

Electron Paramagnetic Resonance of Iron in Indium Arsenide*

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The electron-paramagnetic-resonance spectrum of the $3d^5$ configuration of iron in cubic symmetry has been observed in iron-doped indium arsenide. The spin-Hamiltonian parameters describing this spectrum are $g=2.035\pm 0.002$ and $a=+(421\pm 1)\times 10^{-4}$ cm⁻¹. The inhomogeneously broadened line is approximately 130 G wide. A comparison is made with the Mössbauer effect of Fe⁵⁷ in InAs studied by Bemski and Fernandes. The results are discussed in terms of charge-transfer configuration admixtures introduced by Fidone and Stevens and elaborated by Watanabe and co-workers.

INTRODUCTION

THE properties of the S -state transition group ions Cr⁺, Mn²⁺, and Fe³⁺ as substitutional impurities in covalent crystals have become particularly interesting recently because of the theoretical studies of Watanabe and co-workers¹⁻⁴ and the experimental results for Fe³⁺ in ZnTe by Hensel.⁵ Iron impurities in cubic covalent crystals may exhibit three features as a result of covalency. The g shift is large and positive, the zero-field splitting is larger than in ionic crystals, and a large hyperfine interaction with neighboring nuclei in the crystal is often observed either as resolved structure or as an inhomogeneous broadening of the lines. The explanation for the large positive g shift was first proposed by Fidone and Stevens.⁶ They argued that in addition to considering interactions with excited states of the ion one must also consider interactions with charge-transfer states in which electrons or holes are transferred from the impurity to the neighbors of the impurity in the lattice.

Watanabe and co-workers have analyzed the effects of the admixture of such charge-transfer configurations on the g shift,^{1,2} zero-field splitting,^{1,3} and the ligand hyperfine structure^{1,4} of S -state ions in tetrahedrally coordinated covalent compounds. For iron they conclude that the primary effect arises from the transfer of an electron from the ligands to the impurity. The Coulomb attraction accentuates this effect if Fe³⁺ replaces a divalent ion in the crystal. The striking results of Hensel⁵ for Fe³⁺ in zinc telluride are illustrative of this. Hensel⁵ found a g shift which was positive and larger than any other observed for Fe³⁺ and a zero-field splitting which was larger than any other observed for Fe³⁺ and with the opposite sign from that observed in all other materials investigated. It therefore seems pertinent to study experimentally a number of other S -state impurities in II-VI and III-V compounds.

In III-V compounds, the $3d^5$ configuration of iron is neutral. The electron paramagnetic resonance (EPR) results for iron in III-V compounds are characterized by large positive g shifts, large positive a values, and wide inhomogeneously broadened lines. Previous results have been reported for iron in gallium phosphide⁷ and gallium arsenide.⁸ The EPR spectrum for iron in indium arsenide is reported below. The results are compared with similar $3d^5$ EPR spectra, with the Mössbauer-effect experiments on Fe⁵⁷ in indium arsenide reported by Bemski and Fernandes,⁹ and with the qualitative features of the theory of S -state ions.

RESULTS

Indium arsenide has the zinc blende crystal structure and a band gap of about 0.4 eV, smaller than any III-V compound semiconductor except InSb. Several pieces of a single crystal of InAs doped with iron to a concentration greater than 10^{-4} were examined at 1.3°K using an EPR spectrometer operating at 9.165 Gc/sec. The observed EPR spectrum can be interpreted as arising from a spin of $\frac{5}{2}$ in cubic symmetry and looks very similar to the one observed in iron-doped GaAs⁸ except that the lines are broader in InAs and the resolution is therefore poorer. The spin Hamiltonian for a spin of $\frac{5}{2}$ in cubic symmetry is

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} + (1/6)a[S_{\xi}^4 + S_{\eta}^4 + S_{\zeta}^4 - (1/5)S(S+1)(3S^2 + 3S - 1)],$$

where g is the spectroscopic splitting factor, β is the Bohr magneton, \mathbf{H} is the magnetic field, $3a$ is the zero-field splitting, S is the spin, and ξ , η , and ζ are the cubic axes of the crystal. The two experimentally determined parameters in the spin Hamiltonian, g and a , were obtained from data taken with the magnetic field in a $\langle 100 \rangle$ direction. The resultant values are $g=2.035\pm 0.002$ and $a=+(421\pm 1)\times 10^{-4}$ cm⁻¹. Data obtained when the magnetic field was in a $\langle 111 \rangle$ direction and

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¹ H. Watanabe (to be published).

² H. Watanabe, Bull. Am. Phys. Soc. 8, 439 (1963).

³ G. H. Azarbayejani, H. Watanabe, and C. Kikuchi, Bull. Am. Phys. Soc. 9, 38 (1964).

⁴ I. Chen (private communication in Ref. 1).

⁵ J. C. Hensel, Bull. Am. Phys. Soc. 9, 244 (1964).

⁶ I. Fidone and K. W. H. Stevens, Proc. Phys. Soc. (London) 73, 116 (1959).

⁷ H. H. Woodbury and G. W. Ludwig, Bull. Am. Phys. Soc. 6, 118 (1961).

⁸ M. de Wit and T. L. Estle, Bull. Am. Phys. Soc. 7, 449 (1962); R. Bleckrode, J. Dieleman, and H. J. Vegter, Philips Res. Rept. 17, 513 (1962); B. Goldstein and N. Almeleh, Appl. Phys. Letters 2, 130 (1963); M. de Wit and T. L. Estle, Phys. Rev. 132, 195 (1963).

⁹ G. Bemski and J. C. Fernandes, Phys. Letters 6, 10 (1963).

the observed angular dependence are consistent with these values. The sign of a was determined from relative intensities. The linewidths are $125 \pm 3G$ for the field parallel to $\langle 100 \rangle$ and $132 \pm 3G$ for the field along $\langle 111 \rangle$.

DISCUSSION

The EPR results for iron in InAs are exactly analogous to the results in GaP⁷ and GaAs.⁸ The iron is observed with a $3d^5$ configuration and is in cubic symmetry. Thus the iron must substitute for the indium contributing three electrons to the bonds as does the indium. The remaining five outer electrons of the neutral center are in the $3d$ shell. The cubic crystalline field is weak enough so that Hund's rule is obeyed and an S state with a spin of $\frac{5}{2}$ results. The iron site retains the cubic symmetry of the indium site.

The EPR results and their explanation are apparently in disagreement with the Mössbauer-effect experiments on Fe⁵⁷ in InAs reported by Bemski and Fernandes.¹⁰ Using an Fe⁵⁷ emitter in InAs at room temperature they obtained three pieces of information. They measured an isomer shift¹¹ of $+0.051 \pm 0.004$ cm/sec with respect to a stainless-steel absorber and a quadrupole splitting of 0.045 cm/sec. In addition, their results were independent of the position of the Fermi level. Norem and Wertheim observed very similar results in Ge.¹²

The isomer shift observed by Bemski and Fernandes⁹ is very close to that of Fe³⁺ in ionic crystals.¹³ A decrease in the number of $3d$ electrons will increase $\sum_n |\psi_{ns}(0)|^2$ primarily because of the considerable shielding effect which the $3d$ electrons have on the $3s$ electrons.¹³ The effects of covalency on the isomer shift have been examined by many workers.^{13,14} The varying amounts of $3d$ orbitals in the bonding and antibonding orbitals and the possibility of admixing $4s$ or higher ns orbitals into the occupied orbitals, makes conclusions even of the sense of the covalency effect difficult. Thus, the magnitude of the isomer shift indicates only that the number of $3d$ electrons does not differ from five by an appreciable amount.

The observations by Bemski and Fernandes⁹ of a doublet structure is presumed to arise because of a quadrupole splitting. Such a splitting implies a local symmetry lower than cubic.¹⁵ Since the crystal is cubic, this implies a Jahn-Teller distortion¹⁶ or defect association. A Jahn-Teller distortion is not expected for the $3d^5$ configuration but could be quite significant for $3d^4$ or $3d^6$. A Jahn-Teller distortion would probably lead to a large quadrupole splitting, possibly larger than the one observed. Defect association would cause a quadrupole splitting for any configuration, although the splitting would probably be smaller for $3d^5$ than for $3d^4$ or $3d^6$. In order for only one type of iron to be observed, almost complete association would be required. This suggests that the associated defect is oppositely charged to the original cobalt impurity in the InAs. Close association of a charged defect would lead to a large quadrupole splitting even for the $3d^5$ configuration.

The lack of a dependence on the Fermi level suggests that a neutral center is being observed by the Mössbauer emission. Since ejection of Auger electrons after the electron capture is very probable,¹⁷ the center is not likely to be negatively charged even if the cobalt center were initially. If it is positively charged it will have a high cross section for trapping free electrons and may even capture electrons from the valence band. However, even in the n -type material the neutral center may not be able to trap an additional electron within the 10^{-7} sec lifetime of Fe^{57m}.

It thus does not appear likely that the center observed in the Mössbauer emission⁹ is the same as the center observed by EPR. It seems more likely that some complexity arising because a Co⁵⁷ emitter was used is responsible for the difference. The most likely possibility of those mentioned is defect association. However, the evidence at present does not seem at all conclusive on this point. This can best be cleared up by learning more about the nature of cobalt impurities in InAs and other III-V compounds.

A considerable amount of information is now available on the properties of Cr⁺, Mn²⁺, and Fe³⁺ in covalent crystals.¹⁸ For purposes of comparison, the results for Fe($3d^5$) in covalent crystals are reproduced in Table I. The qualitative features of the table can be summarized

¹⁰ See Ref. 9. The authors of Ref. 9 attribute the $3d^5$ configuration of iron to a negatively charged center, whereas it is neutral as indicated above. Our argument was based on a covalent description of the center but the conclusion is quite general and can be obtained for an ionic description or one of mixed character.

¹¹ The isomer shift results because of slight variations in the Coulomb interaction between the electrons and the nucleus due to the finite nuclear size. The isomer shift is the difference in the transition energy for the emitter and the absorber because of their different chemical forms and is proportional to the difference in total s -electron densities at the nuclei, $\Delta \sum_n |\psi_{ns}(0)|^2$. For a recent discussion of the isomer shift see D. A. Shirley, *Rev. Mod. Phys.* **36**, 339 (1964).

¹² P. C. Norem and G. K. Wertheim, *Phys. Chem. Solids* **23**, 1111 (1962).

¹³ L. R. Walker, G. K. Wertheim, and V. Jaccarino, *Phys. Rev. Letters* **6**, 98 (1961).

¹⁴ G. K. Wertheim and R. H. Herber, *J. Chem. Phys.* **36**, 2497 (1962); J. Danon, *ibid.* **39**, 236 (1963); V. Jaccarino and G. K. Wertheim, in *The Mössbauer Effect*, edited by D. M. J. Compton and A. H. Schoen (John Wiley & Sons Inc., New York, 1962), p. 260.

¹⁵ Although a quadrupole interaction occurs in free space if $S > 1$ and two linearly independent interactions are allowed by cubic symmetry, all such interactions depend quadratically on electronic spin operators and therefore produce no splitting under circumstances when the magnetic-dipole hyperfine splitting is missing. The absence of both types of hyperfine structure occurs because of the rapid electronic relaxation in cubic symmetry. Studies of the temperature dependence might give more information if the relaxation processes become sufficiently slow. A closely related example of this is G. K. Wertheim and J. P. Remeika, *Phys. Letters* **10**, 14 (1964).

¹⁶ H. A. Jahn and E. Teller, *Proc. Roy. Soc. (London)* **A161**, 220 (1937).

¹⁷ H. Pollak, *Phys. Stat. Solidi* **2**, 720 (1962).

¹⁸ See, for example, J. Schneider, S. R. Sircar, and A. Räuber, *Z. Naturforsch.* **18a**, 980 (1963); H. Kimmel, *ibid.* **18a**, 650 (1963); R. S. Title, *Phys. Rev.* **133**, A1613 (1964).

TABLE I. Electron paramagnetic resonance parameters of Fe ($3d^5$) in covalent crystals.

Host crystal	Symmetry	Temp. °K	Freq. Gc/sec	g factor	a in units of 10^{-4} cm $^{-1}$	Linewidth in G	Reference
InAs	T_d	1.3	9	2.035 ± 0.002	$+421 \pm 1$	$125 \pm 3(100)$ $132 \pm 3(111)$	this paper
GaAs	T_d	1.3	9	2.0462 ± 0.0006	$+339.7 \pm 0.3$	54 ± 2	a
GaP	T_d	10		2.025	+390		b
ZnTe	T_d		54.7	2.0967 ± 0.0005	-2613 ± 20		c
ZnS	T_d	77	9	2.0194 ± 0.0003	128 ± 1	0.7	d
		77	9	2.019 ± 0.001	127.4 ± 0.5		e
CdS	C_{3v}	4.2		2.01	≈ 60		f
ZnO	C_{3v}	295	12	2.0060 ± 0.0005	39 ± 5	4	g
		300	9	2.0062 ± 0.0002	41 ± 3		h

^a Reference 8.

^b Reference 7.

^c Reference 5.

^d A. Rüber and J. Schneider, Z. Naturforsch. 17a, 266 (1962).

^e R. S. Title, Phys. Rev. 131, 623 (1963).

^f J. Lambe, J. Baker, and C. Kikuchi, Phys. Rev. Letters 3, 270 (1959).

^g W. M. Walsh, Jr. and L. W. Rupp, Jr., Phys. Rev. 126, 952 (1962).

^h J. Schneider, Z. Naturforsch. 17a, 189 (1962).

by saying that the g shift is large and positive, the zero-field splitting is large, and the linewidths in III-V compounds are large and produced by inhomogeneous broadening. These features can be understood in a qualitative way following the suggestion of Fidone and Stevens,⁶ and Watanabe and co-workers.¹⁻⁴ Because of the high degree of covalency one must take into account not only excited states of the impurity atom or ion itself but, in addition, states involving neighbors to the impurity. These charge-transfer states involve configurations in which an electron is transferred either from the impurity to the neighbors or from the neighbors to the impurity. The latter transfer is to be expected in the case of iron $3d^5$ because of the large positive charge of the ion. As was first pointed out by Fidone and Stevens,⁶ and analyzed in more detail by Watanabe,^{1,2} such a transfer leads to a positive g shift which may be several times larger than the g shift due to the excited states of the ion itself. Azarbayejani *et al.*^{1,3} have shown that this effect can also lead to contributions to the zero-field splitting parameter a . Such calculations are extremely complex and even discerning the qualitative features of the results is very difficult. The most surprising result is probably that of the large negative a value observed for Fe³⁺ in zinc telluride by Hensel.⁵ Presumably, such a result arises because there are numerous terms contributing to a , some positive and some negative, whose relative magnitudes vary with the crystal and impurity. The results for indium arsenide are quite comparable to those for iron in other III-V compounds and are characterized by a large positive g shift, a large positive a value and a large linewidth. Neither the g shift nor a value is as large as that for iron in zinc telluride presumably because iron is neutral in a III-V compound whereas it has a net positive charge in zinc telluride.

It is seen that no simple relationship between the g shift and the zero-field splitting parameter exists for the III-V compounds. The large linewidth for iron in III-V compounds results from unresolved hyperfine structure due to the interaction of the $3d$ electrons with the nuclei of the host lattice in the vicinity of the impurity. Although a detailed experimental description of this interaction would require ENDOR¹⁹ studies it is interesting to note that the ratio of the linewidth observed in gallium arsenide and indium arsenide is approximately equal to the ratio of the weighted means of the magnetic moments of the gallium and indium isotopes. Thus if the hyperfine interaction is predominantly due to the next-nearest neighbors, the required delocalization of the $3d$ electrons is roughly constant. This would be consistent with the results observed for manganese in the II-VI compounds.^{18,20} The next-nearest-neighbor hyperfine structure is the only one observed and it is proportional to the nuclear moment divided by the spin and would indicate roughly constant delocalization. In fact, the results obtained for the hyperfine splitting of iron in the III-V compounds from the linewidth, if attributed to the twelve next-nearest neighbors, are comparable to those for manganese in the II-VI compounds.

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¹⁹ ENDOR stands for electron nuclear double resonance. See G. Feher, Phys. Rev. 103, 834 (1956).

²⁰ G. W. Ludwig and M. R. Lorenz, Phys. Rev. 131, 601 (1963).