

TABLE II. Disintegration energy in Mev.

Disintegration	Calculated	Observed
Na ²⁴ →Mg ²⁴	5.544 ± 0.022	5.528 ^a
Mg ²⁷ →Al ²⁷	2.610 ± 0.020	2.63 ± 0.06 ^b
Al ²⁸ →Si ²⁸	4.647 ± 0.020	4.647 ± 0.014 ^c
Si ³¹ →P ³¹	1.482 ± 0.021	1.471 ± 0.008 ^d

^a K. Siegbahn, Phys. Rev. **70**, 127 (1946).^b Beneš, Hedgran, and Hole, Arkiv Mat. Astr. Fys. **A35**, No. 12 (1948).^c See reference 5.

The (*d*, *p*) reactions of the neon isotopes were investigated, using partially separated isotopic targets deposited on silver sheets. (We are indebted to the Nobel Institute in Stockholm for the preparation of the neon targets.) Attempts to observe the (*d*, *α*) reactions of the neon isotopes proved unsuccessful because of the evaporation of neon from the targets when exposed to beam bombardment. In the case of the magnesium isotopes Mg²⁵ and Mg²⁶, targets were prepared by allowing a suspension of enriched magnesium dioxide to deposit upon platinum backings. Comparison of the data obtained from these targets with those obtained from a target of natural magnesium permitted the positive identification of the particle groups corresponding to the Mg²⁵ and Mg²⁶ isotopes. A similar analysis was used for the isotopes Si²⁹ and Si³⁰. In this case, the targets were prepared by evaporation of enriched silicon dioxide onto platinum backings. (The enriched samples of magnesium dioxide and silicon dioxide were obtained from the Stable Isotopes Division, AEC, Oak Ridge.) The phosphorus targets consisted of copper phosphate and zinc phosphide evaporated onto platinum backings.

In general, the *Q*-values reported in Table I are the result of averaging several measurements. However, in the case of the Ne²²(*d*, *p*), Na²³(*p*, *α*), Al²⁷(*p*, *α*), and P³¹(*p*, *α*) reactions, the value given is based on a single observation. Fortunately, there is sufficient evidence from other sources to indicate that these four measurements may be relied upon.

It is possible to examine the internal consistency of our results using the following closed cycles:

Al ²⁷ (<i>d</i> , <i>α</i>)Mg ²⁵	6.694 ± 0.010 ¹
Mg ²⁴ (<i>d</i> , <i>p</i>)Mg ²⁵	5.097 ± 0.007
Al ²⁷ (<i>p</i> , <i>α</i>)Mg ²⁴	1.597 ± 0.009 (calc)
Al ²⁷ (<i>p</i> , <i>α</i>)Mg ²⁴	1.595 ± 0.007 (obs)
Na ²³ (<i>d</i> , <i>α</i>)Ne ²¹	6.902 ± 0.010 ¹
Ne ²⁰ (<i>d</i> , <i>p</i>)Ne ²¹	4.529 ± 0.007
Na ²³ (<i>p</i> , <i>α</i>)Ne ²⁰	2.372 ± 0.011 (calc)
Na ²³ (<i>p</i> , <i>α</i>)Ne ²⁰	2.372 ± 0.008 (obs)
P ³¹ (<i>d</i> , <i>α</i>)Si ²⁹	8.158 ± 0.011
Si ²⁸ (<i>d</i> , <i>p</i>)Si ²⁹	6.246 ± 0.009 ¹
P ³¹ (<i>p</i> , <i>α</i>)Si ²⁸	1.912 ± 0.011 (calc)
P ³¹ (<i>p</i> , <i>α</i>)Si ²⁸	1.909 ± 0.010 (obs)

The P³¹(*d*, *α*)Si²⁹ *Q*-value has been remeasured as 8.158 ± 0.011 Mev compared with the published value of 8.170 ± 0.020 Mev.¹ A confirmation of this new value can be obtained from a comparison of the *Q*-values of P³¹(*d*, *α*) and Si²⁸(*d*, *p*) groups, corresponding to excited states of Si²⁹, leading to a calculated value of 8.157 ± 0.012 Mev. In addition, the new measurement of the P³¹(*p*, *α*)Si²⁸ reaction confirms the validity of this revised value. However, the recent value of 1.85 ± 0.02 Mev for the P³¹(*p*, *α*)Si²⁸ reaction energy, measured by Freeman and Seed³ using magnetic analysis, is not in agreement with the present results.

The reaction energies measured in this laboratory now link the masses of nuclei from Ne²⁰ to P³². In addition, it is possible to calculate the disintegration energies of Na²⁴, Mg²⁷, Al²⁸, and Si³¹, by choosing the appropriate reactions.

The disintegration energies listed in Table II were calculated using values⁴ of 23.834 ± 0.007 and 1.443 ± 0.002 Mev for the mass differences (2D² - He⁴) and (2H¹ - D²). The agreement with the unpublished results of Motz and Alburger⁵ for Al²⁸ and Si³¹ is highly satisfactory.

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¹ Strait, Van Patter, Buechner, and Sperduto, Phys. Rev. **81**, 747 (1951).² B. B. Kinsey (private communication).³ J. M. Freeman and J. Seed, Proc. Phys. Soc. (London) **A64**, 314 (1951).⁴ Li, Whaling, Fowler, and Lauritsen, Phys. Rev. **83**, 512 (1951).⁵ H. T. Motz and D. E. Alburger (private communication).

Interactions between Nuclear Spins in Molecules

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H AHN and Maxwell¹ have recently reported a spin-echo experiment which indicates the existence of an interaction of the form $4J\hbar\mathbf{I}_1 \cdot \mathbf{I}_2$ between two protons in dichloroacetaldehyde, with $J/2\pi$ being 0.7 cycle per second. An interaction of this form and magnitude has been difficult to understand. The direct magnetic interaction between the two nuclear spins is not of this form but depends on the relative positions of the two nuclei in such a way that when averaged over all orientations of the molecule it equals zero. Hahn and Maxwell¹ suggest that the magnetic shielding² of the nuclear spin magnetic field may modify the spin-spin magnetic interaction in such a way as to prevent its averaging to zero so that an interaction of the desired type is produced. However, they point out that it seems difficult to reconcile the order of magnitude of *J* to be thus expected with the experimental values.

It is the purpose of this note to point out a mechanism which should give rise to an $\mathbf{I}_1 \cdot \mathbf{I}_2$ interaction of the magnitude observed. This mechanism is the magnetic interaction between each nucleus and the electron spin of its own atom together with the exchange coupling of the electron spins with each other. This mechanism can most easily be described for a ¹Σ diatomic molecule, such as HD. It corresponds to the fact that the magnetic interaction of the one nucleus with the electron of its atom will make the electron of that atom tend to lie more frequently antiparallel to the nuclear spin than parallel to it. On the other hand, the two electron spins in the singlet state must be antiparallel to each other so that the electron of the other atom will tend to lie more frequently parallel to the spin of the first nucleus. However, the electron of that atom magnetically interacts with the second nucleus. The combination of these interactions therefore provides a spin interaction between the two nuclei. In terms of perturbation theory the proposed mechanism corresponds to a second-order perturbation by the higher electronic triplet states of molecules with the perturbing interaction being the magnetic interactions of each nucleus with the electron spins. The reason that electron-spin effects enter here, whereas they are omitted in ordinary magnetic shielding² calculations, is that in the present case the magnetic fields from both nuclei vary over the molecule, whereas in the ordinary magnetic shielding case one of the perturbing fields is the externally applied one which is uniform over the molecule and hence affects both electron spins alike.

The effect of the electrons on the interaction of the nuclear spins may be calculated with the following Hamiltonian²⁻⁴ for the molecule

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_3, \quad (1)$$

where

$$\mathcal{H}_1 = \sum_k [1/2m_k][(\hbar/i)\nabla_k + (e/c)\sum_l \gamma_l \mathbf{I}_l \times \mathbf{r}_{kl}/r_{kl}^3]^2 + V + \mathcal{H}_{LS} + \mathcal{H}_{SS} + \mathcal{H}_{II} \quad (2)$$

$$\mathcal{H}_2 = 2\beta \sum_{kl} \gamma_l \{3(\mathbf{S}_k \cdot \mathbf{r}_{kl})(\mathbf{I}_l \cdot \mathbf{r}_{kl})r_{kl}^{-5} - \mathbf{I}_l \cdot \mathbf{S}_k r_{kl}^{-3}\}$$

$$\mathcal{H}_3 = (16\pi\beta/3)\sum_{kl} \gamma_l \delta(\mathbf{r}_k - \mathbf{r}_l) \mathbf{S}_k \cdot \mathbf{I}_l.$$

In the aforementioned, *l* indicates the *l*th nucleus with spin \mathbf{I}_l and

k the k 'th electron with spin S_k , V is the total electrostatic interaction, and r_{kl} is the vector $r_k - r_l$. \mathfrak{S}_{II} corresponds to the direct magnetic interaction of the two nuclei and reduces to zero when averaged over all molecular rotational states. The remaining quantities are defined in the references.²⁻⁴

With the aforementioned Hamiltonian, the energy of the system can be calculated to second order by perturbation theory. The terms which depend on the products of the spins of the two nuclei then correspond to the various spin-spin interactions. The terms arising from the bracketed quantity in \mathfrak{S}_1 are analogous to the magnetic shielding terms calculated by Ramsey² for uniform magnetic fields and are the ones considered by Hahn and Maxwell¹ and found to produce too small an effect. The terms suggested in the present paper are the second-order perturbation terms arising from \mathfrak{S}_2 and \mathfrak{S}_3 and their cross products. The effects of these terms have been calculated approximately for molecular HD with the use of Heitler-London wave functions. The frequency shift arising from second-order perturbations by \mathfrak{S}_2 was found to be $0.5 I_H \cdot I_D$ cycles per second when averaged over all molecular rotational states, which is small and of the same order of magnitude as the terms considered by Hahn.¹ The cross terms between \mathfrak{S}_2 and \mathfrak{S}_3 vanish when averaged over all molecular rotational states. However, the second-order perturbations by \mathfrak{S}_3 give a frequency shift that is relatively large and approximately equal to $70 I_H \cdot I_D$ cycles per second. It is of interest to note that this term, which is the important one, can be written approximately as $0.46 I_H \cdot I_D \Delta\nu_H \Delta\nu_D / (\Delta E / \hbar)$ where the $\Delta\nu$'s are the atomic hyperfine separations, and ΔE is the separation of the lowest singlet and lowest triplet states in molecular hydrogen.

Although a similar calculation in the case of dichloroacetaldehyde is precluded by the lack of a suitable wave function for the molecule, it is quite reasonable from the foregoing calculation that an effect as large as the observed 0.7 cycle per second should be observed since the exchange coupling of the electrons with each other in the successive bonds lying between the two hydrogens is large. In some substances much larger interactions than the aforementioned could probably be obtained if ΔE were sufficiently small.

Experiments to observe this effect in a simple molecule like HD are being planned by the authors. Although such an interaction should also occur in homonuclear molecules such as H₂, it would not be observable in transitions involving no change in molecular rotational state. The authors wish to express their appreciation to Dr. Hahn for sending them an advance copy of the manuscript of his very interesting paper.⁵

¹ E. L. Hahn and D. E. Maxwell, *Phys. Rev.* **84**, 1246 (1951).

² N. F. Ramsey, *Phys. Rev.* **78**, 699 (1950).

³ H. A. Bethe, *Handbuch der Physik* (J. Springer, Berlin, Germany, 1933), Vol. 24/1, p. 386.

⁴ A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc. (London)* **A205**, 136 (1951).

⁵ Subsequent to the submission of this letter the authors have studied the recent article of H. S. Gutowsky and C. J. Hoffman [*J. Chem. Phys.* **19**, 1259 (1951)] in which these authors find multiplet resonance lines with PF₃. The mechanism suggested in the present letter should account for a multiplet structure of the observed nature. This mechanism should produce a larger effect than the one considered by Gutowsky, McCall, and Slichter [*Phys. Rev.* **84**, 590 (1951)] which depends only on electronic orbital contributions arising from \mathfrak{S}_1 in Eq. (2) above.

Possible Natural Radioactivity of Neodymium*

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A NUMBER of investigators have looked for natural radioactivity in neodymium.¹⁻¹² All agree that alpha-activity is absent, and most either reported no beta-activity or ascribed the observed activity to common radioactive impurities. However, Libby,⁷ who used by far the most sensitive detection method, reported a beta-radiation of maximum energy of about 11 kev and specific activity about 60-120 disintegrations per second per

gram. That this activity is truly characteristic of neodymium has been in doubt because Libby did not repurify or fractionate his samples from all other elements to constant specific activity. Takvorian⁹ reported inability to detect activity in neodymium, but an inspection of his data shows that his sensitivity was grossly inadequate. A reference by Broda¹¹ to the unpublished work of Jha (1949) gives no data but implies confirmation of Libby's findings. A recent report by Curran, Dixon, and Wilson¹² states that Libby's data are probably wrong and that the maximum beta-energy may greatly exceed 11 kev. The implication is that radiation attributable to the element was observed, but no indication of the level of activity or degree of chemical purification is given.

One of us¹³ has pointed out that Nd¹⁶⁰ appears to be outside the limits of beta-stability for even-even nuclides, and suggested the possible identification of the radiations found by Libby with those of Nd¹⁶⁰. This would imply the natural occurrence of Pm¹⁶⁰ in equilibrium with Nd¹⁶⁰ in rare earth minerals, a relatively long lifetime for the daughter being required to explain the absence of hard radiations in Libby's samples. An alternate possibility suggested, that Nd¹⁴⁰ is long-lived and occurs naturally, has been eliminated by the subsequent finding¹⁴ that Nd¹⁴⁰ has a 3.3-day half-life with a 2-minute daughter emitting energetic radiations. The determination¹⁵ that Pm¹⁴⁶ undergoes electron-capture decay to Nd¹⁴⁶ removes the possibility¹⁶ that the latter is unstable.

Our measurements were made with a proportional counter accommodating internally solid samples 1650 cm² in area, filled with 68-cm argon and 8-cm ethylene. About 10 percent of the sample is obscured by three longitudinal rods which support the wire from one end so that samples can be inserted from the other end. It is used as a crude spectrometer for low energy radiations by varying the external amplifier gain so as to obtain bias curves. An energy calibration was obtained from the sharp cutoff of the manganese *K* x-rays of Fe⁵⁵ (6 kev), and the highest gain used corresponds to a bias level of 0.3 kev on the energy scale. By combined absorption and bias-curve measurements of the *K* Auger electrons from this transition (5 kev), we have verified that electrons of a very few kev energy are counted with apparent high efficiency and no reduction in energy. The background has been reduced to about 32 counts per minute by shielding with a ring of Geiger counters in anticoincidence, 2 inches of hot-rolled steel, and 3 inches of lead. Since Libby observed 10 counts per minute from an area of 193 cm² at 14 percent geometry, we would expect 270 counts/min from our 1650 cm² at 45 percent geometry if his data were correct, the sample thickness being immaterial for such low energy radiations.

Commercial 99 percent pure neodymium oxide (Lindsay Light and Chemical Company, Chicago) was twice purified in a cation exchange column (Dowex 50) 80 cm long, with very slow citrate elution, scavenged by barium sulfate and zirconium iodate precipitations, precipitated as oxalate, and ignited. A 15-gram layer of the resulting oxide spread uniformly on a copper sheet gave a counting rate about 4 per minute above background at the lowest bias. The bias curves showed that practically all of the excess radiations were more energetic than 11 kev. Moreover, the sensitivity of the copper-lined counter to external gamma-radiation (Co⁶⁰) is increased about 11 percent by the Nd₂O₃ coating, which just about accounts for the excess observed, since most of the residual background is presumably due to gamma-radiation. No growth of activity was observed in two months. We conclude that not more than 1 count/min of either soft or hard radiation is contributed by the neodymium. Accordingly, the maximum specific beta-activity is 0.003 disintegration per second per gram of element, corresponding to a minimum half-life of 2×10^{16} years for Nd¹⁶⁰.

In spite of the negative results of this experiment we feel that it is still likely that Nd¹⁶⁰ is unstable but with a highly forbidden decay and very long lifetime. In the discussion of the limits of beta-stability,¹³ Nd¹⁶⁰ and Ca⁴⁸ were given similar special mention as being apparently outside of the stability region, and another