CURRENT PROBLEMS IN RESEARCH

Electron Spin Resonance

Its use is leading to a new understanding of impurity centers in semiconductors such as silicon.

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The phenomenon of electron spin resonance depends upon the fact that an electron, like a bar magnet, has a magnetic moment. If an electron is placed in a magnetic field its energy is proportional to the strength of the field and differs according to whether its magnetic moment is aligned parallel or antiparallel to the field. Moreover, modern physics tells us that only these two orientations occur in nature. In electron spin resonance, electrons are flipped from one orientation to the other by an additional high-frequency magnetic field. The probability of a flip is maximal when the difference in energy between the two orientations is given by Planck's constant h times the frequency ν of the alternating field:

$$\Delta E = h\nu$$

Experimentally, the sample is exposed to microwave radiation (an alternating magnetic field having $\nu \sim 10{,}000$ Mcy/sec) and the main magnetic field is varied until the resonance condition, Eq. 1, is satisfied, as illustrated in Fig. 1.

One might imagine that all electrons can undergo spin resonance transitions. This is not the case; electrons frequently occur in pairs which are aligned in such a way that the intrinsic magnetism of the one cancels that of the other. Electron pair bonds consist of such pairs, as do closed shells of electrons. Unpaired electrons, which show spin resonance, are nevertheless quite common. They are found in partly filled inner shells of elements, in the *d* shell of iron-group elements, and in the *f* shell of rare-earth elements. They are found if an electron pair bond is ruptured to form a free radical. They occur as conduction electrons in semiconductors and in metals.

The energy levels of unpaired electrons are influenced by electric and magnetic fields of their crystalline environment as well as by the magnetic field at the disposal of the experimenter. A major use of spin resonance is its use in probing these fields, and in favorable cases a quite detailed picture of the environment of the unpaired electrons can be obtained. A fundamental feature of the resonance spectrum which reflects the crystalline environment is the g factor, which in simple cases is given by

$$g = (h/\beta)\ (\nu/H) \qquad (2)$$

Since Planck's constant h and the Bohr magneton β are constants, g essentially is the ratio of the resonant frequency to the resonant magnetic field. The symmetry of the g factor (more precisely, the symmetry of the g tensor) is determined by the symmetry of the crystalline environment. The departure of g from the value for a free electron, 2.0023, is determined by the strength of the crystalline electric field and by the coupling between the spin and the orbital motion of the electron.

Another of the main tools for investigating the crystalline environment is the structure on spin resonance lines. Such structure is of two types, "fine" structure and "hyperfine" structure. Fine structure occurs in the spectra of resonant centers containing several unpaired electrons whose magnetic moments are coupled parallel to one another. In the general case where $2S$ electrons are coupled together, the resulting magnetic moment can assume $2S + 1$ orientations, between which there are $2S$ allowed transitions. (As before, one electron has two possible orientations and but one allowed transition.) The occurrence of different transitions at different values of applied magnetic field corresponds to fine structure.

Hyperfine structure is associated with the presence of nuclei which have magnetic moments. In such cases the unpaired electrons are exposed to a local magnetic field produced by nearby magnetic nuclei. Because of this variable local field, the resonance condition is satisfied for different electrons at different values of the applied magnetic field, although the total field for resonance remains the same. Frequently the resonant centers are unpaired electrons occupying an orbital of a particular element. The hyperfine structure then consists of $2I + 1$ lines, where I is the nuclear spin of the element. It provides a simple and frequently unambiguous means of indentifying the origin of the resonant absorption.

A spectrum which displays both fine and hyperfine structure is shown in Fig. 2. Since five unpaired electrons are coupled together in this center, there are five fine-structure transitions, which differ in intensity. The impurity nucleus (Cr^{53}) has a spin of 3/2. Because this nucleus can assume any one of four orientations, each fine-structure transition is split into four hyperfine lines. In addition, the symmetry of the resonance pattern allows one to deduce the symmetry of the crystalline environment of the chromium ion.

Status of the Field

The first paper reporting spin resonance appeared immediately after World War II (*1*). This timing was not accidental; the experiments were made feasible by advances in the microwave art which accompanied the development of radar for wartime use.

Early studies were concerned with salts of the transition metal ions. An outstanding accomplishment was the elucidation of the spin resonance spectra of transition metal ions in ionic crystals (*2*). In such crystals the transition metal ion typically is surrounded by six negatively charged ions at the corners of an octahedron. The spectra have been accounted for in terms of the energy-level scheme of the isolated ion as perturbed by a crystalline field. The particular form a spectrum assumes depends on the symmetry of this field and on its strength relative to parameters which describe the isolated ion.

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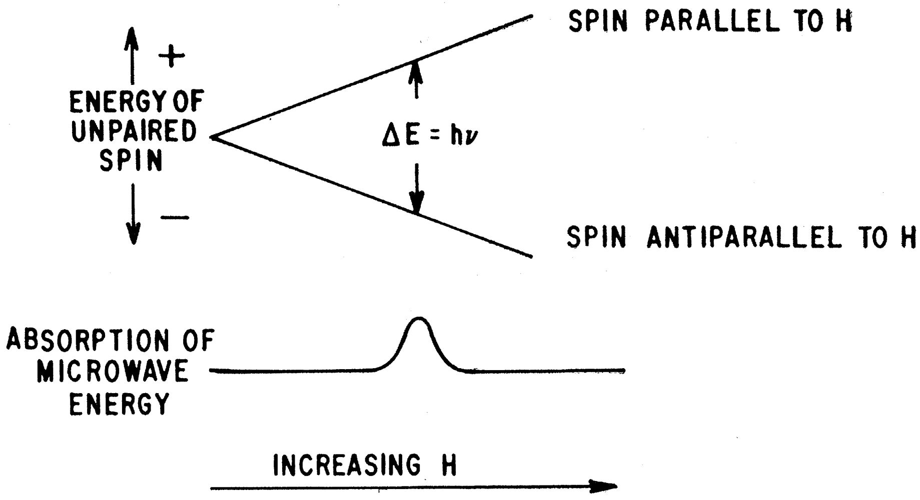


Fig. 1. The resonance condition for a single unpaired electron, which has just two allowed orientations.

As the field of spin resonance has come of age, the basic phenomena have become better and better understood; attention today is directed primarily to the application of spin resonance to problems in a variety of systems. Of great current interest are biological systems. Here, for example, one monitors free-radical intermediates, hoping to gain increased understanding of fundamental processes such as photosynthesis and oxidation—reduction reactions. Several detailed accounts of such work have appeared recently (*3*). A second type of system of current interest is the alkali halide crystal containing paramagnetic centers, which may, for example, give it color. My main interest is in yet another type of system, the semiconductor crystal containing a magnetically active impurity (*4*). I now turn to a discussion of this last type of system, with particular reference to the elemental semiconductor silicon.

Silicon

The element silicon is in column IV of the periodic table, as are carbon and germanium. The configuration of the free atom is $3s^23p^2$; there are four electrons in the valence shell, which can participate in chemical bonding. Thus, it is not surprising that the basic arrangement of atoms in a silicon crystal is tetrahedral, as shown in Fig. 3. Each atom can be thought of as forming electron pair bonds with four neighbors, by means of its valence-shell electrons.

As a semiconductor, silicon is characterized by the fact that the allowed energy levels for electrons fall into discrete bands. The highest normally filled band, termed the valence band, is separated from the lowest unoccupied band, the conduction band, by an energy gap. Silicon containing no impurities or other defects is diamagnetic at low temperatures, since filled bands, like closed shells, contain no unpaired electrons. All spin resonance which has been observed is associated directly or indirectly with the presence of defects. The study of defects is of particular interest because of the decisive role they play in the electrical, optical, magnetic, and other properties of the semiconductor.

Silicon has several characteristics which make it particularly tractable to the resonance technique. Its technology is well advanced; single crystals of controlled impurity content can be grown in accord with exacting specifications. The energy band structure and other properties are understood in considerable detail. The atoms are arranged in a highly symmetrical fashion, making interpretation of spectra simple.

Three types of defects have been

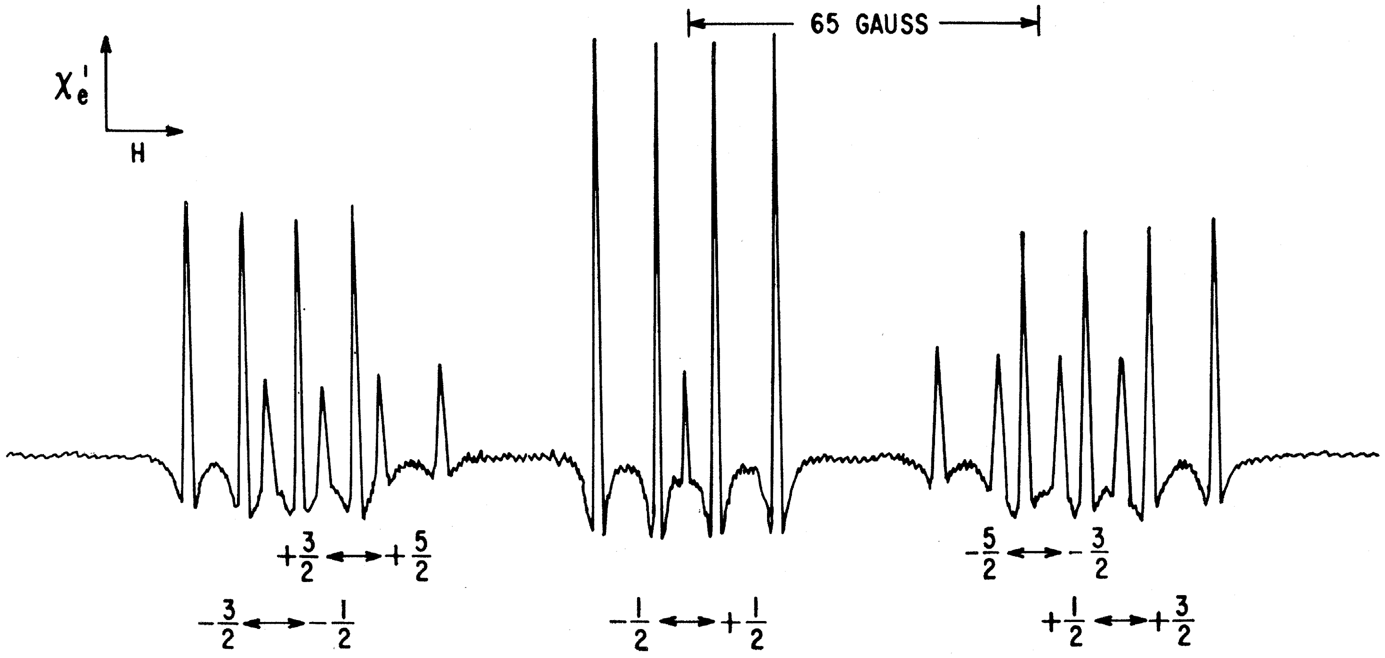


Fig. 2. Spectrum of Cr^+ in silicon. The five fine-structure lines, which are labeled, are each split into four components by hyperfine interaction with chromium-33.

studied by spin resonance in silicon in some detail. These are (i) shallow donor impurities, (ii) transition metal ions, and (iii) defects resulting from radiation damage. Resonance experiments have contributed quite substantially to the understanding of each type of defect. I shall describe these experiments, hoping that the reader will gain an appreciation of the versatility and power of the resonance technique.

Shallow Donor Impurities

The shallow donor impurities are elements of column V of the periodic table—phosphorus, arsenic, and antimony—which have one more valence shell electron than silicon has. This extra electron is bound but weakly to the donor; at high temperatures it may be thermally ionized (donated) to the conduction band, where it contributes to the conduction process. Since the donor electron travels in an orbit encompassing many atoms, its properties are related more closely to those of the host lattice than to the particular impurity to which it is bound.

Kohn and Luttinger have investigated the orbits (or, more precisely, the wave functions) of the donor electron, using a hydrogenic model (*5*). That is, they treat the donor electron as if it were bound to a single positive charge in a medium having the dielectric constant of the lattice. The periodic potential of the lattice is also taken into account. They find that the donor wave function can be approximated by wave functions of the conduction band multiplied by functions which resemble the orbits of the hydrogen atom. The dimensions of the wave function of lowest energy are quite large, of the order of 20 angstrom units, or about nine times the nearest neighbor distance.

Electron spin resonance of the shallow donors is associated with the donor electron, which is unpaired; no resonance can be observed from donors which have lost this electron. Resonance was first observed for phosphorus and arsenic donors. They were identified by the characteristic hyperfine splitting of the resonance line into two and four components for phosphorus and arsenic, respectively. Moreover, the magnitude of the hyperfine splitting gave a direct measure of the amplitude of the wave function at the donor nucleus. The small experimental value confirmed the Kohn-Luttinger theory that the donor wave function is spread out rather than concentrated near the nucleus.

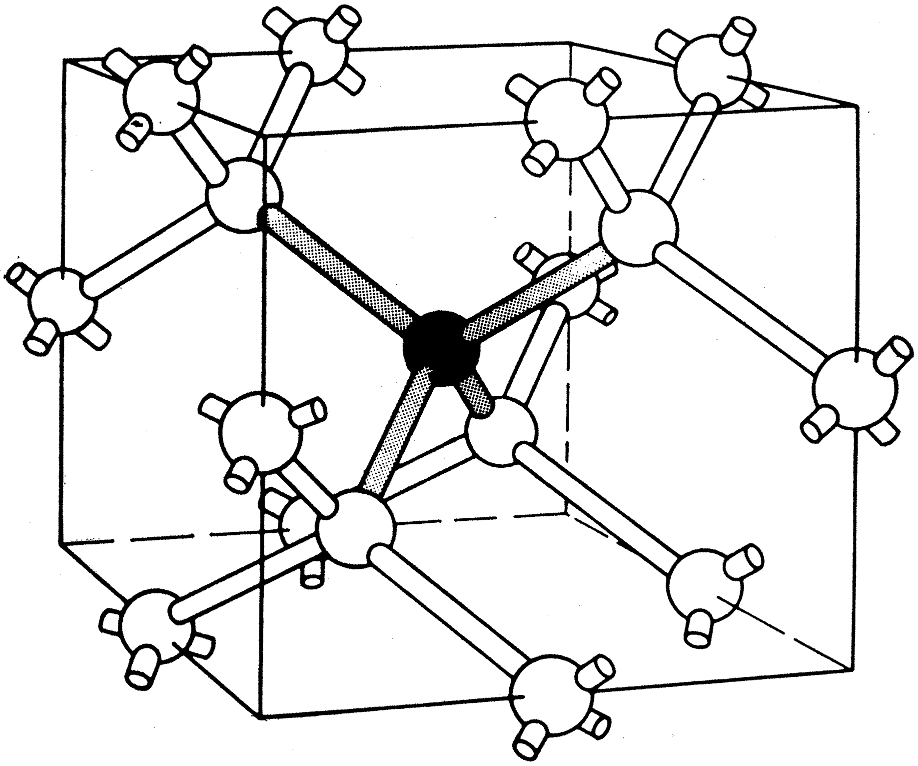


Fig. 3. Basic arrangement of atoms in the silicon lattice. [Courtesy G. D. Watkins and J. W. Corbett]

The resonance spectrum of phosphorus donors is shown in Fig. 4 as a function of the phosphorus concentration (*6–8*). As the phosphorus concentration is increased, additional lines appear, and at sufficiently high concentrations only one line is observed. These quite dramatic changes in the signal represent the increased interactions between donors as their mean separation decreases. The low concentration at which the effects occur again points to the spread-out character of the wave function.

A direct measure of the extent of the wave function has been provided by Feher's elegant ENDOR experiments (*7*). ENDOR stands for electron-nuclear double resonance. In this technique one uses the intensity of the electron spin resonance line as a means of detecting transitions in which a nuclear moment reorients. A feature of this technique is that one can detect and study hyperfine interactions which do not lead to resolved structure on the electron resonance line. For example, one can study the hyperfine interaction with silicon-29, an isotope of silicon of 4.7-percent abundance, having a nonzero nuclear magnetic moment. This interaction is responsible for the width of the phosphorus hyperfine lines in Fig. 4.

The detection of hyperfine interactions by ENDOR is illustrated in Fig. 5. The ENDOR transitions of the phosphorus are at frequencies between 50 and 70 megacycles per second, while at the lower frequencies one sees transitions of silicon-29 occupying various lattice sites. The strength of the silicon-29 interaction (that is, the ENDOR frequency) is a direct measure of the probability of finding the donor electron at the particular lattice site. One thus has a direct measure of the extent of the donor wave function.

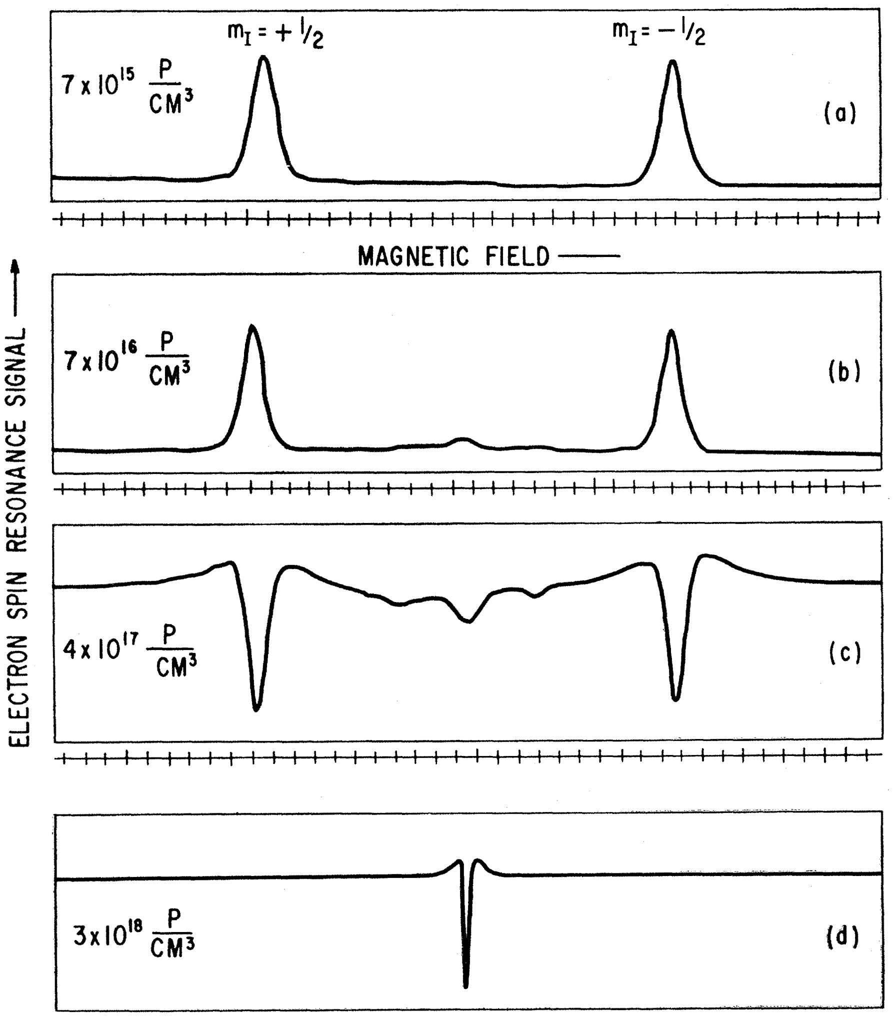
Resonance measurements have also contributed to the understanding of the fundamental properties of the conduction band of silicon. For example, from the ENDOR results and the Kohn-Luttinger theory, it was possible to learn something about the lowest energy states in the conduction band—in particular, the values of the crystal momentum which characterizes these states. It was also possible to deduce the magnetic properties of electrons occupying the conduction band, as distinguished from the properties of donor electrons, which are bound.

Donor resonances have also been put to use in studying other problems, two of which I will briefly mention. One problem is nuclear polarization—obtaining nuclei with their magnetic moments pointing in a definite direction in space. A second application is that of studying the dynamics governing the transfer of electrons from one impurity to another, or from the conduction band to an impurity.

Transition Metal Ions

While much was known about shallow donor impurities in silicon prior to the initial resonance measurements, transition metal impurities presented an enigma. Part of the difficulty lay in their low solubility, which is only about 1 part per million at the temperature corresponding to the solubility maximum. This solubility is comparable to the concentration of undesired impurities which found their way into samples. Equally serious, the electrical properties of samples containing transition metals changed with time, presumably because of precipitation or other processes involving the transition metal. Finally, the electrical properties of different metals were similar, and it was difficult to decide whether one was dealing with the desired element or whether another was contaminating the sample. From electrical measurements it was clear that many of the transition metals acted as donor impurities, and that the donor electron was tightly bound relative to that of the column-V elements (the shallow donors). However, it was by no means clear whether the transition metals were substitutional or interstitial, and whether they were isolated in the lattice or associated with other defects. Moreover, almost nothing was known about their electronic structure. Spin resonance has contributed a good deal to the answering of these questions. The experimental studies have been made primarily by H. H. Woodbury and me, while F. S. Ham has contributed considerably to their interpretation (*9*).

Transition metal ions typically contain several unpaired electrons in their *d* shell. As a result, it may be possible to detect and study several different



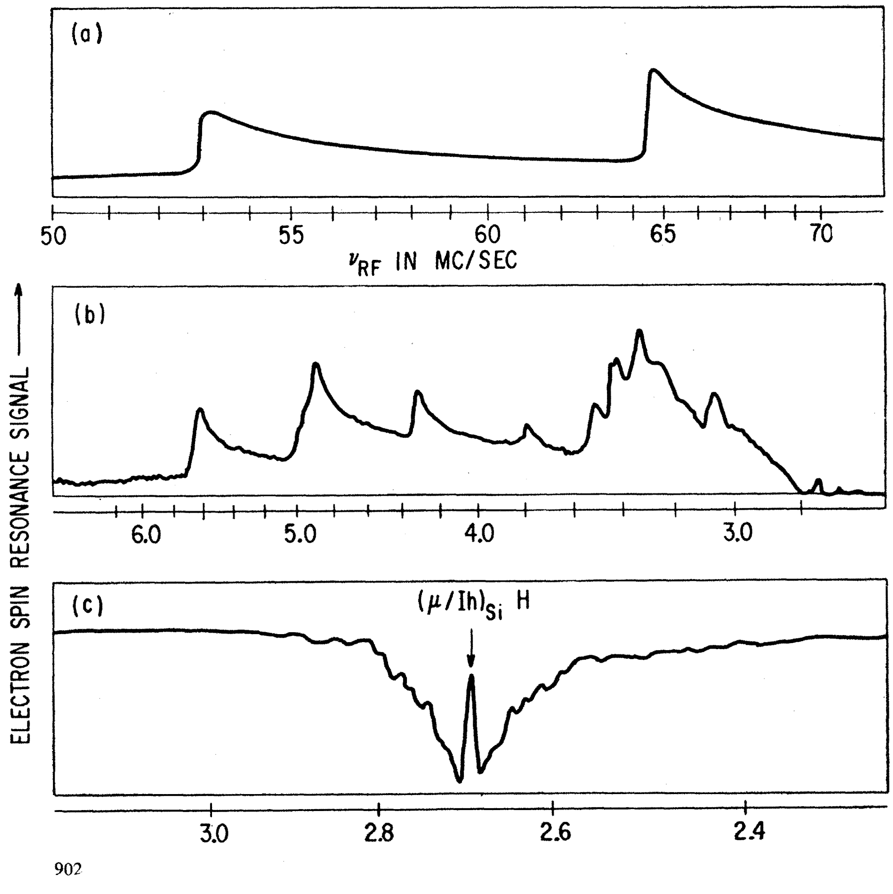


Fig. 4 (top). Spectrum of phosphorus donors. The signal changes with increasing donor concentration as interactions between nearby donors become more important. Fig. 5 (bottom). ENDOR transitions in phosphorus-doped silicon. *a*, Phosphorus-31 transitions; *b* and *c*, silicon-29 transitions. [After G. Feher (*7*)] charge states by spin resonance. In silicon there is a particularly simple way of obtaining these different charge states; one need only introduce the transition metal element (by diffusion) into crystals containing the proper concentration of a shallow acceptor or shallow donor impurity. In essence, the latter impurities furnish a sink for electrons or a reservoir for electrons, respectively. In the case of manganese we have produced four different charge states, Mn$^-$, Mn^0, Mn$^+$, and Mn^{++}, all of which show resonance. These are obtained by diffusing manganese into silicon containing phosphorus (a donor), no other impurities, a low concentration of boron (an acceptor), and a higher concentration of boron, respectively.

Early resonance measurements on transition metal ions of the 3*d* or iron group showed that it was possible to obtain ions unassociated with other defects. An example is Cr$^+$, whose spectrum is shown in Fig. 2 for the applied magnetic field parallel to a cubic crystalline direction. As the crystal is rotated in the field, the five fine-structure transitions move back and forth in a fashion indicating that the unpaired electrons

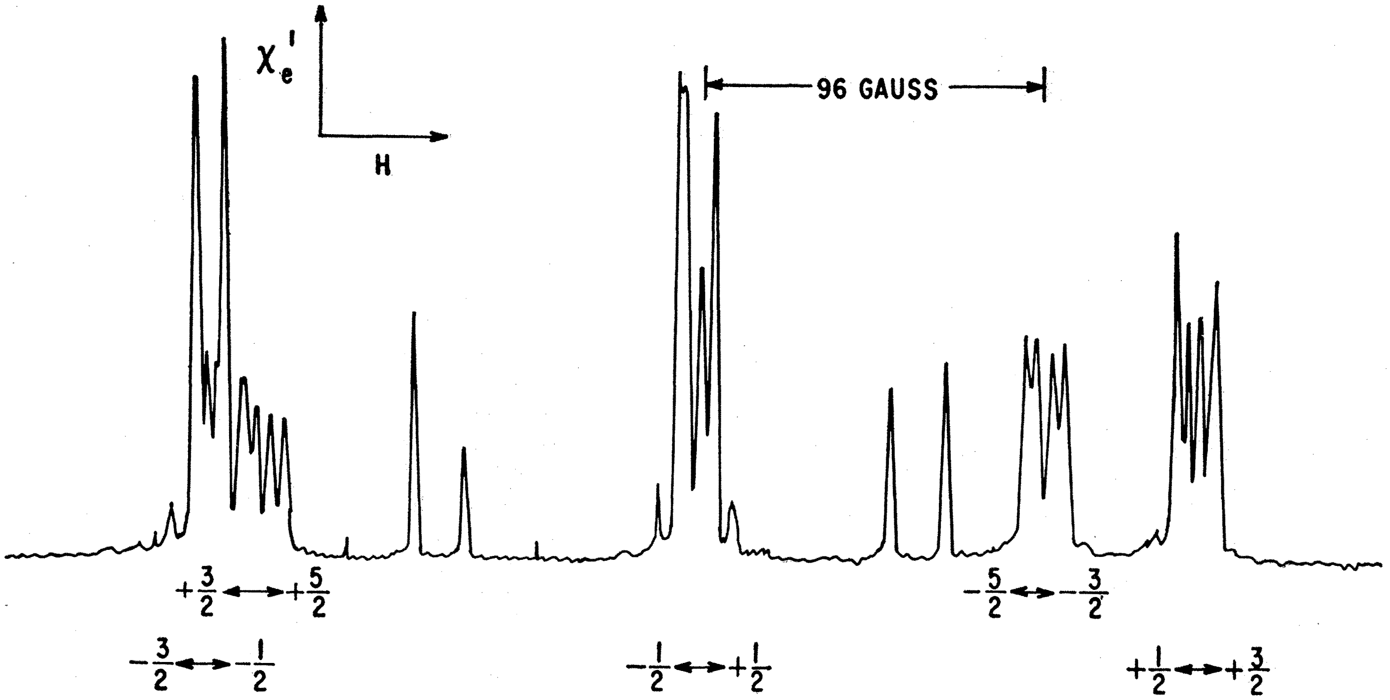


Fig. 6. Spectrum of chromium-gallium pairs. Each fine-structure line is split by hyperfine interaction with gallium-69 in this sample, which contains nonmagnetic chromium isotopes.

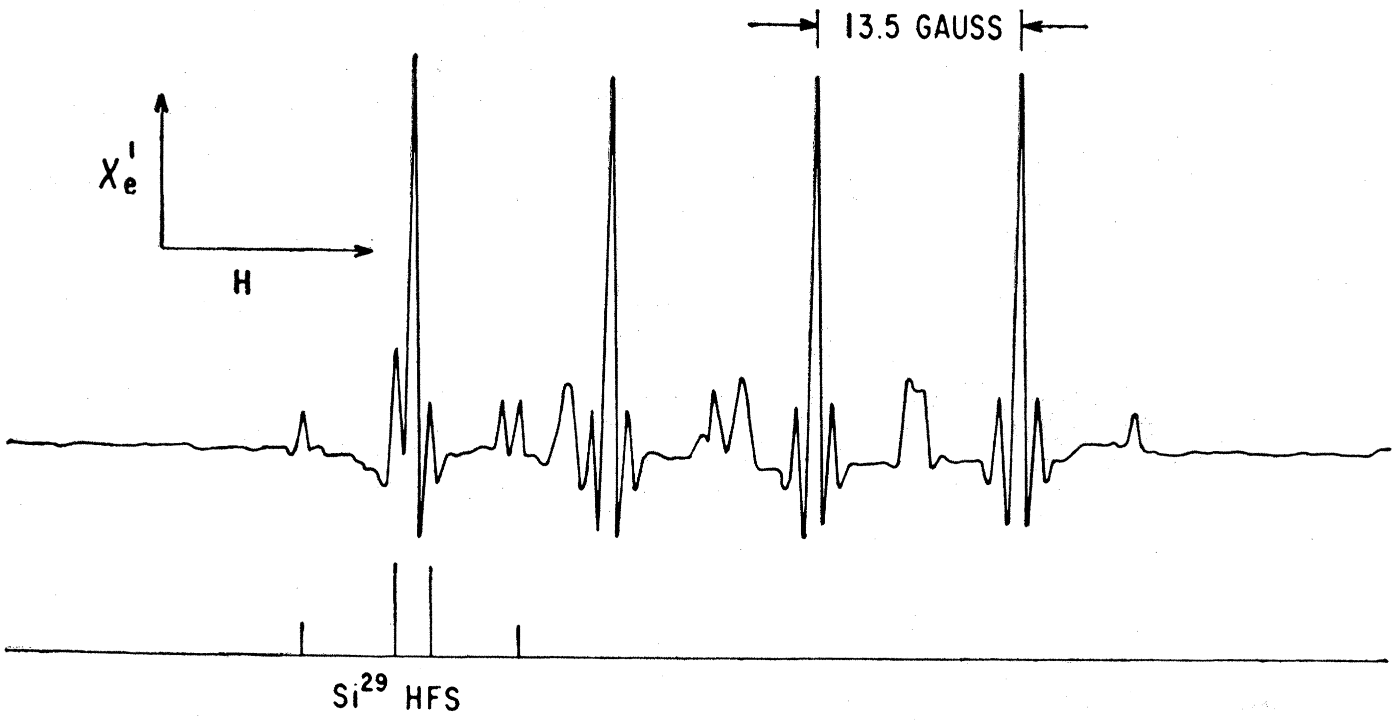


Fig. 7. Spectrum of substitutional Cr^0. The intensity of the inner silicon-29 lines shows that they arise from 12 equivalent positions for silicon-29 (the second-neighbor positions of Fig. 3).

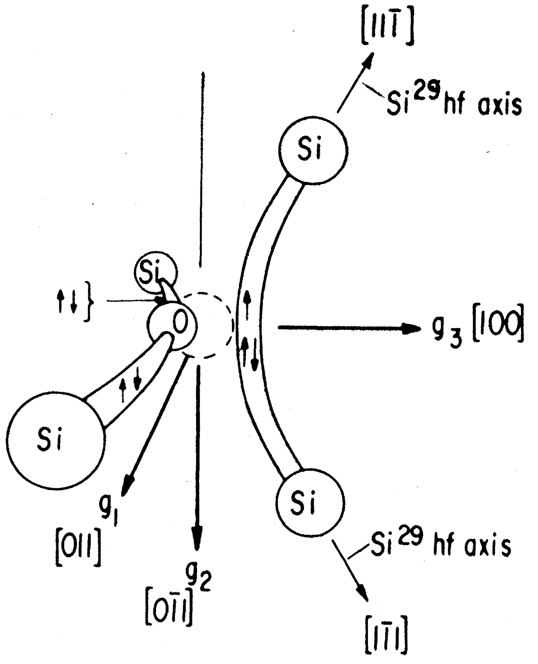


Fig. 8. The Si-*A* center, depicted as a vacancy trapped at an interstitial oxygen atom. The unpaired electron is in an orbit encompassing two silicon atoms. [After G. D. Watkins and J. W. Corbett (*15*)]

are in a crystalline environment of purely tetrahedral symmetry; there can be no second defect nearby. Consistent with this picture, the unpaired electrons show strong hyperfine interaction with but one nucleus, which can be indentified as chromium by its spin and magnetic moment.

Other experiments showed that transition metal ions tend to associate with other defects—in particular, with acceptor ions. For example, samples containing chromium and gallium initially showed a strong Cr^+ spectrum. However, when such samples were allowed to stand at room temperature, the intensity of the Cr^+ resonance decreased, while an entirely new spectrum appeared. The new spectrum, shown in Fig. 6, still originates from unpaired electrons of chromium. In other respects it is quite different. It shows additional hyperfine structure which has been identified as arising from a gallium nucleus. Moreover, the symmetry of the spectrum is lower than cubic, and from it one deduces that the chromium-gallium pairs are aligned along particular crystallographic directions.

Acceptor impurities such as gallium are known to be substitutional and immobile at room temperature. The ability of transition metal ions to diffuse through the lattice and associate with acceptors is strong evidence that they occupy interstitial sites. Additional evidence that this is the case was provided by experiments in which the transition metal ions were exposed to vacancies. (Vacancies can be produced, for example, by displacing lattice atoms with high-energy electrons.) After exposure to vacancies, new spectra were found for the transition metal ions. The symmetry of the patterns indicated that, again, the ions occupied sites of tetrahedral symmetry. However, ions in the new sites showed hyperfine interaction with silicon-29 in four nearest-neighbor positions and in 12 second-nearest-neighbor positions (see Fig. 7). This arrangement of neighbors is characteristic of substitutional sites but not of interstitial sites. Thus, vacancies are trapped by interstitial transition metal ions, which thereby become substitutional.

The detection of spin resonance for an increasing number of interstitial ions of the iron-group elements led to a model for their electronic structure. I will describe this model after a few introductory words about *d* orbitals.

A *d* electron has available to it five orbital states. It can be shown, on very general grounds, that in an environment of either octahedral or tetrahedral symmetry these states split into two groups, a doublet and a triplet, which have different energies. It is known that in ionic crystals the triplet is lower in energy than the doublet when the symmetry about the transition metal is octahedral, while it is higher in energy when the symmetry is tetrahedral.

One question to be answered in formulating a model for the electronic structure of 3*d*-group ions in silicon concerned the order of the triplet and the doublet states, since silicon is a covalent rather than an ionic crystal. A second question was whether each one-electron state of lower energy was filled with two electrons before any electrons entered the higher-energy one-electron states. A third question was the distribution of electrons between the 3*d* shell and the valence shell. There were two main types of experimental information to help in deciding these questions. One was the number of unpaired electrons, or, more precisely, the number of magnetic levels ions displayed through their resonance spectra. The second was the presence or absence of orbital degeneracy in the ground state of the ions; orbital degeneracy was revealed by its effect on resonance parameters, such as the *g* factor.

The basic model that evolved is essentially this: the triplet is lower in energy, but electrons enter the doublet before a second electron enters each triplet state. Moreover, all valence shell electrons of the ion are transferred to the 3*d* shell.

This model has been quite successful in accounting for qualitative features of the spectra. However, a quantitative look at resonance parameters has shown that the wave functions of the transition metal ions are not purely 3*d* functions. Rather, they are hybridized, in a fashion which is not yet clear, with orbitals of their silicon neighbors. Very recently resonance lines of the transition metal ions have been observed to split in an electric field (*10*). This splitting is related to the hybridization of orbitals (*11*), and future study of it may bring answers to some of the remaining questions.

Radiation Damage Centers

Profound changes in the properties of silicon crystals can be brought about by bombarding them with particles, such as electrons, which have been accelerated to such a high velocity that they are capable of displacing atoms from their normal lattice positions. The interest in studying damaged crystals arises in part from the desire to understand the properties of fundamental defects such as the vacant lattice site and the interstitial atom.

There have been extensive studies of the optical and electrical properties of damaged crystals (*12*). Until recently the observed effects were discussed in terms of vacancies and interstitials. Resonance measurements have shown, however, that these primary defects are unstable under common experimental conditions.

An important step in the understanding of radiation damage in silicon was the study by Bemski (*13*), and studies by Watkins and his collaborators (*14*), of resonant absorption associated with a center called the Si-*A* center. This center shows a large hyperfine interaction with silicon-29 occupying two positions. The magnitude of the interaction suggests that the unpaired electron occupies a broken-bond orbital involving these two positions. Broken-bond orbitals are to be expected around a vacancy. A further clue to the identity of the Si-*A* center was the observation that it can be produced in much higher concentration in crystals which contain a considerable amount of oxygen than in crystals which are essentially oxygen-free.

The model for the Si-*A* center which has evolved is depicted in Fig. 8. The center may be thought of as an interstitial oxygen atom which has trapped a lattice vacancy. Of the four silicon atoms adjacent to the vacancy, two bond to the oxygen, while the other two bond to each other. The unpaired electron is situated in an antibonding orbital involving the latter pair of silicon atoms.

Recent electrical and optical measurements on damaged silicon have confirmed the belief that results are sensitive to the presence or absence of oxygen. It is now a widely accepted view that vacancies are mobile in silicon below room temperature and that they tend to associate with oxygen impurities, as indicated by the resonance measurements.

A number of other resonant centers have been detected in damaged silicon crystals by Watkins and his collaborators (*14, 15*). In crystals containing the donor phosphorus but little oxygen the dominant center has been identified as a vacancy trapped adjacent to a phosphorus atom. Thus, vacancies will associate with a variety of impurities in silicon.

The resonance study of damaged silicon is still in progress. It now appears that the isolated vacancy is at long last available for study. It has been tentatively identified in crystals which were bombarded and maintained at low temperature to prevent it from moving (*15*).

Concluding Remarks

In studying silicon a number of specialized techniques have been coupled with standard spin resonance methods. Among these are electron-nuclear double resonance and examination of spectra in the presence of uniaxial stress, electric fields, or visible or infrared light. A great variety of defects have been detected and studied, including shallow donors, transition metal ions, and radiation damage centers. Impurities have been identified, and the nature of impurity sites has been clarified. Information has been obtained about fundamental properties of the host lattice and about whether impurities are substitutional or interstitial, about their electronic structure, and about the size and details of the orbits occupied by the unpaired electrons.

It is clear that, in the future, spin resonance techniques will be increasingly used for studying the more complicated chemical and biological systems. The characteristics of high sensitivity and high selectivity make spin resonance an ideal technique for monitoring elusive processes as well as for searching out new phenomena.

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