

FIG. 1. Deuteron signal from HD.

The method of observation consisted of the application of an intense 15- μ sec rf pulse at the resonant frequency to a tuned coil containing the sample in the static magnetic field. The intensity and duration of the pulse were such as to cause the net nuclear magnetic moment vector to nutate 90°. This enabled the observation of maximum signal amplitude due to the free ringing or precession of the moment vector when the $15-\mu$ sec pulse was removed.⁵ The homogeneity of the static field was good enough to allow the observation of the nuclear free-ringing signal or "tail" with its modulation pattern⁶ for 100,000 μ sec. The ultimate limitation on the observation of the fine structure modulation in the nuclear signal was the relaxation time.

The modulation pattern on the "tail" in the D resonance in HD at 4.4 Mc/sec is shown in Fig. 1. It is a simple beat pattern of two signals of equal amplitude. The two spin groups correspond to the two possible orientations of the neighboring H magnetic moment. Figure 2 shows the pattern observed in the H resonance at the same frequency. This is the slightly more complicated but typical beat pattern of three signals of equal frequency separation and amplitude. The three groups in this case correspond to the three possible orientations of the neighboring D magnetic moment. In addition to the fine structure modulation, both tails decay due to the normal relaxation processes.

The most accurate value for the separation δ , 43.5 ± 1 cps, was obtained from the fifth minimum on a picture of the H resonance at 4.4 Mc/sec. The ± 1 cps is the estimated maximum limit of error. The limits in the D resonance at 4.4 Mc/sec and the H resonance at 30.0 Mc/sec were somewhat greater. To within the latter limits, all separations observed in the D resonances and the H resonances agreed with the value quoted above.

The samples used consisted of substantially pure HD gas sealed in a glass bulb of 0.1 cc volume, in amount such that the pressure at room temperature would be about 300 atmospheres. The samples were prepared by admitting a known volume of the



FIG. 2. Proton signal from HD.

gas at known pressure and temperature through 25 cm of capillary to the bulb where the gas was frozen by immersing in liquid helium. While the bulb was still immersed and the gas still frozen, the upper end of the capillary was sealed off. The observations were then made at liquid nitrogen temperature.

We are greatly indebted to Mr. David G. White of the Department of Chemistry for the preparation of the gas which was subsequently sealed off. The method of preparation involved the reaction of D₂O with lithium aluminum hydride in a manner similar to that described by Fookson, Pomerantz, and Rich.⁷ In the present work the final fractionation process was omitted. Two of their samples prepared by the same method as the present samples were analyzed mass spectrographically before fractionation and were found to contain 98.1 percent and 97.0 percent hydrogen deuteride, respectively.

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The Theory of Secondary Emission*

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S EVERAL authors^{1,2} have treated the problem of the inter-action between energetic primary electrons and the weaklybound lattice electrons of a solid. However, owing to considerations involving the orthogonality of Bloch wave functions, certain conclusions based upon these theories are incorrect.

The differential cross section for the process in which a primary electron undergoes a transition from a state K to a state K', within a solid angle $d\Omega'$, is given by

$$d\sigma(\mathbf{K} \rightarrow \mathbf{K}') = \Sigma_{\mathbf{g}} d\sigma_{\mathbf{g}}, \tag{1}$$

where

$$d\sigma_{\mathbf{q}} = [4m^{2}e^{4}K'/\hbar^{4}S^{4}K] \times |\Sigma_{\mathbf{m}}a_{\mathbf{m}+\mathbf{q}}(\mathbf{k})a_{\mathbf{m}}^{*}(\mathbf{k}')|^{2}d\Omega'. \quad (2)$$

Here, S = K - K', m and q are vectors with integer components, and **k** and **k'** are wave vectors corresponding to initial and final states of the lattice electron. The a_m are the coefficients in the Fourier expansion of the eigenfunctions for a cubic lattice of lattice constant a.

These have the form

$$\Psi_{\mathbf{k}}(\mathbf{r}) = V^{-\frac{1}{2}} \exp[i\mathbf{k}\cdot\mathbf{r}]\Sigma_{\mathbf{m}}a_{\mathbf{m}}(\mathbf{k}) \exp[i(2\pi/a)\mathbf{m}\cdot\mathbf{r}].$$
(3)

It is found that for each q the following conservation relation holds:

$$\mathbf{S} + \mathbf{k} - \mathbf{k}' + 2\pi \mathbf{q}/a = 0. \tag{4}$$

For given K, K', k, and q, k' is uniquely specified by Eq. (4), and the summation indicated in Eq. (1) is equivalent to an integration over final states \mathbf{k}' .

Because of the presence of S^4 in the denominator of Eq. (2) $d\sigma_q$ is appreciable only when **K**' has values for which S is near its minimum Smin. For primary energies above several hundred ev, S_{\min} is considerably smaller than any of the other terms in Eq. (4), and, in the region of interest, \mathbf{k}' is given approximately by

$$\mathbf{k}' \approx \mathbf{k} + 2\pi \mathbf{q}/a. \tag{5}$$

It is consequently assumed for purposes of integration over Ω' that $a_{\mathbf{m}}(\mathbf{k}')$ can be replaced by $a_{\mathbf{m}}(\mathbf{k}+2\pi\mathbf{q}/a)$. This approximation leads to the total cross section of the Wooldridge theory:

$$\sigma_{\mathbf{q}} = \frac{16\pi m^2 \epsilon^4}{\hbar^4} \frac{|\Sigma_{\mathbf{m}} a_{\mathbf{m}+\mathbf{q}}(\mathbf{k}) a_{\mathbf{m}}^*(\mathbf{k} + 2\pi \mathbf{q}/a)|^2}{\left[(2\pi \mathbf{q}/a) \cdot (2\pi \mathbf{q}/a + 2\mathbf{k})\right]^2}.$$
 (6)

However, expressions for secondary yields and energy losses based upon this cross section actually vanish since, in this approximation, σ_q is zero, a fact not recognized in previous theories. This is an immediate consequence of the orthogonality relation between the lattice eigenfunctions belonging to **k** and $\mathbf{k}+2\pi\mathbf{q}/a$,

$$\int \psi_{\mathbf{k}} \psi_{\mathbf{k}+2\pi \mathbf{q}/a}^{*} d\tau = 0. \tag{7}$$

Substitution of Eq. (3) into Eq. (7) yields

 $\frac{1}{V} \sum_{\mathbf{m}, \mathbf{n}} a_{\mathbf{n}}(\mathbf{k}) a_{\mathbf{m}}^{*}(\mathbf{k} + 2\pi \mathbf{q}/a) \int \exp[(2\pi i/a)(\mathbf{n} - \mathbf{q} - \mathbf{m}) \cdot \mathbf{r}] d\tau$ (1-) * (1- 1-0 - - (-) - 0

$$= \Sigma_{\mathbf{m}} a_{\mathbf{m}+\mathbf{q}}(\mathbf{k}) a_{\mathbf{m}} (\mathbf{k}+2\pi \mathbf{q}/a) = 0.$$
 (8)

Substitution of Eq. (8) into Eq. (6) yields a zero cross section. In order to obtain a finite result, it is necessary to take into account the variation of $a_{\mathbf{m}}(\mathbf{k}')$ with **K'**. This can be accomplished by a Taylor series expansion of $a_{\rm m}({\bf k}')$ about the point ${\bf k}' = {\bf k} + 2\pi {\bf q}/a$. This results in a cross section which for sufficiently high energies has the same form as that obtained by Bethe³ for the ionization of atoms, namely,

$$\sigma_{\mathbf{q}} = (A/E) \ln(E/E'), \qquad (9)$$

where E is the energy of the primary electron and A and E' are parameters characteristic of the medium. A similar expression is obtained for the rate of energy loss by electrons passing through solids. These results are entirely different from those obtained on the basis of Eq. (4), which have previously been interpreted^{1,2} to mean that both the rate of production of secondaries and the rate of energy loss should be practically independent of the energy of the primary. Actually, these quantities are zero in the approximation leading to Eq. (4), and as indicated by Eq. (9) and the equivalent expression for the energy loss, they decrease rapidly with energy.

It should be pointed out that the above considerations do not apply to the case of free electrons (q=0), which has been treated by Baroody⁴ and by Dekker and van der Ziel², since values of S in the neighborhood of S_{\min} are forbidden because they correspond to transitions to occupied states.

The questions outlined here will be treated in more detail in a forthcoming paper.

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Alpha-Particle Ionization in Mixtures of the Noble Gases

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URING the course of experiments to determine for polonium alpha-particles the absolute value of W, the average energy required to produce an ion pair in various gases, erratic results soon showed that the effect of minute gaseous impurities in such measurements is much greater than is commonly recognized. Accordingly, experiments have been carried out where a contaminant in measured quantities could be added to the gas under investigation and the effect of the impurity on the total ionization observed. Preliminary experiments on helium and neon have shown rather striking results.

In the measurements a short collimating system directed the polonium alpha-particles along the axis of a long cylindrical ionization chamber. The effective path length was about 20 cm. The ions produced by each alpha-particle were collected and measured by 'a method already described.1 From a knowledge of the capacity of the system and the change of potential of the system produced by the ionization from each alpha-particle, the absolute number of ion pairs produced may be determined. The

FIG. 1. Ion pairs collected per alpha-particle as a function of argon concentration in helium. Runs \triangle and O represent commercial "spectroscopically pure" He. Run \times represents this He after further purification.

average energy W to produce an ion pair is, of course, the energy of the polonium alpha-particle (5.298 Mev) divided by this number.

The ionization chamber was pumped and baked for twelve hours at a temperature above 200°C at the beginning of the measurements, and extreme care was taken to minimize gaseous impurities from the system.

The graph in Fig. 1 shows the effect on the ionization produced per alpha-particle of adding extremely small quantities of argon to pure helium. The ionization per alpha-particle at first increases rapidly with increasing argon concentration and then more slowly, apparently approaching finally a saturation value. The points on the curve may be indefinitely repeated by adding argon in measured quantities and then removing it by repeated passage over coconut charcoal at liquid air temperature.

The addition of argon to pure neon gives a curve of the same type as that shown in Fig. 1, but with higher ionization values throughout. Data for helium and neon with argon as an impurity are shown in Table I.

TABLE I. Polonium alpha-ionization measurements in helium and neon.

Gas	Ion pairs per Po alpha-particle	W=average energy per ion pair, ev/ion pr
Purest helium used	128,300	41.3
Helium +0.13% argon	178,400	29.7
Purest neon	146,000	36.3
Neon +0.12% argon	203,000	26.1

It is of interest to note that, for the purest gases used here, the number of ion pairs produced per alpha-particle is much smaller, and the W correspondingly larger, than the results heretofore given in the literature. In fact, the value of W for helium commonly given in the literature, about 30 ev/ion pair, is in much closer agreement with the above value for helium saturated with argon as an impurity. This suggests the presence of impurities in previous determinations.

Experiments with a small radium source placed in a standard position with regard to the chamber show a similar increase in gamma-ray ionization as the argon concentration in helium is increased. Here the total relative current through the chamber was measured, rather than the effect of single gamma-rays.

A plausible explanation² for the increase in ionization observed, both for alpha-particles and gamma-rays, is that this increase results from a transfer of energy from the metastable states in

