

## Spin Resonance of Impurity Atoms in Silicon

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(Received April 11, 1955)

An explanation is proposed for the weak satellite lines observed in the microwave electron spin resonance of Group V impurity atoms in silicon. The satellites occur halfway between the main hyperfine lines. It is proposed that the satellites represent the resonance of pairs of impurities close enough together for their exchange interaction to be very large compared to the hyperfine coupling. Mathematical details are worked out.

THE microwave spin resonance of Group V impurity atoms in silicon such as As or P has been studied by Fletcher, Yager, Pearson, Merritt, Holden, and Read.<sup>1</sup> They find the resonance consists of  $2I+1$  equally spaced lines of equal intensity, where  $I$  is the nuclear spin of the impurity atom. They interpret the splitting of the electron line as arising from the hyperfine interaction with the nuclear magnetic moment. The theoretical splitting has been worked out by Kohn and Luttinger.<sup>2</sup> Although the wave function of the electron bound to the impurity atom is complicated in silicon, they are able to obtain excellent agreement with the experimental splitting. Thus the main features of the resonances appear to be well understood. Fletcher and his co-workers find, however, that a close examination reveals that there are very weak satellite lines half-way between each of the main pairs.

Although Fletcher *et al.* propose in their second paper that the lines are from forbidden transitions, in a private communication they point out that the observed intensity is too high for this explanation. The purpose of this note is to propose a possible alternative explanation.

In essence, our proposal is that the satellite lines arise from the resonance of impurity atoms sufficiently close together that they should be considered as pairs whose electron spins are coupled strongly by the exchange interaction. In this case the electrons act as a unit which effectively responds to the average magnetic field produced by the hyperfine coupling to the two nuclei involved. As a consequence, the pattern for pairs consists of lines spaced at half the interval of single impurities, but extending over the same total range. Let us examine the mathematical details.

We consider a system of pairs of impurities in a static magnetic field  $H_0$ . The Hamiltonian is

$$\mathcal{H} = a(\mathbf{I}_1 \cdot \mathbf{S}_1 + \mathbf{I}_2 \cdot \mathbf{S}_2) + A \mathbf{S}_1 \cdot \mathbf{S}_2 + \gamma_e \hbar (S_{1z} + S_{2z}) H_0 + \gamma_n \hbar (I_{1z} + I_{2z}) H_0,$$

where  $\mathbf{I}_1$  and  $\mathbf{I}_2$  are the nuclear spins,  $\mathbf{S}_1$  and  $\mathbf{S}_2$  are the electron spins,  $\gamma_e$  and  $\gamma_n$  are the electron and nuclear gyromagnetic ratios, and  $a$  is the hyperfine coupling

constant evaluated theoretically by Luttinger and Kohn. The term  $A \mathbf{S}_1 \cdot \mathbf{S}_2$  represents the electron exchange interaction between pairs of electrons.<sup>3</sup> In its absence, we obtain energy levels which to a first approximation may be described by the quantum numbers  $m_1$  and  $m_2$  for the two nuclei, and  $M_1$  and  $M_2$  for the electrons. We find for the energy

$$E = a(m_1 M_1 + m_2 M_2) + \gamma_e \hbar (M_1 + M_2) H_0 + \gamma_n \hbar (m_1 + m_2) H_0.$$

The interaction  $\gamma_e \hbar (S_{1x} + S_{2x}) H_x \cos \omega t$  will then induce transitions in which  $\Delta M_1 = \pm 1$ ,  $\Delta M_2 = 0$  or  $\Delta M_1 = 0$ ,  $\Delta M_2 = \pm 1$ , giving us a set of lines at energies  $\gamma_e \hbar H_0 + a m_1$ , where  $m_1 = I, I-1, \dots, -I$ . There are then  $2I+1$  lines all told, of spacing  $a$ .

When  $A \gg a$ , it is appropriate to consider the electrons as forming a system described by quantum numbers  $S$  and  $M$ , where  $S = 1, 0$  and  $M = S, S-1, \dots, -S$ , but the nuclei are still described by  $m_1$  and  $m_2$ . Now the states  $S=1$  and  $0$  are the well-known singlet or triplet states. Then the diagonal terms become (since the triplet is symmetric and the singlet anti-symmetric)

$$E = a(\frac{1}{2} m_1 M + \frac{1}{2} m_2 M) + \frac{1}{2} A [S(S+1) - \frac{3}{2}] + \gamma_e \hbar M H_0 + \gamma_n \hbar (m_1 + m_2) H_0.$$

The term  $\gamma_e \hbar H_x (S_{1x} + S_{2x}) \cos \omega t$  gives us transitions  $\Delta S = 0$ ,  $\Delta M = \pm 1$ , so that we get lines at  $\gamma_e \hbar H_0 + \frac{1}{2} a (m_1 + m_2)$  which will give  $4I+1$  lines. The spacing is  $a/2$  rather than  $a$ . The intensity will *not* be uniform. To compute the intensity pattern we must find the number of ways of getting the same sum  $m_1 + m_2 = M_F$ . This procedure is a straight forward problem which can be solved by vector addition of the two angular momenta  $I$  to form  $F = 2I, 2I-1, \dots, 0$ . For each value of  $F$  we get a given value of  $M_F$  once. Moreover, each value of  $F$  occurs only once. Thus,  $M_F = 2I$  occurs once,  $M_F = 2I-1$  occurs twice, etc. The relative intensity of lines starting from one end of the pattern will then be 1-2-3-4...4-3-2-1. Therefore in the case of As we get an intensity pattern 1-2-3-4-3-2-1. The three lines of intensity 2-4-2 will be seen. The 1-3-3-1 lines will be

<sup>1</sup> Fletcher, Yager, Pearson, Holden, Read, and Merritt, *Phys. Rev.* **94**, 1392 (1954); Fletcher, Yager, Pearson, and Merritt, *Phys. Rev.* **95**, 844 (1954).

<sup>2</sup> W. Kohn and J. M. Luttinger, *Phys. Rev.* **97**, 883 (1955).

<sup>3</sup> We have omitted the magnetic dipole coupling between the electrons as being small compared to the exchange interaction.

masked by the resonance of single As impurities. Thus the central *satellite* should be twice as large as the outer satellites.

As the concentration increases, we would have resonances coming from clusters of more than two, but we might expect such clusters to be rather infrequent in the concentration range in which clusters of two are rare. The extreme case is the one in which the exchange coupling is so strong that we have a metal with completely nonlocalized electrons. Thus our case of interacting pairs is simply the first step in the process of turning the sample into a metal.

We note, finally, that if  $A \sim kT$  or larger, there should be a temperature dependence of the satellite intensity of  $\exp(-2A/kT)$ , assuming the triplet states are higher in energy. The presence of satellites should also be a

function of concentration (approximately proportional to  $c$  for low concentrations) and possibly of the mechanical treatment of the material if it causes the distribution of As in the lattice to be appreciably altered.

The predicted greater intensity of the central satellite for As is confirmed experimentally. The weakness of the lines makes it difficult to check the intensity ratio accurately, although Dr. Fletcher states that the experimental values scatter in the vicinity of the theoretical prediction.

The author wishes to thank Dr. Fletcher for interesting conversations. This paper grew out of discussions on another problem with Professor David Pines and Professor John Bardeen. The author is indebted to them for numerous stimulating conversations and helpful comments.

## Melting Curves of He<sup>3</sup>, He<sup>4</sup>, H<sub>2</sub>, D<sub>2</sub>, Ne, N<sub>2</sub>, and O<sub>2</sub> up to 3500 kg/cm<sup>2</sup>\*

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(Received April 13, 1955)

New and more accurate measurements were made on the melting pressure-temperature relationship of seven substances below 120°K and up to 3500 kg/cm<sup>2</sup>. New regions were covered for He<sup>3</sup> and O<sub>2</sub>. The blocked-capillary method was used. The data were fitted to the Simon-type equation,  $P = a + bT^c$ , with more success than to a quadratic,  $P = A + BT + CT^2$ . Rather straightforward shifts were obtained in the melting curves of the isotope pairs, He<sup>3</sup>-He<sup>4</sup> and H<sub>2</sub>-D<sub>2</sub>. Superpressuring in the O<sub>2</sub> measurements was unusually great.

### 1. INTRODUCTION

OUTSIDE of the pioneering work of Simon and his collaborators,<sup>1,2</sup> there is a surprisingly small amount of data on melting<sup>3</sup> temperatures as a function of pressure over a wide range and in the region below 100°K. They covered He, H<sub>2</sub>, Ne, N<sub>2</sub>, and A up to about 5000 kg/cm<sup>2</sup> using the blocked capillary technique first used by Kamerlingh Onnes and van Gulik.<sup>4</sup> Bridgman<sup>5</sup> also determined the the melting curves of N<sub>2</sub> and A to about 6000 kg/cm<sup>2</sup> but used the discontinuity in the specific volume as the criterion of melting. His  $P$ - $T$  curves lay below those of Simon *et al.*; he felt that their data were in error as a result of the shear stress in the capillary plug. Recently, Robinson,<sup>6</sup> using the freedom of a pellet as the criterion of melting, measured A and N<sub>2</sub> to about 9400 kg/cm<sup>2</sup>; his  $P$ - $T$

curve for A lay below those of both Simon<sup>2</sup> and Bridgman,<sup>5</sup> while his N<sub>2</sub> curve lay between those of Simon and Bridgman (if one believes Robinson's actual data rather than his conclusions).

Helium has been studied in the 4000-7300 atmos (35-50°K) region by Holland, Huggill, and Jones<sup>7</sup> and in the 140-780 atmos (4-12°K) region by Dugdale and Simon.<sup>8</sup> All of these He data agree substantially with those of Simon.<sup>1,2</sup>

An interesting isotopic comparison resulted from the observations of Chester and Dugdale<sup>9</sup> on H<sub>2</sub> and D<sub>2</sub>. They found the D<sub>2</sub>  $P$ - $T$  curve to be consistently 170 kg/cm<sup>2</sup> lower than the H<sub>2</sub> curve up to their maximum pressure of 2800 kg/cm<sup>2</sup>. However, their quantitative results were expressed only as the difference between the two isotopes and are therefore inadequate for general use.

One of the most debated points concerning solid-gas equilibria is the maximum temperature at which solid exists.<sup>10-13</sup> According to Simon,<sup>10</sup> the substance most

\* Work done under the auspices of the U. S. Atomic Energy Commission.

<sup>1</sup> F. Simon, *Z. physik. Chem.* **B2**, 340 (1929).

<sup>2</sup> Simon, Ruhemann, and Edwards, *Z. physik. Chem.* **B6**, 62 (1929); **B6**, 331 (1930).

<sup>3</sup> Used in its most general sense: solid to either fluid phase, liquid or gas.

<sup>4</sup> H. Kamerlingh Onnes and W. van Gulik, *Leiden Comm.* 184a (1926).

<sup>5</sup> P. W. Bridgman, *Phys. Rev.* **46**, 930 (1934); *Proc. Am. Acad. Arts Sci.* **70**, 1-32 (1935).

<sup>6</sup> D. W. Robinson, *Proc. Roy. Soc. (London)* **A225**, 393 (1954).

<sup>7</sup> Holland, Huggill, and Jones, *Proc. Roy. Soc. (London)* **A207**, 268 (1951).

<sup>8</sup> J. S. Dugdale and F. E. Simon, *Proc. Roy. Soc. (London)* **A218**, 291 (1953).

<sup>9</sup> P. F. Chester and J. S. Dugdale, *Phys. Rev.* **95**, 278 (1954).

<sup>10</sup> F. E. Simon, *Z. Elektrochem.* **35**, 618 (1929); *Trans. Faraday Soc.* **33**, 65 (1937); *Proc. Roy. Soc. (London)* **A218**, 291 (1953).