

<sup>6</sup>F. R. Gamble, J. H. Osiecki, M. Cais, R. Pisharody, F. J. DiSalvo, and T. H. Geballe, *Science* **174**, 493 (1971).

<sup>7</sup>E. Ehrenfreund, A. C. Gossard, F. R. Gamble, and T. H. Geballe, *J. Appl. Phys.* **42**, 1491 (1971).

<sup>8</sup>K. Murakawa, *Phys. Rev.* **98**, 1285 (1955).

<sup>9</sup>The powder particles are typically in the form of flakes. Depending on particle size and packing and the manner in which the sample was cooled, substantial orientation of the flakes was sometimes achieved, with the *c* axis parallel to the external magnetic field. In these cases we could also measure  $K_{||}$ . This was achieved in the NbS<sub>2</sub> sample but not in our NbS<sub>2</sub>(Py)<sub>1/2</sub> sample, probably because of shape differences.

<sup>10</sup>W. H. Jones, Jr., T. P. Graham, and R. G. Barnes, *Phys. Rev.* **132**, 1898 (1963).

<sup>11</sup>In the absence of (anti-) shielding calculations for Nb, use was made of Murakawa's (Ref. 8) and Burns's [G. Burns, *J. Chem. Phys.* **31**, 1253 (1959)] estimates for  $R$  and  $\gamma_{\infty}$ , respectively.

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<sup>13</sup>See, for example, M. H. Cohen and F. Reif, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5, p. 360.

<sup>14</sup>A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1965), Vol. IIA, p. 291.

<sup>15</sup>R. Huisman, R. de Jonge, C. Haas, and F. Jellinek, *J. Solid State Chem.* **3**, 56 (1971).

<sup>16</sup>L. G. Wesson, *Tables of Electric Dipole Moments* (MIT Press, Cambridge, Mass., 1949), p. 23.

<sup>17</sup>A qualitatively similar situation occurs in transition-metal hydrides. Bonding between hydrogen levels and conduction-band states induces bonding states far below the Fermi energy. [S. Alexander (private communication); see also, D. E. Eastman, J. K. Cashion, and A. C. Switendick, *Phys. Rev. Letters* **27**, 35 (1971); and E. Ehrenfreund, Ph.D. thesis (The Hebrew University, Jerusalem, Israel, 1970) (unpublished).]

## Electron-Spin Resonance of Rare-Earth Ions in the Actinide Cubic Metal Th<sup>†</sup>

D. Davidov, R. Orbach, C. Rettori,\* D. Shaltiel,† and L. J. Tao  
*Department of Physics, University of California, Los Angeles, California 90024*

and

B. Ricks§  
*Department of Physics, University of California, San Diego, California 92037*  
(Received 25 August 1971)

The electron-spin resonance of Gd, Er, and Dy of nominal concentrations between 40 and 3250 ppm in the actinide metal Th is reported. The temperature dependence of the linewidth yields values for the exchange coupling  $J_{fs}$  between the rare-earth localized moment and the conduction electrons. We find  $J_{fs}$  to be almost independent of the  $4f$  occupation number, in agreement with the values of  $J_{fs}$  obtained previously by others from superconducting-transition-temperature measurements in the same alloys.

### I. INTRODUCTION

We wish to report the observation of the electron-spin resonance (ESR) of the rare earths Er, Dy, and Gd in the cubic actinide metal thorium (the observation of Er in Th has been reported previously).<sup>1</sup> The temperature dependence of the linewidth, as well as the sign of the  $g$  shift, yield values for the localized-moment-conduction-electrons exchange coupling  $J_{fs}$ . We find that  $J_{fs}$  is positive, and almost equal for the three solutes. This behavior can be understood using the usual model of a total exchange interaction generated from a positive atomic-like contribution expected to be nearly independent of the  $4f$  occupation number, and a (negative) covalent mixing contribution which does vary across the rare-earth series, but which is expected to be small in comparison to the atomiclike term.<sup>2</sup> The values of  $J_{fs}$  so derived are in agreement with the

values of  $J_{fs}$  obtained by fitting the Abrikosov-Gorkov model<sup>3</sup> with the experimental decrease of the superconducting transition temperature  $T_c$  of Th when alloying with the same rare earths, as measured by Guertin.<sup>4</sup>

### II. SAMPLE PREPARATION

The ESR measurements were conducted at 3-cm wavelength and as a function of temperature in the liquid-helium range ( $1.4 \leq T \leq 4.2$  °K). The apparatus and technique of measurement are described elsewhere.<sup>5</sup>

The samples were arc melted from thorium of 99.99% purity and rare earths of minimum 99.9% purity in an argon atmosphere. After melting, the samples were prepared by two different methods:

(i) *Rapid quenching*. The rapid quenching was accomplished by splattering the molten alloys on a cold copper wall with a jet of He gas. The "splat-

TABLE I. Nominal concentrations of the rare-earth elements (in ppm) in thorium for samples whose ESR was observed.

Gd	Dy	Er
1300	3250	2600
330	860 <sup>a</sup>	570
330 <sup>a</sup>	450	570 <sup>a</sup>
95	180 <sup>a</sup>	230
95 <sup>a</sup>	180	230 <sup>a</sup>
		100
		100 <sup>a</sup>
		40

<sup>a</sup>Splat-cooled samples.

cooled" samples formed small thin pieces which were directly used in the ESR measurements.

(ii) *Filing of the arc-melted alloys into powder.*

This was accomplished by filing the samples either in a glove box in an argon atmosphere, or in air. It was found that the experimental results were the same for both cases, indicating that oxidation is negligible. The nominal concentration of the rare-earth element in the sample varied from 3250 to 40 ppm. The list of samples whose ESR was observed is given in Table I.

### III. EXPERIMENTAL RESULTS

#### A. Th:Gd

The ESR spectrum for Th:Gd is a single line with a metallic resonance shape. The peak

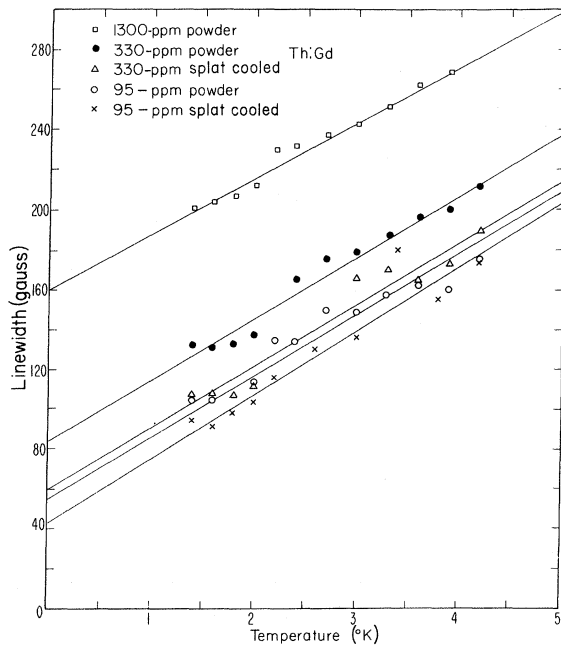


FIG. 1. Electron-spin-resonance linewidth of Gd in Th:Gd as a function of temperature.

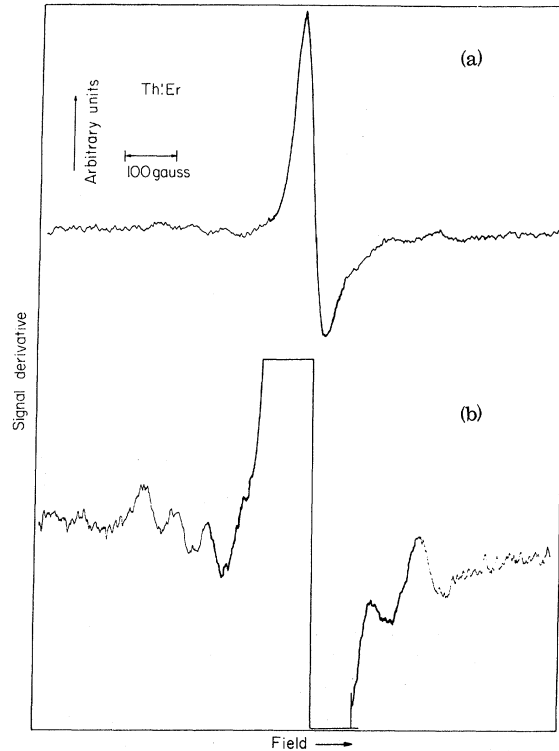


FIG. 2. Electron-spin-resonance spectrum of splat-cooled sample of 230-ppm Er in Th at 1.4 °K. The central line corresponds to Er isotope with  $I=0$ . The surrounding satellites [they are clearly seen in the enhanced spectrum (b)] arise from Er isotope with  $I=\frac{1}{2}$ .

amplitude ratio<sup>6</sup>  $A/B$  equals, approximately, 2.7. The field for resonance, for all Gd concentrations, is appropriate to a  $g$  value of  $2.07 \pm 0.01$ . The temperature dependence of the linewidth can be fitted to the formula  $a + bT$  (Fig. 1) where  $b$  is concentration independent (at low concentrations) and equal to  $31 \pm 5$  G/deg. This behavior indicates that the Th:Gd alloy is probably not bottlenecked.<sup>7</sup> The residual linewidth  $a$  depends on Gd concentration as well as on the method of sample preparation. It is clearly seen from Fig. 1 that decreasing the Gd concentration decreases  $a$ . At the same Gd concentration the values of  $a$  are smaller for the splat-cooled samples than for the powdered samples. This behavior is also observed for Th:Er and Th:Dy alloys.

#### B. Th:Er

The spectrum for the 230-ppm Th:Er splat-cooled sample is exhibited in Fig. 2. It is of the same character as that of Ag:Er and Au:Er published previously.<sup>8</sup> A strong "central" line (corresponding to Er isotopes with  $I=0$ ) is surrounded by several hyperfine line satellites (corresponding

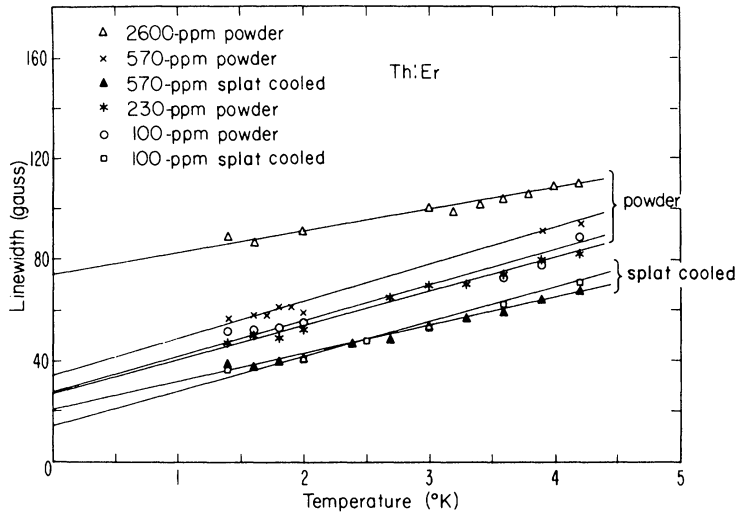


FIG. 3. Electron-spin-resonance linewidth of Er ( $I=0$  isotope) in Th:Er as a function of temperature.

to the  $\text{Er}^{167}$  isotope with  $I = \frac{7}{2}$ . Using the second-order hyperfine splitting formula, we find the hyperfine constant  $A^{167}$  to be  $75 \pm 2$  G. The resonance field of the central ( $I=0$ ) line corresponds to a  $g$  factor of  $6.84 \pm 0.05$ , appropriate to a  $\Gamma_7$  crystal-field ground state.<sup>8</sup> The slope of the linewidth of the central line versus temperature (Fig. 3) is  $b = 14 \pm 3$  G/deg. The values for  $a$  exhibit the same dependence on concentration and sample preparation as for Th:Gd.

#### C. Th:Dy

The ESR spectra of Th:Dy exhibit the same character as the spectra of Ag:Dy published previously.<sup>9</sup> A single isotropic line was observed, with the field for resonance appropriate to a  $g$  value of  $7.61 \pm 0.1$ . This value is very close to that expected for the cubic  $\Gamma_7$  state of the Dy  $4f^9$  configuration ( $g = 7.55$ ). The observed linewidth increases linearly with temperature. The standard deviation, however, is larger than in the Th:Er and Th:Gd samples (Fig. 4). The average value of  $b$  is equal to  $33 \pm 7$  G/deg. The line shape for all the samples measured was appropriate to a localized moment in a metal with a peak amplitude ratio  $A/B$ , varying between 2 and 3. One expects<sup>9</sup> additional resonance splittings arising from the hyperfine interactions between the  $\Gamma_7$  electronic state and the nuclear isotopes  $\text{Dy}^{161}$  ( $I = \frac{5}{2}$ ) and  $\text{Dy}^{163}$  ( $I = \frac{5}{2}$ ). This hyperfine splitting is not resolved because of the low relative intensity of the hyperfine lines, as well as the large residual width (relative to the expected hyperfine splittings:  $A^{161} = 57$  G,  $A^{163} = 80$  G). Numerical calculations show that for a Lorentzian linewidth of 200 G the  $\text{Dy}^{161}$  and  $\text{Dy}^{163}$  isotopes increase the linewidth by 20%. This partly explains the larger residual linewidth of Th:Dy relative to Th:Er (both Dy and Er have a doublet ground state).

#### IV. ANALYSIS OF EXPERIMENTAL RESULTS

The exchange interaction of the type  $J_{fs}(\vec{S} \cdot \vec{s})$  between the localized spin  $\vec{S}$  and the conduction-electron's spin  $\vec{s}$ , leads to a thermal broadening of the linewidth given by the formula<sup>1</sup>

$$b = \frac{\pi g k_B}{\mu_B} \left( \frac{g_J - 1}{g_J} \right)^2 (J_{fs} \eta)^2 \frac{K(\alpha)}{(1 - \alpha)^2}, \quad (1)$$

where  $k_B$  is the Boltzmann factor,  $\mu_B$  is the Bohr magneton,  $g_J$  is the Landé  $g$  factor,  $\eta$  is the "bare" density of states for one spin direction at the Fermi level, and  $\alpha$  is the enhancement factor. Both  $\alpha$

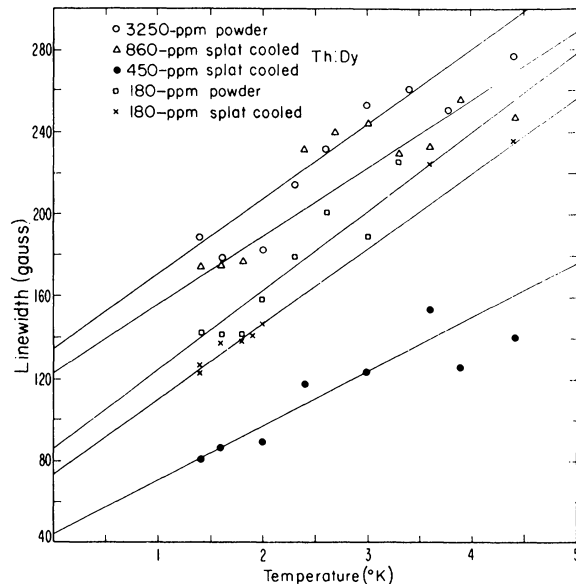


FIG. 4. Electron-spin-resonance linewidth of Dy in Th:Dy as a function of temperature.

TABLE II. Comparison of  $J_{fs}$  determined from the ESR experiment [for  $K(\alpha)=0.4$ ] and the values of  $J_{fs}$  determined from measurements on the suppression of the superconducting transition temperature, using the Abrikosov-Gorkov (AG) formula.

	$b$ (G/deg)	$g$ value expt	$J_{fs}$ (eV)	$\Delta g$	$\Delta T_c/\Delta c$ (°K/at. % rare earth)	$J_{fs}$ (eV)	$\Delta g$
			ESR $K(\alpha)=0.4$	calc $K(\alpha)=0.4$		AG	expt
Th: Gd	31 ± 5	2.07 ± 0.015	+0.042	0.055	2.7	0.045	+0.08 ± 0.015
Th: Er	14 ± 3	6.84 ± 0.05	+0.046	0.077	0.2	0.030	+0.07 ± 0.05
Th: Dy	33 ± 7	7.61 ± 0.1	+0.044	0.11	0.5	0.030	+0.06 ± 0.1

<sup>a</sup>Relative to the  $g$  value in insulators:  $g_{Gd}=1.993$ ;  $g_{Er}=6.77$ ;  $g_{Dy}=7.55$ .

and the function  $K(\alpha)$  are defined by Narath and Weaver<sup>10</sup> and by Shaw and Warren.<sup>11</sup>

Following Maple<sup>12,13</sup> we can estimate the various quantities appearing in Eq. (1). The value  $\eta$  can be determined from specific-heat measurements according to the relation

$$\gamma_e = \frac{2}{3} \pi^2 k_B^2 \eta (1 + \lambda). \quad (2)$$

Here,  $\lambda$  is the electron-phonon mass enhancement, which we estimate using McMillan's strong-coupling model.<sup>14</sup> We find  $\lambda=0.53$ . The specific-heat parameter  $\gamma_e$  was measured experimentally<sup>15</sup> to be  $\gamma_e=4.3$  mJ/mole deg<sup>2</sup>. Using Eq. (2), we find  $\eta=0.55$  states/eV atom spin.

Susceptibility measurements, corrected for core and diamagnetism contributions,<sup>13</sup> yield a value of  $\chi_e=10^{-4}$  emu/mole for the spin susceptibility of the conduction band.<sup>16</sup> The density of states appropriate to this value,  $\eta_x$  (calculated using the free-electron model), is much larger than the value of  $\eta$  obtained from specific-heat data. We attribute this discrepancy to exchange enhancement of the conduction-electron susceptibility. Using the relation  $\chi_e=2\mu_B^2 \eta/(1-\alpha)$  we find  $\alpha=0.6$ . Values of  $K(\alpha)$ , as a function  $\alpha$ , have been calculated by various authors.<sup>10,11</sup> For the case of alkali metals, Shaw and Warren<sup>11</sup> calculate  $K(\alpha)=0.45$  for  $\alpha=0.6$ , while the calculation of Narath yields  $K(\alpha)=0.6$ . This difference in  $K(\alpha)$  results from different assumptions about the character of the electron-electron interaction, as well as its  $q$  dependence. It has been stressed by Shaw and Warren<sup>11</sup> that  $K(\alpha)$  is very sensitive to the latter property.

Substituting the appropriate values of  $g$ ,  $g_J$ ,  $\alpha$ ,  $\eta$ , and  $K(\alpha)=0.4$  in Eq. (1), one can compute the absolute value of the exchange interaction  $J_{fs}$ . The sign of  $J_{fs}$  is determined as follows.

For Er and Dy, the cubic  $\Gamma_7$  ground states yield theoretical  $g$  values of 6.77 and 7.55, respectively. The  $g$  value of Gd in nonmetallic hosts is 1.993 ± 0.005. The  $g$  values obtained experimentally for the Th alloys, however, are slightly larger (more positive), indicating positive values for  $J_{fs}$  for all the three alloys. The derived values of  $J_{fs}$  are listed in Table II.

Using the values of  $J_{fs}$  determined above [taking  $K(\alpha)=0.4$ ], one can calculate the  $g$  shift due to the

exchange interaction with the conduction electrons according to the formula

$$\Delta g = g \frac{g_J - 1}{g_J} J_{fs} \eta \frac{1}{1 - \alpha}. \quad (3)$$

The calculated  $g$  shift can explain (within the limits of experimental error) the observed  $g$  values for Th:Er and Th:Dy (Table II). However, Eq. (3) cannot account for the large  $g$  shift ( $\Delta g=0.08$ ) obtained experimentally for Th:Gd (the experimental error in  $g$  for Gd is ±0.015, as compared to ±0.05 and ±0.08 for Er and Dy, respectively).

The deviation of the experimental  $g$  shift of Th:Gd (or, perhaps, even for Th:Er and Th:Dy) relative to the calculated exchange-shifted value can be attributed to two possible reasons:

(i) An inappropriate choice of  $\alpha$  or  $K(\alpha)$ . The value of  $\alpha$  was determined macroscopically by taking the ratio of the corrected susceptibility to the specific heat. However, the effective value of  $\alpha$  may be different microscopically if there is a local enhancement of the susceptibility in the immediate vicinity of the paramagnetic ions. Narath and Weaver<sup>17</sup> have indicated that the value of  $\alpha$  of the impurity atom determined microscopically (by NMR) may be different from the value of  $\alpha$  of the host atom determined macroscopically. There may also be an error in the determination of  $K(\alpha)$ , since this parameter is very sensitive to the  $q$  dependence of the electron-electron interaction and may, therefore, be completely different for Th than for other materials, for the same  $\alpha$ .

(ii) An additional positive contribution to the  $g$  shift which does not originate from the exchange interaction (e.g., the spin-orbit coupling of the host). Such a contribution has been anticipated previously for Au:Gd.<sup>18</sup>

Should we assume that the  $g$  shift ( $\Delta g=0.08$ ) observed experimentally for Th:Gd originates from the exchange interaction alone, we can calculate  $K(\alpha)$  and  $J_{fs}$  from Eqs. (1) and (3) [and thus, determine these values independent of previous calculations of  $K(\alpha)$ ]. It is found in this manner that  $K(\alpha)=0.21$ . The value of  $J_{fs}$  obtained for Th:Gd is 0.058 eV, to be compared to 0.042 eV which would be obtained for  $K(\alpha)=0.4$ ; the difference is less than 40%.

It is of great interest to compare these values of

$J_{fs}$  with those obtained by means of other experimental techniques. When small amounts of rare-earth impurities are alloyed with Th metal, the critical superconducting temperature of the latter is reduced appreciably from its pure value of  $T_c = 1.4$  °K. This behavior has been interpreted in terms of the Abrikosov-Gorkov pair-breaking theory.<sup>3</sup> At low paramagnetic-ion concentrations, the transition temperature  $T_c$  is depressed linearly with concentration. In the absence of crystal-field splittings, it is given by the formula<sup>3,19</sup>

$$\left| \frac{\Delta T_c}{\Delta c} \right| = J_{fs}^2 (g_J - 1)^2 \eta J(J+1) \frac{\pi^2}{8k_B}, \quad (4)$$

where  $c$  is the concentration. The measured values<sup>4</sup> of  $\Delta T_c/\Delta c$  are listed in Table II. From (4), one can extract values of  $J_{fs}$  (these are also listed in Table II, column 6) which lie within 30% of those determined by magnetic resonance techniques (Table II, column 3). If, however, one goes to the opposite extreme, and assumes a very large crystal-field splitting such that only the  $\Gamma_7$  ground state is important for Dy and Er, the equivalent to (4) would yield values of 0.048 and 0.045 eV for  $J_{fs}$  in Th:Dy and Th:Er, respectively. These values are closer to the ESR values found in our work (column 3 of Table II) than those generated by (4). Clearly, the real situation lies somewhere between these extremes. Fulde *et al.*<sup>20</sup> have examined the intermediate case. States at energies much greater

than  $T_c$  can contribute to a reduction in  $T_c$  by virtue of pair-breaking off-diagonal ("Van Vleck") exchange-induced transitions. Unfortunately, no information is available for the magnitude of the crystal-field splitting in Th, so that application of this theory is not possible. Our two extremes bracket the result, and when accurate values are known for the crystal-field parameters, the measured  $\Delta T_c/\Delta c$  can be used to obtain  $J_{fs}$  accurately.

An examination of the ESR results for  $J_{fs}$  (column 3 of Table II) demonstrates an independence of the  $4f$  occupation number. It should be stressed that near independence of the exchange interaction on the  $4f$  occupation number has been obtained previously in LaAl<sub>2</sub>,<sup>19</sup> as well as for rare earths (Gd, Er) in Au<sup>8,18</sup> and in Rh.<sup>21</sup> This independence can be understood from the fact that  $J_{fs}$  arises from (i) a (positive) atomiclike contribution, expected to be nearly independent of  $4f$  occupation number<sup>22</sup> and (ii) a negative covalent mixing contribution<sup>22</sup> which is believed to be small because of the stability of the Er, Dy, and Gd  $4f$  shells. The measured (positive) sign of  $J_{fs}$  is consistent with this argument.

In conclusion, we have demonstrated that the magnitudes of the exchange interaction  $J_{fs}$  of dilute alloys of Er, Dy, and Gd in Th, derived both from resonance and suppression of  $T_c$  measurements, are in agreement. We also confirm the near independence of  $J_{fs}$  on the  $4f$  occupation number.

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\*On leave from the Department of Physics, University of Buenos Aires, Argentina.

<sup>‡</sup>On leave from the Hebrew University, Department of Physics, Jerusalem, Israel.

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PHYSICAL REVIEW B

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## Absolute Spin Susceptibilities and Other ESR Parameters of Heavily Doped *n*-Type Silicon. I. Metallic Samples\*

J. D. Quirt<sup>†</sup> and J. R. Marko

*Department of Physics, University of British Columbia, Vancouver 8, B. C., Canada*

(Received 16 August 1971)

Results are presented for the measured electron spin resonance (ESR) spin susceptibilities of "metallic" phosphorus-doped silicon with  $N_D \geq 1 \times 10^{19}$  donors/cm<sup>3</sup>. These results agree closely for the case of  $N_D \gtrsim 4 \times 10^{18}$  donors/cm<sup>3</sup> with values calculated on the basis of a "rigid-band" model of noninteracting Pauli electrons. Evidence for a non-Pauli temperature-dependent-susceptibility component was found in the lower portion of our sample-concentration range. Static-susceptibility data are used together with our results to obtain the diamagnetic susceptibility which exhibits a concentration dependence consistent with the predictions of Kjeldaas and Kohn. Measurements of  $g$  values and linewidths are presented as evidence for the proposal that the Fermi level enters the host conduction band at a concentration  $N_D \approx 2 \times 10^{19}$  donors/cm<sup>3</sup>. These data are also used to verify Elliot's theory of impurity-scattering spin relaxation and to demonstrate  $g$ -value anisotropies characteristic of the silicon conduction band.

### I. INTRODUCTION

In a previous publication<sup>1</sup> we have presented relative magnetic-spin-susceptibility data for silicon samples having phosphorus impurity concentrations  $N_D$  near to or in excess of  $N_D^c \sim 3 \times 10^{18}$  donors/cm<sup>3</sup>. The critical donor impurity concentration  $N_D^c$  has been associated<sup>2</sup> with a semiconductor-metal or "Mott" transition in these materials. Our susceptibility measurements indicated the existence of qualitative differences in the concentration and temperature dependences of samples with concentrations above and below  $N_D \sim 10^{19}$  donors/cm<sup>3</sup>, respectively. For the purposes of the present discussion and because of the details of these dependences, we have designated these concentration regions as "metallic" and "impurity banded," respectively. This classification is similar to that previously proposed by Holcomb and Alexander<sup>2</sup> based on the assumption that an "impurity banded" to "metallic" transition occurs when the Fermi energy enters the normal conduction band of the host lattice.

We have now extended our measurement techniques to obtain absolute spin-susceptibility values. This article will outline and briefly discuss these techniques prior to a presentation and discussion of the data for specifically "metallic" samples. It will be seen that the spin susceptibility approaches that of a Pauli electron gas when the donor concentration is above roughly  $4 \times 10^{19}$  donors/cm<sup>3</sup>. There is

evidence of a non-Pauli-like temperature-dependent susceptibility in the lower portion of our sample-concentration range. Further, diamagnetic susceptibilities, obtained through the use of previous static-field data,<sup>3</sup> exhibit a concentration dependence reasonably consistent with the predictions of the Kjeldaas-Kohn calculation.<sup>4</sup>

In the course of our susceptibility measurements it was possible to accurately measure the linewidths and  $g$  values of the observed signals. These data will also be presented and discussed in the light of previous theories and the "rigid-band" model inferred from our susceptibility results.

### II. EXPERIMENTAL DETAILS

Our electron spin resonance (ESR) measurements were carried out on powdered silicon samples in a standard  $x$ -band microwave spectrometer utilizing phase-sensitive detection relative to a modulated magnetic field. The samples were prepared by mortar and pestle grinding of slices cut from purchased<sup>5</sup> single-crystal boules. Sample concentrations were obtained by four-point-probe resistivity measurements<sup>6</sup> of the slices prior to grinding. The "surface" ESR line produced by the grinding was eliminated by an HF-HNO<sub>3</sub> etch and a subsequent heating to 600 °C in air.<sup>7</sup> All powders were separated into portions of relatively uniform powder size. The data to be presented here were obtained through the use of powders having particle sizes ranging