must be positive. This last condition is required in order that spin states of high multiplicity, which favor ferromagnetism, have the lowest energy. It seems certain that for many of the non-ferromagnetic substances containing a high concentration of magnetic atoms the exchange integrals are negative. In such cases the lowest energy state is the one in which the maximum number of antiparallel pairs occur. An approximate theory of such substances has been developed by Néel,[1] Bitter,[2] and Van Vleck[3] for one specific case and the results are briefly described below.

Consider a crystalline structure which can be divided into two interpenetrating lattices such that atoms on one lattice have nearest neighbors only on the other lattice. Examples are simple cubic and body-centered cubic structures. Let the exchange integral for nearest neighbors be negative and consider only nearest neighbor interactions. Theory then predicts that the structure will exhibit a Curie temperature. Below the Curie temperature the spontaneous magnetization *vs.* temperature curve for one of the sub-lattices is that for an ordinary ferromagnetic material. However, the magnetization directions for the two lattices are antiparallel so that no net spontaneous magnetization exists. At absolute zero all of the atoms on one lattice have their electronic magnetic moments aligned in the same direction and all of the atoms on the other lattice have their moments antiparallel to the first. Above the Curie temperature the thermal energy is sufficient to overcome the tendency of the atoms to lock antiparallel and the behavior is that of a normal paramagnetic substance.

Materials exhibiting the characteristics described above have been designated "antiferromagnetic." Up to the present time the only methods of detecting antiferromagnetism experimentally have been indirect, e.g., determination of Curie points by susceptibility and specific heat anomalies. It has occurred to one of us (J.S.S.) that neutron diffraction experiments might provide a direct means of detecting antiferromagnetism. In an antiferromagnetic material below the Curie temperature a rigid lattice of magnetic ions is formed and the interaction of the neutron magnetic moment with this lattice should result in measurable coherent scattering. Halpern and Johnson[4] have shown that the magnetic and nuclear scattering amplitudes of a paramagnetic atom should be of the same order of magnitude and this result has been qualitatively verified by experimental investigators.[5] At the time of the above suggestion, an experimental program on the determination of the magnetic scattering patterns for various paramagnetic substances (MnO, MnF_2, $MnSO_4$ and Fe_2O_3) was underway at Oak Ridge National Laboratory and room temperature examination had shown (1) a form factor type of diffusion magnetic scattering (no coupling of the atomic moments) to exist for MnF_2 and $MnSO_4$, (2) a liquid type of magnetic scattering (short-range order coupling of oppositely directed magnetic moments) to exist for MnO and (3) the presence of strong coherent magnetic diffraction peaks at forbidden reflection positions for the α-Fe_2O_3 lattice. The latter two observations are in complete accord with the antiferromagnetic notion since the Curie points for MnO and α-Fe_2O_3 are respectively[6] 122°K and 950°K.

Figure 1 shows the neutron diffraction patterns obtained for powdered MnO at room temperature and at 80°K. The room temperature pattern shows coherent nuclear diffraction peaks at the regular face-centered cubic reflection positions and the liquid type of diffuse magnetic scattering in the background. It should be pointed out that the coherent nuclear scattering amplitudes for Mn and O are of opposite sign so that the diffraction pattern is a reversed NaCl type of pattern. The low temperature pattern also shows the same nuclear diffraction peaks, since there is no crystallographic transition in this temperature region,[7] and in addition shows the presence of strong magnetic reflections at positions not allowed on the basis of the chemical unit cell. The magnetic reflections can be indexed, however, making use of a magnetic unit cell twice as large as the chemical unit cell. A complete description of the magnetic structure will be given at a later date.

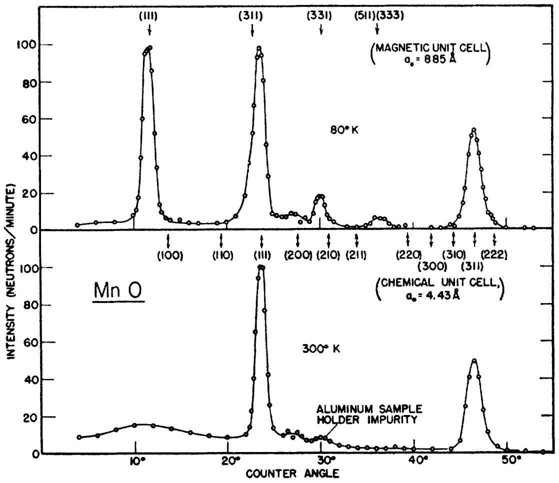

FIG. 1. Neutron diffraction patterns for MnO at room temperature and at 80°K.

In conclusion it appears that neutron diffraction studies of antiferromagnetic materials should provide a new and important method of investigating the exchange coupling of magnetic ions.

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[*] This work was supported in part by the ONR.

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[2] F. Bitter, Phys. Rev. **54**, 79 (1938).

[3] J. H. Van Vleck, J. Chem. Phys. **9**, 85 (1941).

[4] O. Halpern and M. H. Johnson, Phys. Rev. **55**, 898 (1939).

[5] Whittaker, Beyer, and Dunning, Phys. Rev. **54**, 771 (1938); Ruderman, Havens, Taylor, and Rainwater, Phys. Rev. **75**, 895 (1949); and also unpublished work at Oak Ridge National Laboratory.

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Imprisonment of Resonance Radiation in Mercury Vapor

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August 29, 1949

THE term "imprisonment of resonance radiation" describes the situation wherein resonance radiation emitted in the interior of a gas-filled enclosure is strongly absorbed by normal gas atoms before it can get out; the eventual escape of a quantum of radiation then takes place only after a number of successive atomic absorptions and emissions. The phenomenon was first observed by Zemansky[1] who measured the time of decay, T, of diffuse resonance radiation from an enclosure of optically excited mercury vapor, after the exciting beam of 2537A light was cut off. T was found to depend upon gas density and enclosure geometry; at densities around 10^{15}/cc, T attained values of the order of 10^{-4} sec., a thousand times greater than the natural lifetime of an excited 6^3P_1 atom.

On the theoretical side, a number of treatments[2-6] have been presented. The early work[2-4] is reviewed in reference 6. In the latter paper (as well as in that of Bieberman[5]), the transport of resonance quanta is described by a Boltzmann-type integro-differential equation for the density of excited 6^3P_1 atoms; the solution of this equation by the Ritz variational method gives accurate values for the decay time, T. It was found that T depends not only on vapor density and enclosure geometry, but also on the spectral line shape of the resonance radiation, as pointed out earlier by Kenty;[4] explicit results were obtained for the case of Doppler broadening and plane-parallel enclosure geometry. Most recently, unpublished calculations have extended the analysis to enclosures of the form of infinite circular cylinders and to a variety of line shapes.

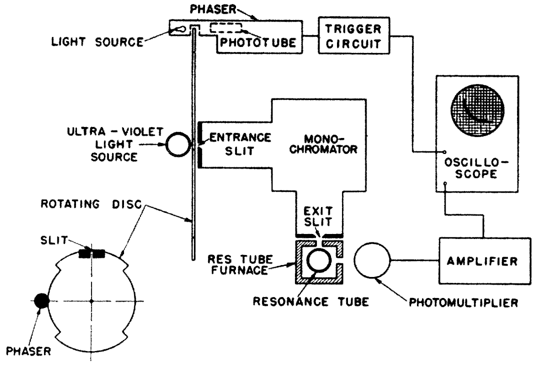

Fig. 1. Schematic diagram of apparatus.

With regard to the comparison of the theory with Zemansky's results, we may remark that, while order-of-magnitude agreement is obtained, the quantitative comparison is not altogether satisfactory. Actually, as pointed out in reference 6, both the geometry of the enclosures, as well as the limited pressure range over which the measurements were taken, are not very suitable for comparison purposes. For these reasons and because of the considerable advances in experimental techniques—i.e., in the preparation of impurity-free gas systems, in the measurement of radiation intensities by use of the photo-multiplier tube, and in the measurement of time by synchroscope techniques—we have performed a modernized version of Zemansky's experiment under conditions of vapor density and enclosure geometry appropriate for comparison with theory.

The apparatus is shown schematically in Fig. 1. The 2537A light is obtained from a mercury discharge source and isolated by a monochromator. The light is turned on and off by a sectored disk rotating (at about 10,000 r.p.m.) past the entrance slit of the monochromator. It is then incident on the resonance tube, a carefully evacuated and sealed-off silica glass cylinder containing a small quantity of mercury. A phaser is used to synchronize the triggering of the oscilloscope sweep circuit with the rotation of the disk. To adjust the pressure of mercury vapor, which is in equilibrium with the liquid mercury, the resonance tube (1.3 cm in diameter, 13.5 cm long) is placed in a specially designed furnace whose temperature can be varied at will. The diffuse radiation coming from the resonance tube is incident on a photo-multiplier, and the resulting signal is amplified and displayed on an oscilloscope. Observation of the decay trace for various furnace temperature gives directly the decay time T as a function of vapor density N.

The experimental results are indicated by the black circles in Fig. 2. For N less than 1.5×10^{16}/cc, the line shape is determined predominantly by Doppler broadening; for this case the theory has been worked out[7] and is represented by the solid curve. For N greater than 1.5×10^{16}/cc, the dual complications of pressure broadening and hyperfine structure render the calculations more difficult; in this region, upper and lower limits to the theory are given. Agreement between measurements and theory is seen to be quite satisfactory. Zemansky's observation that the time

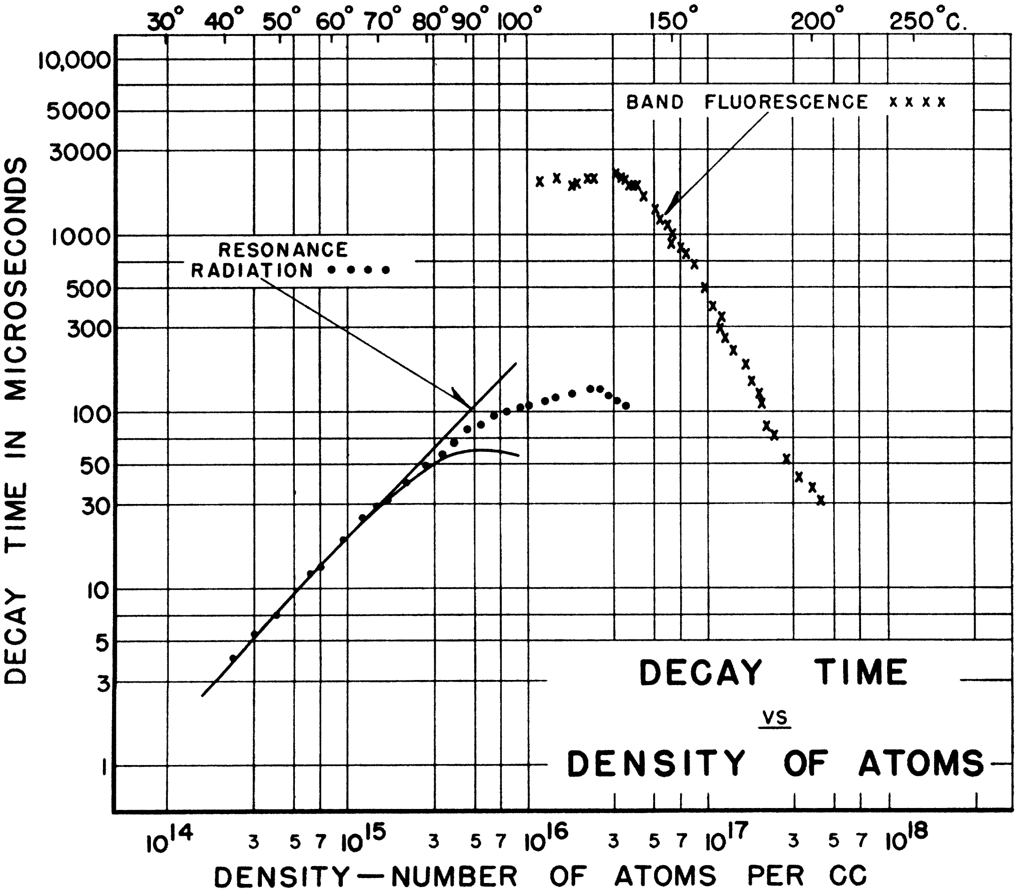

Fig. 2. Black circles represent experimental measurements of decay time of resonance radiation; the solid curves, the upper and lower limits of the theoretical prediction. The crosses represent measurements of the band fluorescence of Hg_2, which is discussed in the following letter.

constant is appreciably lowered for N greater than 7×10^{15}/cc is not confirmed. Further experimental details and results will be presented in a later publication.

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[6] T. Holstein, Phys. Rev. **72**, 1212 (1947).
[7] The formula used is: $T=\frac{5}{8}k_0R(\pi\log k_0R)^{\frac{1}{2}}$, where R is the cylinder radius and k_0 the absorption coefficient at the center of a Doppler broadened line. For mercury vapor k_0 is given in terms of vapor density N and absolute temperature θ by the expression: $k_0=(2.19\times 10^{-12}N)/\theta^{\frac{1}{2}}$ cm^{-1}.

Persistence of Band Fluorescence in Mercury Vapor

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WHEN mercury vapor is excited with 2537A resonance radiation it emits not only the resonance line itself but also a continuous spectrum[1] whose main constituents are two bands in the visible and near ultraviolet regions. The visible band extends from 4000A to 5300A with a maximum intensity at 4850A; the near ultraviolet band is contained in a range from 3000A to 3700A with maximum intensity at 3350A.

The persistence of this band fluorescence after the removal of the exciting light, first discovered by Phillips,[2] was investigated rather extensively by Lord Rayleigh with the aid of a moving-vapor-stream technique. In an experiment[3] in which the pressure, although not measured, was presumably kept at a minimum, this author observed a decay time of 1.8 millisec. for the fluorescence.

Interpretations of the different observations in terms of excited states of Hg_2 have been advanced by a number of authors. Of these, the most recent, due to Mrozowski,[4] is illustrated in Fig. 1. Optical transitions from the excited levels to the ground state give rise to the two bands previously mentioned, as well as to the 2540A band, closely adjacent to the resonance line. Two of these transitions, $({}^31_u-{}^1\Sigma_g{}^+)$ and $({}^30_u{}^+-{}^1\Sigma_g{}^+)$, are presumed to occur with a probability of the same order as that of the corresponding atomic transitions $({}^3P_1-{}^1S_0)$, i.e., $\sim 10^7$ sec.$^{-1}$. The transition $({}^30_u{}^--{}^1\Sigma_g{}^+)$ is forbidden for pure Case c classification of the molecular levels; the experimentally observed presence of the 4850A band is to be attributed to a small deviation from Case c, presumably in the direction of Case b. Rough estimates indicate that the lifetime of the ${}^30_u{}^-$ state may well be of the order of the persistence time (1.8 millisec.) observed by Lord Rayleigh. One is thus led to assume that the ${}^30_u{}^-$ state acts as the primary reservoir of long-lived molecular excitation; the identity of decay times of both the visible and near ultraviolet bands is explained as arising from the continual replenishment of the ${}^31_u$ level from the ${}^30_u{}^-$ level by collisions of the second kind.

In our experiment on imprisoned resonance radiation, described in the preceding letter, band fluorescence first showed up at densities of about $N=10^{16}$/cc, giving rise to a composite trace on the oscilloscope. From this trace one could discern two decay processes, the shorter of which we associated with resonance radiation, the longer with molecular fluorescence. This interpretation was confirmed by the use of glass transmission filters with which we could eliminate resonance radiation and observe a simple exponential decay of the fluorescence alone; the near ultraviolet and visible bands were found to decay at the same rate. Measured values of the common time constant are given in Fig. 2 of the preceding letter. We note that the low pressure limit of T agrees quite well with Lord Rayleigh's value (1.8 millisec.).

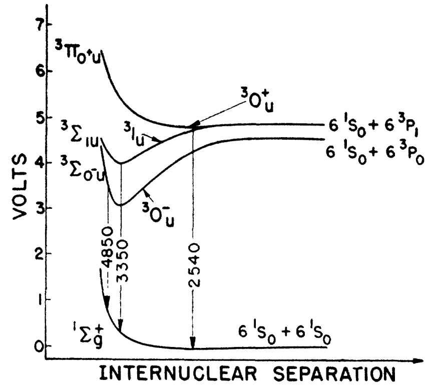

FIG. 1. Energy level diagram of Hg_2 according to Mrozowski (see reference 4(b), Fig. 1), with slight alterations. For large internuclear distances, the levels are described in terms of states of the separated atoms; for intermediate and small internuclear distances, this classification is replaced by those of Hund's Cases c and a, respectively.

It might be supposed that the decrease in T with increasing density is actually due to the simultaneous increase of temperature according to the saturated vapor pressure curve of mercury.[5] The absence of such an effect was demonstrated in a preliminary experiment in which, at a given pressure, two different observation temperatures were provided by the use of two furnaces of somewhat differing design. It was found that, at constant pressure, the time constant actually ***increases*** with temperature. This observation is in sharp disagreement with the interpretations based in Fig. 1, according to which a rise in temperature would enhance the probability of jumps from the ${}^30_u{}^-$ level to the ${}^31_u$ level by collisions of the second kind. An effect of this type would shorten the observed time constant since the ${}^31_u$ state is presumed to decay immediately (10^{-7} sec.), emitting the 3350A band.

According to Fig. 1, we would also expect the ratio of the intensities of the two bands, I_{4850}/I_{3350}, to decrease with increasing temperature. This has indeed been observed by Lord Rayleigh[3] and by Mrozowska.[6] The latter author, in addition, observed I_{4850}/I_{3350} to increase with pressure at constant temperature. In our experiments, in which the pressure and temperature varied interdependently according to the saturated vapor curve, an increase in I_{4850}/I_{3350} was also observed with increasing furnace temperature. The effect of pressure variation on the intensity ratio has not been explained in terms of the energy level scheme in Fig. 1.

Further experiments in which the pressure and temperature can be varied independently are now in progress.

[1] See, for example, W. Finkelnburg, *Kontinuerliche Spektren* (Verlag. Julius Springer, Berlin, 1938), Section 60, for a short survey and bibliography.
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Nuclear Magnetic Resonance Shift in Metals*

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THE purpose of this letter is to report the observation of a shift in the nuclear magnetic resonance frequencies from expected values in five metals, Li, Na, Al, Cu, and Ga, in magnetic fields ranging from five to ten thousand gauss, using an automatic search type radiofrequency spectrometer.[1] The magnitudes of the signals observed were in all cases at least twenty times noise amplitude, and in all cases the resonance frequencies, for constant magnetic field, were higher by tenths of a percent than the resonance frequencies observed in salts of the corresponding metals. The absolute accuracy of the frequency measurements was about 0.01