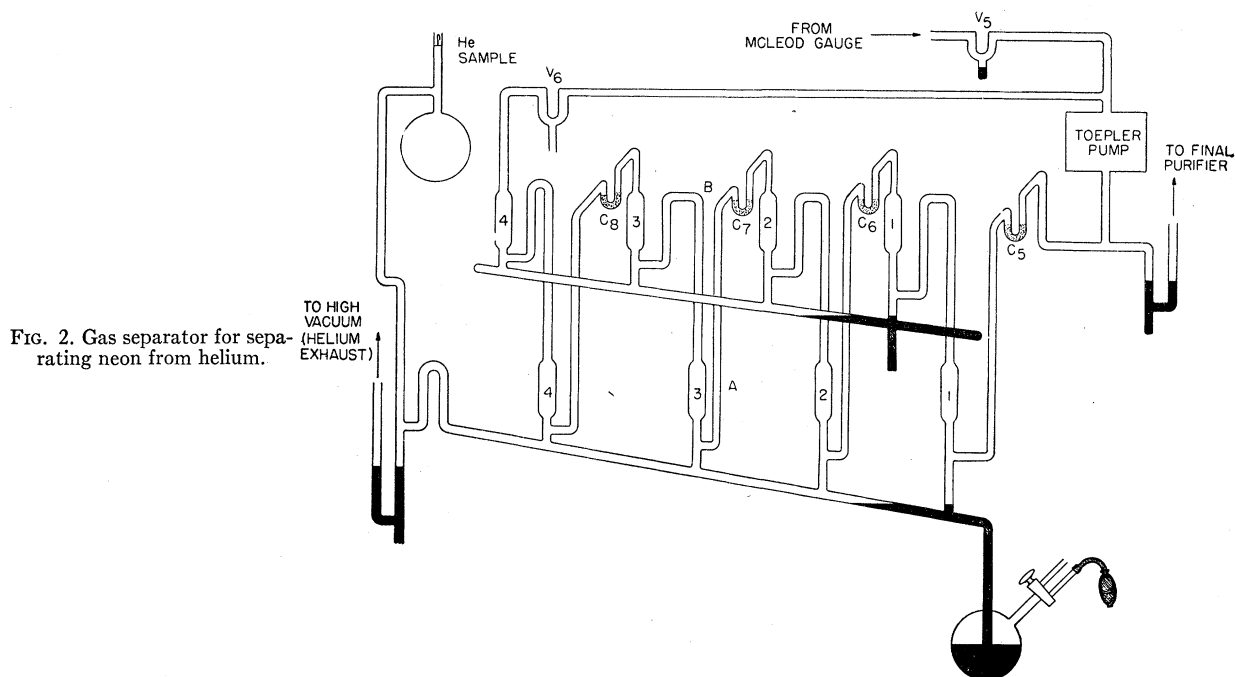


Fig. 2. Gas separator for separating neon from helium.

$\text{Ne}^{21}/\text{Ne}^{20}$ ratio is 370 times normal. Any impurity at mass 20 or 22 would cause an effect in the opposite direction. The $\text{Ne}^{22}/\text{Ne}^{20}$ ratios are approximately normal in the pitchblende and the monazite, but in the euxenite the Ne^{22} abundance is about 50 times the normal abundance. It is possible that the errors in the $\text{Ne}^{22}/\text{Ne}^{20}$ ratios for the pitchblende and the monazite mask small variations which would be revealed by a more careful investigation. The relatively small change in the $\text{Ne}^{21}/\text{Ne}^{20}$ ratio in the pitchblende was caused by the presence of a large quantity of normal neon in the sample, as it may be seen that the absolute excess of Ne^{21} is greater in the pitchblende than it is in either of the other two samples. This normal neon probably had its origin in "memory" in the mass spectrometer. Shortly before the pitchblende sample was analyzed a large sample of normal neon was run; apparently a sufficient quantity remained in the instrument to interfere with the pitchblende analysis.

The values for the excess Ne^{21} can be relied on as a measure of the quantity of the gas in the sample to within a factor of two. The relative values are reliable within twenty percent.

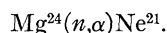
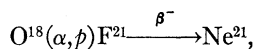
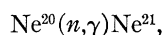
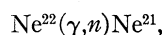
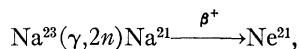
The variations in isotopic abundance found here are much greater than those which could be produced by any natural chemical isotopic fractionation or by fractional diffusion of isotopes. These variations must be attributed to a natural nuclear process. It appears that the most likely process for producing this excess Ne^{21} is the nuclear reaction $\text{O}^{18}(\alpha, n)\text{Ne}^{21}$. All three minerals contain oxygen as a major constituent and the

(α, n) reaction on oxygen is well-known.⁸ The yield of this reaction on O^{16} is zero, since for this isotope the Q for the reaction is -12.2 Mev. The yield from O^{17} may be expected to be less than that from O^{18} , since this isotope is less abundant and the Q values are similar ($+0.6$ and -0.7 , respectively); it is difficult in this experiment to see the effect of the reaction with O^{17} because of the relatively large amount of normal Ne^{20} present.

A calculation of the quantity of Ne^{21} which would be produced in the pitchblende by this reaction by the polonium α -particles, if we use the yield for oxygen given by Roberts, indicates that about 9×10^{-8} cc/g would be produced if the target could be considered to be pure oxygen, all the reaction to be with the isotope O^{18} , and the age of the mineral taken to be the helium age. The helium age is used rather than the lead age because it probably includes a better measure of the ability of the mineral to retain inert gases. The fact that the mineral was not pure oxygen will reduce the amount of Ne^{21} which might be expected by a factor of about three, while the fact that there are seven other α particles emitted from uranium will increase this estimate by a factor of about eight. The differing energies of the natural α particles will not affect the order of magnitude of this estimate. Thus the expected amount is in approximate agreement with the actual quantity 1.4×10^{-7} cc/g which was found.

⁸ J. H. Roberts, U. S. Atomic Energy Commission Report MDDC-731, 1947 (unpublished). A summary of the studies which have been made of (α, n) reactions was made by H. L. Anderson, Preliminary Report No. 3, Nuclear Science Series, National Research Council (unpublished).

Other possible reactions which might produce an excess of Ne^{21} are



The photoreactions may be excluded since the only gammas present which might be sufficiently energetic are the neutron capture gamma rays which are only about 10^{-6} times as abundant as the α particles, since the α -particle production rate is about 10^7 times the neutron production rate² and there are only a few gammas per capture. The high probability of absorption of these gammas by other processes, particularly by electron pair formation, plus the high threshold for these reactions eliminates competition by photoreactions. The relatively small ($4 \times 10^{-25} \text{ cm}^2$) cross section for neutron capture in Ne^{20} precludes the formation of approximately equal amounts of Ne^{21} by neutron capture in this isotope. The high threshold (4.66 Mev) for the (α, p) reaction plus the fact that the emitted proton will have to traverse the Coulomb barrier of the nucleus makes this reaction seem less likely than the (α, n) reaction. The (n, α) reaction on magnesium to produce Ne^{21} has a threshold of about 2 Mev. Also, because of the Coulomb barrier of about 6 Mev, the emission of low-energy α -particles is improbable. Therefore even higher neutron energies are required. If all the neutrons formed in the mineral reacted in this way with magnesium, about ten times as much Ne^{21} would be produced by this process as by the $\text{O}^{18}(\alpha, n)$ mechanism. However, because of the fact that magnesium is usually present in these minerals only to a few tenths of a percent and because of the small number of neutrons with sufficient energy, it should be expected that this magnesium reaction is much less likely.

It is interesting to calculate the amount of Ne^{21} which may be formed by this (α, n) reaction in ordinary rocks. The monazite contained about six percent thorium, while the average uranium and thorium concentrations of igneous rocks are about four and twelve parts per million respectively.⁹

Thus the α activity of these average rocks is about 1/2500 of that in the monazite. If it is assumed that the abundance of normal neon in these rocks is the same as in monazite, then in these rocks the ratio of excess Ne^{21} to normal Ne^{20} will be 1.6×10^{-4} . Thus the Ne^{21} produced by nuclear reactions contributes about 6 percent of the Ne^{21} in ordinary rocks if their ages are the same as that of the monazite. However, the age of the earth

is about ten times the age of the monazite, and during the early history of the earth, the abundance of uranium was greater and the α activity due to U^{235} was about equal to that of U^{238} . Thus it may be seen that a large fraction of the Ne^{21} in rocks was probably formed in this way. Now if the neon in the earth's atmosphere were obtained by out-gassing of the crust at some time later than the very early stages of the earth's history, it might be expected that an appreciable fraction of the atmospheric Ne^{21} was formed by this natural nuclear reaction. The rate of production of Ne^{21} in rocks can be estimated from the data presented in this paper to be of the order of $10^{-20} \text{ cc STP/g yr}$. Taking the abundance of potassium in igneous rocks as 2.6 percent¹⁰ the rate of production of A^{40} from the disintegration of K^{40} can be estimated to be $9 \times 10^{-14} \text{ cc STP/g yr}$. Thus the present ratio of the rate of production of A^{40} to the rate of production of Ne^{21} is about 10^7 . Four thousand million years ago this ratio was about twice this, because of the difference between the decay constants of K^{40} and the isotopes of uranium.

This figure may be compared with the ratio of A^{40} to Ne^{21} in the atmosphere, 2.0×10^5 , as calculated from the data of Paneth.¹¹ Therefore, if the atmosphere was formed by out-gassing of the crust and if argon and neon were out-gassed to the same extent, this calculation indicates that between 1 and 2 percent of the Ne^{21} in the atmosphere today originated from this nuclear reaction. In this calculation it is assumed that the ratio of potassium to uranium plus thorium throughout the region of the crust which is out-gassed is the same as the average calculated for igneous rocks relatively near the surface. If deep rocks contribute significantly this assumption may not be valid. Furthermore, it is possible that the uranium and thorium minerals in these rocks, e.g., zircon, may lose gas more readily owing to damage of the crystal structure by alpha-particles. If for these reasons the contribution of excess Ne^{21} to the atmosphere is greater it may be noted that this effect will affect estimates of the cosmic abundances of neon based on interpolating the odd isotope abundance curve at mass 21 and then multiplying by the observed atmospheric isotopic abundances.¹²

The excess Ne^{22} found in the euxenite can probably be attributed to the similar reaction $\text{F}^{19}(\alpha, n)\text{Na}^{22}$. The high yield for this reaction reported by Roberts⁸ indicates that the extra Ne^{22} could be produced by only a few tenths percent of fluorine provided it were located within a few microns of the alpha source. However, it is not known whether fluorine can be expected to be this favorably located. For this reason it would be very difficult to calculate whether or not it is reasonable to expect this much Ne^{22} to be produced by this process. The evidence is not sufficiently strong to exclude the

¹⁰ See reference 9, p. 423.

¹¹ F. A. Paneth, *Quart. J. Roy. Meteorol. Soc.* **65**, 303 (1939).

¹² Harrison Brown, *Revs. Modern Phys.* **21**, 625 (1949).

⁹ K. Rankama and T. G. Sahama, *Geochemistry* (University of Chicago Press, Chicago, 1950), pp. 570, 632.

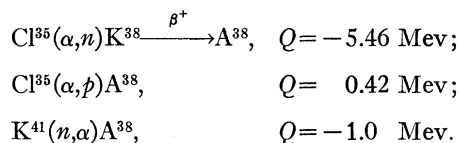
reactions $F^{19}(\alpha, p)Ne^{22}$ and $Mg^{25}(n, \alpha)Ne^{22}$ although it is believed that these reactions are less likely.

2. Variations in the Isotopic Abundances of Argon

Mass spectrometric determinations were made of argon extracted from pitchblende, Ceylon monazite, and euxenite. The results of these measurements are shown in Table II.

The constancy of the ratios when aliquots of the gas are taken from charcoal at different temperatures and when the pressure in the source changes because of the depletion of the reservoir together with the fact that the known impurity peaks did not change when the pressure of the gas in the reservoir was increased by decreasing its volume indicates that the ratios observed were not seriously affected by background impurities.

In every case the abundance of A^{36} is below normal; this is probably caused by the decay of small amounts of potassium present in the mineral. The anomalously low A^{36}/A^{38} ratio found in pitchblende, and to a much smaller extent in the other minerals, is in agreement with the measurements of Fleming and Thode.³ The situation here is quite similar to the excess Ne^{22} in euxenite. The reactions which should be considered are



The Q values were calculated from reaction energies given by Roberts,⁸ and atomic masses were given by Collins, Nier, and Johnson.¹³

Again the first two reactions require the presence of significant quantities of chlorine within range of the α -particles. The yield of the (α, n) reaction is low, primarily because of the high threshold for the reaction; most of the alphas will have energies below the threshold. For those with energies just above the threshold

TABLE II. Data on argon extracted from radioactive minerals.

Sample	Wt. of sample	Age $\times 10^{-6}$ yr	Per-cent uranium	Per-cent thorium	Isotope ratios		Excess A^{38} cc STP/g ^b
					36/40 ^a	36/38 ^a	
Atmospheric ^c					0.00338	5.35	
Belgian Congo Pitchblende	20.0 g	650 ^d	44	0	0.00233 ± 0.0005	1.61 ± 0.04	2 $\times 10^{-8}$
Ceylon Monazite	53.2 g	535 ^f	0.3	7.8	0.00266 ± 0.0005	4.71 ± 0.20	6 $\times 10^{-10}$
Madagascar Euxenite	109.6 g $\sim 600^f$	60 ^e	6	3.5	0.00321 ± 0.0005	4.72 ± 0.15	9.5 $\times 10^{-11}$

^a The errors shown represent the mean deviations of the peak heights.

^b Mass spectrometer calibrated with krypton tracer.

^c See reference 7.

^d Alfred O. Nier, Phys. Rev. **55**, 153 (1939).

^e Helium age as calculated from the quantity of helium obtained from the mineral and the uranium content.

^f Uranium-lead ages. These ages were measured in this laboratory.

the cross section will be small. The (n, α) reaction on potassium seems unlikely because of the nine-Mev barrier that the α -particle must penetrate in order to leave the nucleus. However, this reaction has the advantage that the potassium need not be intimately associated with the uranium or thorium. From the amount of radiogenic A^{40} present, the potassium concentration is in the range of a few-tenths percent or less. This fact also makes this reaction unlikely. Thus, though the evidence is not definite, the (α, p) reaction on chlorine seems the most likely possibility.

IV. ACKNOWLEDGMENTS

The writer wishes to express appreciation to C. Patterson for instruction in the chemical techniques used in the lead analyses and for the use of some purified reagents, to G. Tilton for several uranium analyses, to D. F. Peppard and J. P. Marble who supplied mineral samples, to O. Joensuu for emission spectrometric lead analyses, and to R. J. Hayden who was responsible for the construction of the mass spectrometer used in this investigation and who prepared the krypton tracers which were used.

Especial thanks must be given to M. G. Inghram whose counsel and encouragement guided this work from its inception to its completion.

¹³ Collins, Nier, and Johnson, Phys. Rev. **84**, 717 (1951).