Radioactive Preparation of Defects in Solids

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An experimental study has been made of the use of radioactive materials in preparing defects in solids. Paramagnetic resonance was used to study such defects. The systems studied utilized tritium and krypton 85. Solid tritium was studied at 4.2°K. It was found that atomic tritium was formed and showed a characteristic hyperfine splitting of 543 gauss. The krypton 85 was also studied at 4.2°K. This should yield atomic rubidium but no paramagnetic resonance characteristic of this atom was found.

1. INTRODUCTION

ONE of the major areas of interest in solid-state physics is concerned with the study of a relatively dilute system of defects in solids. Such defects may be due to the addition of some chemical impurity, for example. The technique of preparing defects by the effects of high radiation is also widely used. The production of color centers by x rays is a well-known example of this method. In the present study we wish to examine experimentally the possibility of preparing defects by a method of radioactive decay. This means that we attempt to make a solid as perfectly as possible but containing some radioactive atoms which decay to a different element. This results in a foreign impurity being introduced.

This method is particularly useful when the defects are unstable and must be kept at low temperatures or in cases where the defect cannot be formed by the usual techniques. One can imagine a variety of systems for studying this method, but in the present work we shall deal only with the problem of defects in frozen gases as discussed below.

There has been considerable interest in the study of atoms trapped at low temperatures in various matrices.[1] Such centers have been prepared by rapid freezing of gas discharge products and also by radiation damage at low temperatures. The techniques of paramagnetic resonance have been used to make measurements on these atomic centers.

In the present work a similar type of experiment is reported except that in this case radioactive decay is used to prepare atomic centers. In this technique a frozen matrix is made which contains some radioactive material. This radioactive material decays, and the daughter product gives rise to an atomic center. Such centers can then be studied by paramagnetic resonance, and also, in some cases, optical absorption measurements may be made.

There are two general schemes which can be used to yield fairly simple systems. The first is one in which an active element decays into a noble gas atom, and the second in which a noble gas atom becomes an atom of an active element. The first scheme is represented by the use of solid tritium or tritium in solid neon. We have

$$H_2^3 \xrightarrow[\beta]{} He^3 + H^3.$$

It is seen that this process leads to the formation of atomic tritium. The atomic He^3 is inert and so the tritium remains atomic. The second scheme is represented in the use of solid krypton containing Kr^{85}; in this case we can have solid krypton with the process

$$Kr^{85} \xrightarrow[\beta]{} Rb^{85}.$$

Atomic rubidium will be formed. Both of these schemes were attempted experimentally. Only the tritium scheme led to observable atomic species, however.

In order to consider the feasibility of such experiments we take the case where we wish to make paramagnetic resonance studies of the atomic center at liquid helium temperatures. This means that one wants to have perhaps 10^{13} or more atomic centers to make good paramagnetic resonance studies. If we consider using 100 millicuries of a radioactive material, this means that 3×10^9 centers will be made per second. Thus a few hours of decay will yield a sufficient number of atomic centers. At this stage, only beta emitters are considered, so that the shielding problem is not overly difficult.

In the ideal experiment one would want the formation of the atomic center to occur with no other disordering processes present. Unfortunately this is almost precluded in the experiment. There is a recoil associated with the decay, and in addition the emitted particle will cause some radiation damage to the lattice. Such effects should be minimal in the case of tritium since the beta particle has only 20 kev of energy. In the case of Kr^{85}, the beta is about 0.6 Mev and so significant recoil of the Rb^{85} will occur. Thus the initial Kr^{85} may be in a simple lattice site but the Rb^{85} can end up in a different lattice site. In addition, the beta particle can cause damage to the inert Kr lattice. In spite of this, the systems may still be simple enough to be of considerable interest.

2. EXPERIMENTAL METHOD

The technique of paramagnetic resonance was used to detect the presence of the trapped atoms. The equip-

[1] C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, Phys. Rev. 112, 1169 (1958).

ment consisted of an X-band (10 000 Mc/sec) resonance spectrometer, 12-in. magnet, and helium Dewar system. The magnetic field was modulated at 5 kc/sec and a coated ceramic microwave cavity was used. Since the measurements were made at 4.2°K one may anticipate that a major problem in the detection would be saturation of the electron paramagnetic absorption since spin-lattice relaxation times can be very long at this temperature. It is therefore desirable to use low microwave power in making measurements, and to do this superheterodyne detection was employed. The microwave power level was kept at about 1 μw or less for most measurements. In general the derivative of the absorption was observed. In cases where saturation was a problem the derivative of dispersion was observed.

The system was arranged so that a sample tube could be lowered into the microwave cavity at liquid helium temperatures, and also the sample tube could be removed and kept in a liquid helium storage Dewar. Samples could be kept at this temperature for about two weeks. The gases of interest were frozen in the bottom of the sample tube and the tube was then placed in the cavity and measurements were made.

The sample tube can present some problems, since it suffers some radiation damage and this can introduce spurious signals. Some measurements were made on various tubing materials to evaluate this problem. Materials were x rayed at 77°K for several hours and then examined for paramagnetic resonance at 4.2°K. Some results are shown in Figs. 1 and 2. It is seen that x-rayed vycor glass gives an atomic hydrogen signal. This is deduced from the hyperfine splitting of about 510 gauss which is the same as one would expect from atomic hydrogen.[1,2]

The rest of the broad resonance signal in vycor cannot be readily identified. The existence of such absorption

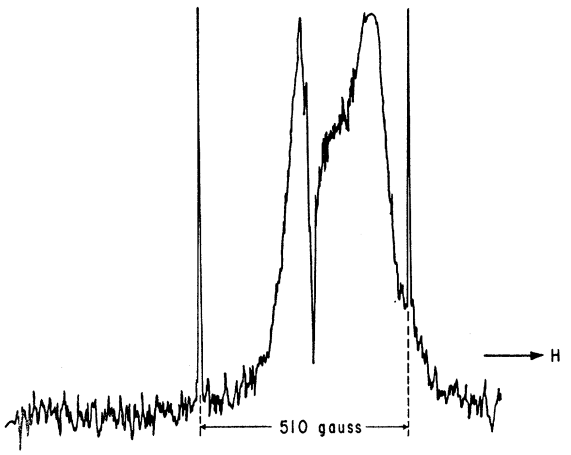

FIG. 1. Paramagnetic resonance signal from Vycor glass, x rayed at 77°K and measured at 4.2°K. The derivative of the dispersion signal is displayed. The spectrum is centered about 3200 gauss.

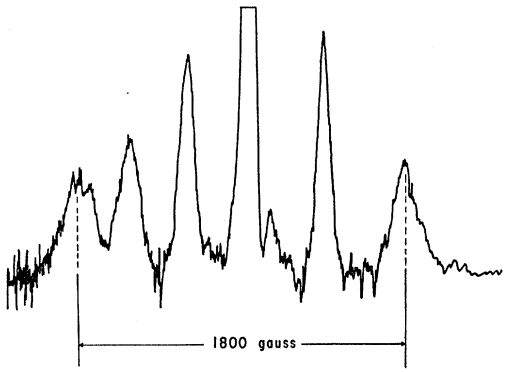

FIG. 2. Paramagnetic resonance signal from quartz, x rayed at 77°K and measured at 4.2°K. The derivative of the dispersion signal is displayed. The spectrum is centered about 3200 gauss.

due to x-ray induced defect is not surprising however. In the present work we wish only to note the presence of such signals so as to avoid confusion with the species being sought. In view of the large signals produced by x rays, vycor was not used as a sample holder. In the case of quartz, a complex absorption pattern was observed as shown in Fig. 2. This absorption would be characteristic of a species with hyperfine structure related to $I=5/2$. One does not know whether this is due to a defect or a foreign impurity. It may be noted that a spectra characteristic of $I=5/2$ has been found in x-rayed quartz crystals at 300°K.[3] This spectra had a hyperfine splitting of only 5 gauss and was attributed to a resonance associated with trapping of a charge near an Al^{27} impurity which has $I=5/2$. In our case the splitting is very much larger and is certainly a different entity. It is possible, however, that the center may also be associated with Al^{27}.

In any case the resonance was quite weak and so it was possible to use quartz as a container in the tritium experiment. Quartz was not acceptable for the Rb^{85} experiment since Rb^{85} has $I=5/2$ also and this would confuse the measurements. It was found that teflon, x rayed at 77°K, showed a weak resonance around $g=2$. Since the Rb^{85} resonance should show large hyperfine splitting with lines well away from $g=2$, teflon was used as a sample holder in this case. It should be noted that this problem of sample holder can also be avoided by placing the sample in a microwave cavity with no container used other than the cavity. In our present case this was not necessary.

3. EXPERIMENTAL RESULTS

a. Tritium

In this set of experiments 1 cc of tritium at STP was used. This is about 2.6 curies so that atomic tritium is formed at the rate of 10^{11}/sec. The half-life of tritium is 12 years. This amount of gas was frozen in a quartz tube

[2] N. Ramsey, *Molecular Beams* (Clarendon Press, Oxford, 1956), p. 265.

[3] J. H. E. Griffiths, J. Owen, and I. M. Ward, Nature **173**, 439 (1954).

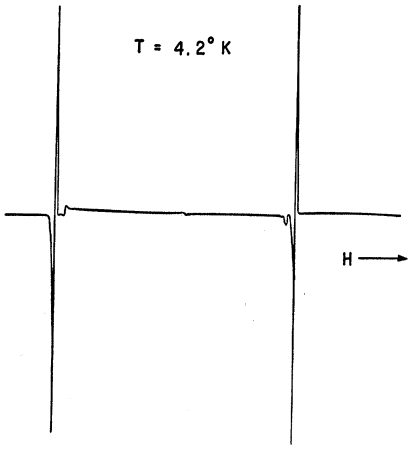

FIG. 3. Paramagnetic resonance observed from solid tritium, about 10 minutes after freezing at 4.2°K. The derivative of absorption is displayed. The splitting is 543 gauss.

at 4.2°K and placed in the microwave cavity. Measurements were begun after about 5 minutes. The spectrum anticipated for atomic tritium was observed. This is shown in Figs. 3 and 4. We note a hyperfine splitting of 543 gauss, as expected[2] from the hyperfine structure of free atomic tritium. This means that the tritium, although frozen in a solid matrix, behaves almost as a free atom as far as the hyperfine splitting is concerned. The parameters for the spectrum are: $g=2.002+0.002$ and $A=1515\pm2$ Mc/sec.

No problem with the quartz sample container was involved here since the tritium signal was so strong that a weak background would not matter. Also the amount of radiation damage was probably much smaller than that produced by the heavy x-ray irradiation used in testing the sample container.

One expects that the He^3 which is formed will be in the form of a neutral atom. If a large fraction remained ionized, with only a single electron, it would be paramagnetic with a large hyperfine splitting. A search was made for such an absorption but no evidence of this was found. A weak absorption with a splitting of about 510 gauss was noted. This signal did not grow with time and is apparently due to a trace of atomic hydrogen trapped in the frozen matrix.

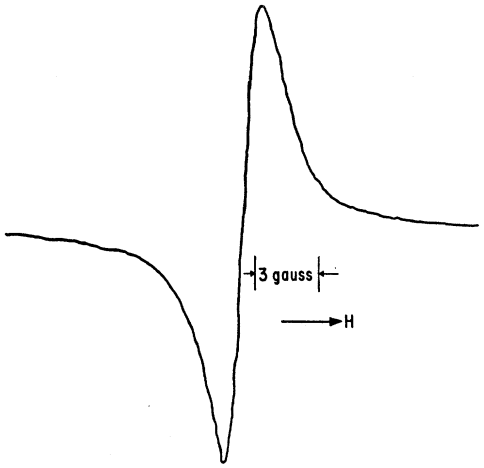

FIG. 4. Detailed trace of the low field line of the tritium doublet.

The atomic tritium signal should grow with time linearly, assuming no recombination occurs. This growth is seen in the steady increase of the paramagnetic resonance signal as shown in Fig. 5.

The uncertainty in measurement does not permit a firm statement on whether or not the growth was strictly linear. It should be noted that the starting time for the curve is somewhat uncertain since the material was cooled slowly to helium temperature over a period of about 3 minutes. The correct starting time for the curve would be the instant that the tritium became solid. Since one could not see the tritium, this point is uncertain. Thus within the limits of the experiment, no unusual behavior can be noted in the growth curve.

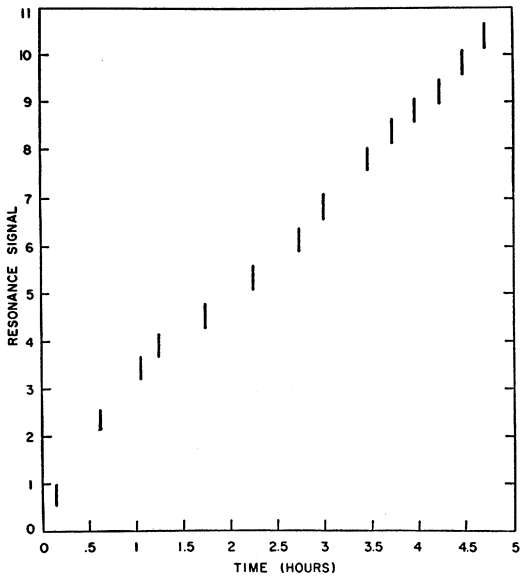

FIG. 5. Growth of the tritium resonance signal with time after freezing at 4.2°K.

An important question which arises is this. Is the atomic tritium observed due to the decay process or is it due to self radiation damage, since the solid tritium is being bombarded by its own 20-kev electrons? In order to examine this question the following experiment was conducted. The tritium was warmed back to 300°K and mixed with a liter of neon gas. Neon and tritium have boiling points at 27°K and 25°K, respectively, so that one might be able to obtain a frozen matrix of neon containing the tritium. The ionizing effects of the electrons will then act on the neon and the self damage on the tritium should be much less.

The results of this test are shown in Fig. 6. A tritium signal of about the same strength is obtained for the

neon-tritium mixture as the tritium alone. In addition, however, some additional fine structure is seen on the tritium signal. This fine structure can be ascribed to interaction with the Ne^{21} isotope. This nucleus has a magnetic moment of -0.66 nuclear magnetons, $I=3/2$, and is 0.3% abundant.[4] This means that if one assumes an interaction between nearby Ne^{21} atoms with the tritium one can estimate roughly the expected intensity of this fine structure. If one assumes the tritium can interact with 10 surrounding neon atoms, the fine structure lines should have an intensity which is down about a factor of 100 from the main line. The observed ratio is more nearly 50, but considering the uncertainties involved, the agreement is reasonable enough. This additional effect shows that the tritium was in a changed environment so that it was mixed with the neon. Thus the results indicate that one is indeed observing the formation of atomic tritium by the simple radioactive decay mechanism.

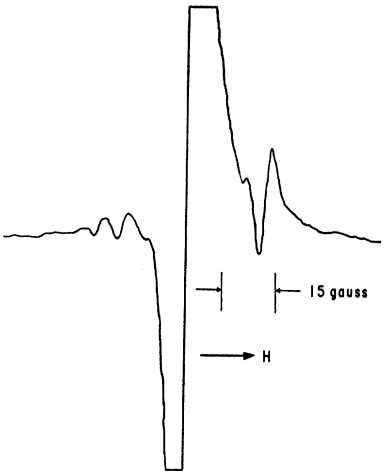

FIG. 6. Details of the low-field line of the tritium doublet when tritium is in a neon matrix. The line is about 50 times larger than the fine structure shown on the low-field side of the line. The line just to the high-field side is due to atomic hydrogen.

b. Krypton 85

The atomic rubidium experiment was attempted using 200 mC of Kr^{85}. This was contained in 20 cc of stable krypton. Atomic Rb^{85} should yield a paramagnetic resonance spectrum of 6 lines since it has $I=5/2$. The spacing between lines should be about 300 gauss if it behaves as a free atom.

Initial experiments were again carried out in quartz since it was believed that the signal would be strong enough to see above any radiation damage effects. It was found that only the very weak quartz radiation damage signal appeared after 10 hours at which time 10^{14} rubidium atoms would be present. Because the quartz signal has a wide spread in magnetic field, a teflon container was used since its radiation damage signal would not overlap the expected Rb^{85} spectrum. Again no signal was observed which could be ascribed to Rb^{85}. This absence of paramagnetic absorption could be due to the fact that when Kr^{85} decays it yields Rb^{85+} at first and this ion is not paramagnetic. One expects, however, that Rb^{85+} should be neutralized by the capture of an electron and become paramagnetic. Thus the reason for the lack of a result may lie in some details of the experimental technique.

4. CONCLUSION

It is seen that the tritium case seems to be quite straightforward as an example of radioactive preparation of defects. In this case we have dealt with a very simple example. Since one can obtain a wide variety of tritiated compounds, this method may have a fairly general applicability. Again it must be emphasized that the host material should not be readily damaged by the 20-kev electron if this method is to be of value. The use of materials with specific hydrogen sites tritiated makes possible definitive production of defects in such materials. This is of value in studies aimed at identifying species formed by high-energy radiation damage.

The failure to observe any paramagnetic resonance for the Kr^{85} system is not understood at present except in terms of some possible experimental problem such as saturation of the paramagnetic resonance due to a long spin-lattice relaxation time. It is quite possible that an optical observation of the Rb^{85} in solid krypton might overcome this problem. One should expect strong optical absorption in the red and near infrared. Such observations would be of interest in connection with reported observations made on alkali atoms deposited from the vapor phase.[5]

[4] J. T. LaTourrette, W. E. Quinn, and N. F. Ramsey, Phys. Rev. **107**, 1202 (1957).

[5] M. McCarty and G. W. Robinson, Mol. Phys. **2**, 415 (1959).