

EPR investigation of manganese clusters in silicon

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Manganese centers were investigated in silicon specimens with initial doping concentrations between $1.5 \times 10^{15} \text{ P cm}^{-3}$ and $6 \times 10^{15} \text{ B cm}^{-3}$. All known Mn centers could be observed but the cluster $\text{Mn}_{i3}\text{Mn}_i$ was missing in highly-boron-doped material, indicating that this center is negatively charged. A new center of trigonal symmetry was observed for an initial doping of $6 \times 10^{15} \text{ B cm}^{-3}$ and identified as a Mn_{i3}^{2+} cluster. The EPR signal of this center is strongly light sensitive in contrast to the other known Mn clusters.

I. INTRODUCTION

Manganese forms a large variety of different defects in silicon and is an important representative of the transition metals in general. Up to the present, the isolated interstitial manganese defects Mn_i^{2+} , Mn_i^+ , Mn_i^0 , and Mn_i^- and the substitutional Mn_s^+ and Mn_s^{2-} (Refs. 1 and 2) as well as some complexes with other impurity atoms³ and two different Mn clusters⁴⁻⁶ have been observed.

Ludwig, Woodbury, and Carlson⁴ were the first to report on the occurrence of the Mn_{i4} cluster, which was described later in more detail by Kreissl and Gehlhoff.⁵ Differences between the two groups concerning the effective spin of the center was resolved more recently by Kreissl, Gehlhoff, and Vollmer,⁶ who demonstrated quite clearly by a comparison between experimental and simulated spectra that $S=6$ is the only reasonable choice. So far, however, it was not possible to decide whether the cluster is centered around a lattice atom or an empty interstitial site.

In their publication Kreissl, Gehlhoff, and Vollmer also report on another manganese cluster with trigonal symmetry. From their analysis they conclude that this cluster consists of four atoms forming a distorted tetrahedron (a triangular pyramid). The triangular base consists of three equivalent neutral interstitial atoms while the fourth atom is ionized. According to Beeler, Anderson, and Scheffler⁷ a neutral manganese atom in a cubic environment is in a 4T_1 state for both the substitutional and the interstitial site. The local field at an atom in a cluster is of lower than cubic symmetry, so that orbital moments are quenched.^{1,5} Consequently, an effective spin $S=3/2$ is assigned to each of the three equivalent atoms and the fourth atom must have an effective spin $S=1$ to yield the observed total spin $S=11/2$ (strong ferromagnetic exchange coupling of the spins is expected). The d shell of neutral Mn is occupied by seven electrons in the interstitial and by three electrons in the substitutional position, respectively. Therefore, to obtain $S=1$, the ionized atom should be negative in an interstitial and positive in a substitutional position, respectively. Although the authors prefer a cluster model of four interstitial atoms they cannot exclude the possibility of a substitutional position on the basis of their measurements.

II. EXPERIMENT

To resolve this question, we have investigated in the present work a wide range of specimens with initial doping

concentrations from $1.5 \times 10^{16} \text{ P cm}^{-3}$ to $6 \times 10^{15} \text{ B cm}^{-3}$. The base material was floating zone silicon. Samples with dimensions $3 \times 3 \times 10 \text{ mm}^3$ were cut from [111]-oriented disks with the long axis in a [110] direction. Manganese was chemically deposited on the surface from a manganese chloride solution. The samples were annealed for 1–2 h at 1260°C in a vertical furnace under an atmosphere of high-purity He and quenched in water with a layer of oil on top.

A Bruker spectrometer, series ER200D, operating in the X-band (9.41 GHz), was used for the EPR measurements. The specimens were mounted with their long axis perpendicular to the magnetic field, which could be turned around to sweep out the entire (110) plane. The measurements were carried out in dispersion, the magnetic field was modulated with 50 kHz, and the temperature was near the boiling point of liquid helium.

III. RESULTS AND THEIR INTERPRETATION

A. The $\text{Mn}_{i3}\text{Mn}_x$ cluster

Immediately after quenching, the EPR signals of isolated Mn_i^0 and Mn_i^- were observed in all specimens. On annealing at room temperature the signal intensities of isolated interstitial impurities decreased simultaneously with the formation of the clusters. After storing the specimens at room temperature for a few weeks, $\text{Mn}_{i3}\text{Mn}_x$ clusters could be detected in specimens with initial doping concentrations between $1.5 \times 10^{16} \text{ P cm}^{-3}$ and $7 \times 10^{14} \text{ B cm}^{-3}$ but not for $6 \times 10^{15} \text{ B cm}^{-3}$.

From these two observations we draw the following conclusions.

(1) The clusters are formed by migrating interstitial impurities because only for these the mobility at room temperature is sufficiently high. Therefore, since a kick-out mechanism would be energetically unfavorable, the clusters are most likely composed entirely of interstitials.

(2) The charge of the ionized atom in the cluster is negative, i.e., the correct characterization of the cluster is $\text{Mn}_{i3}^0\text{Mn}_i^-$.

Since, as explained in the Introduction, the interstitial ion must be negative and the substitutional ion positive to yield the total spin of the cluster, the two statements (1) and (2) support each other. The question where the negative charge comes from in the originally p -type specimens still remains

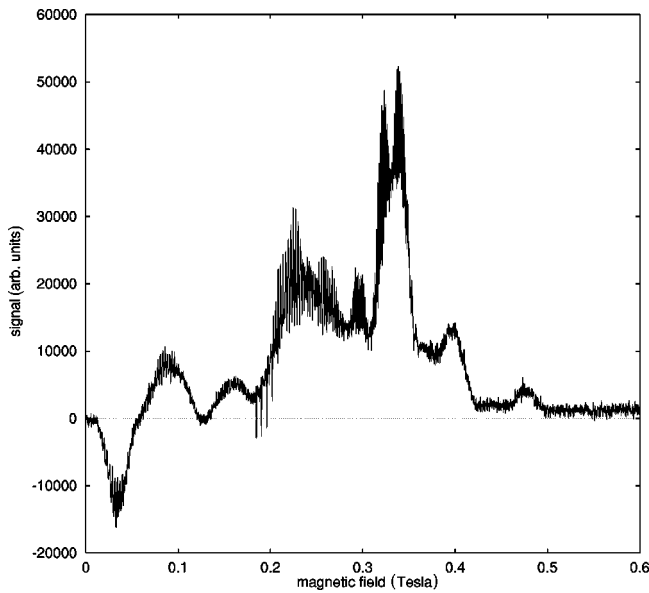


FIG. 1. EPR spectrum of the Mn_{i3}^{2+} cluster with the magnetic field in the $[100]$ direction.

open. One possibility is that another unidentified donor impurity which is not EPR-active is present in the sample. Preliminary deep-level transient spectroscopy (DLTS) experiments on the same specimens show indeed a manganese correlated donor level near midgap.

B. New centers in highly boron-doped material

In the specimen with $6 \times 10^{15} \text{ B cm}^{-3}$ we observed, immediately after quenching, a high concentration of isolated Mn_i^0 defects, a rather weak signal from Fe impurities, and also the spectrum of the cubic manganese cluster Mn_{i4}^0 . From photo-EPR measurements that were carried out later, we infer that the sample also contained MnB pairs. As the Mn concentration in the sample is higher than the shallow doping concentration, all boron atoms have been absorbed in pairs. In the dark, these pairs are in a neutral state in which they are not EPR-active. This was in fact intended and was the reason for our choice of the highest boron concentration: For higher concentrations our spectra would be masked by a large number of lines from positively charged MnB^+ centers.

In addition to these well-known defects we observed the spectra of a so far unknown center. Like the $\text{Mn}_{i3}^0\text{Mn}_i^-$ cluster, this new center formed at room temperature in the course of few weeks from the isolated interstitials. Figures 1, 2, and 3 show the EPR spectra when the magnetic field is applied in the directions $[100]$, $[111]$, and $[011]$, respectively. The whole range of angles between $[100]$ and $[011]$ was scanned with a step size of 5° and in the vicinity of the $[111]$ direction, which is most suitable for fitting theoretical model parameters, with an even smaller step size.

Obviously the new spectrum consists of hyperfine groups for which the hyperfine splitting is small compared with the fine-structure splitting. The positions (centers of gravity) of the fine structure groups are plotted in Fig. 4 (single symbols) versus angle. From the measured spectra represented in Figs. 1–3 and from the total angular dependence of Fig. 4,

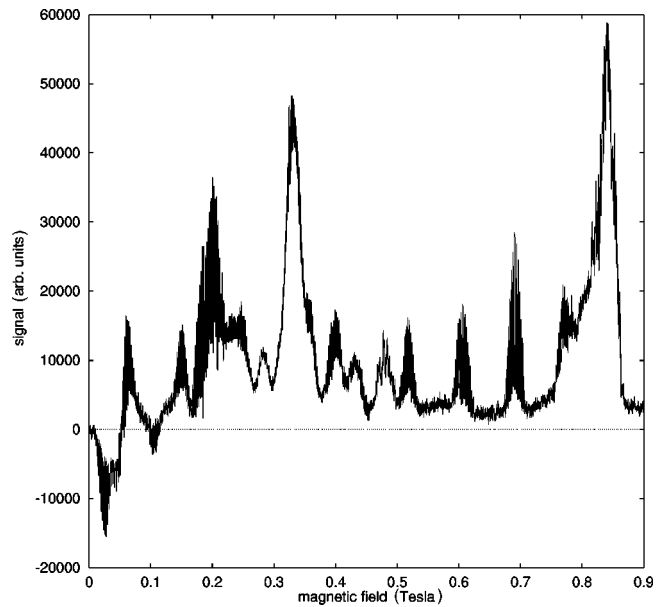


FIG. 2. EPR spectrum of the Mn_{i3}^{2+} cluster with the magnetic field in the $[111]$ direction.

which shows a maximum separation of the different groups in the $[111]$ direction, we conclude that the new center has trigonal symmetry.

A further clue concerning its structure is given by the hyperfine structure of the different groups some of which are well resolved as seen in Fig. 2. The most intensive one (near 0.7 T) is plotted again on a more extended scale in Fig. 5. As the direction of the magnetic field is presumed to be parallel to the center axis we do not expect that the structure is influenced by forbidden transitions.

The group consists of 16 equidistant hyperfine lines whose intensities closely match the pattern

$$1:3:6:10:15:21:25:27:27:25:21:15:10:6:3:1.$$

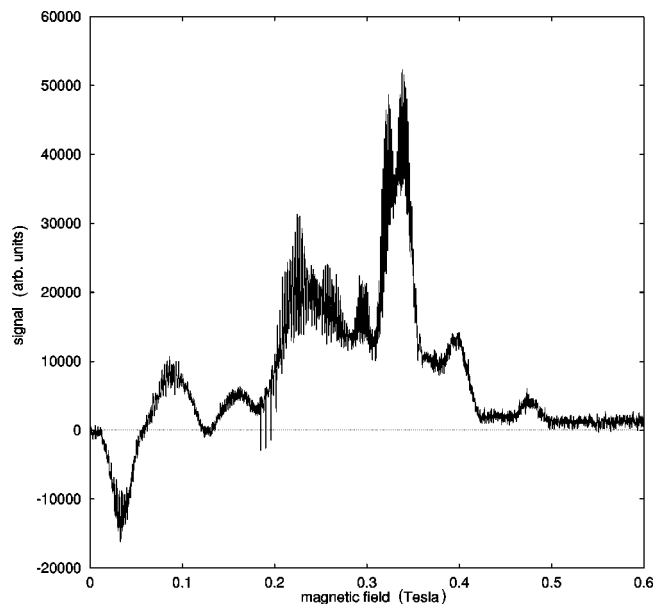


FIG. 3. EPR spectrum of the Mn_{i3}^{2+} cluster with the magnetic field in the $[110]$ direction.

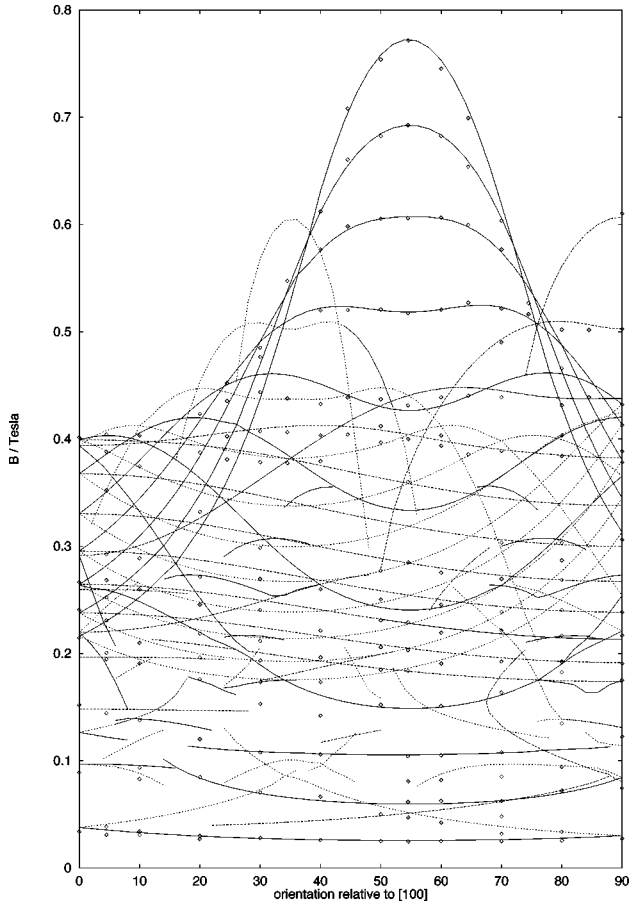


FIG. 4. Calculated angular dependence of the Mn_{i3}^{2+} cluster using Eq. (1) together with the experimental values (single points). Full lines are used for centers which are $\parallel \mathbf{B}$, broken lines for centers which are not $\parallel \mathbf{B}$ if \mathbf{B} lies in the $[111]$ direction.

This indicates that three Mn atoms (nuclear spin of each atom $I=5/2$ and $2NI+1$ lines for N atoms) in equivalent positions are involved in the center and it is straightforward to assume a triangular arrangement in one of the four $\{111\}$ planes. The hyperfine constants determined from the measured spectra at different angles between the magnetic field and the symmetry axis are

$$|A_{\parallel}| = (20.7 \pm 0.2) \times 10^{-4} \text{ cm}^{-1},$$

$$|A_{\perp}| = (30.0 \pm 3.0) \times 10^{-4} \text{ cm}^{-1}.$$

Having thus established the axial symmetry of the new center and omitting for the moment the hyperfine interaction, we can now describe the EPR spectrum according to Muller *et al.*⁸ by the following Hamiltonian:

$$\begin{aligned} \mathbf{H} = & \mu_B g_{\parallel} B_z \mathbf{S}_z + \mu_B g_{\perp} (B_x \mathbf{S}_x + B_y \mathbf{S}_y) \\ & + \mathbf{D}[\mathbf{S}_z^2 - \frac{1}{3}S(S+1)] + \frac{\sqrt{2}}{36} a[\mathbf{S}_z, (\mathbf{S}_+^3 + \mathbf{S}_-^3)]_+ \\ & + \frac{1}{180} (F-a) \{35\mathbf{S}_z^4 - [30S(S+1) - 25]\mathbf{S}_z^2 \\ & - 6S(S+1) + 2S^2(S+1)^2\}, \end{aligned} \quad (1)$$

where $[\mathbf{AB}]_+ = \mathbf{AB} + \mathbf{BA}$.

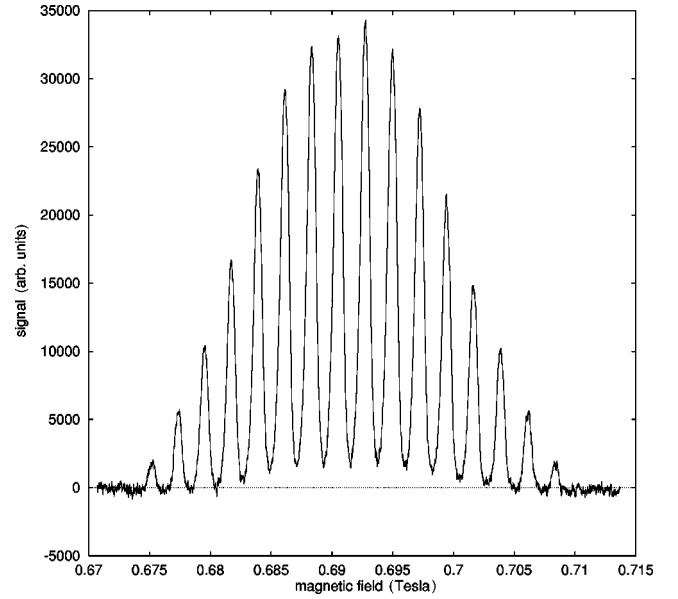


FIG. 5. Hyperfine structure of a $[111]$ center with \mathbf{B} in the $[111]$ direction.

The indices x, y, z refer to a coordinate system whose z axis is parallel to the symmetry axis of the center. If B is applied in the $[111]$ direction it is parallel to z for one of the four possible center orientations. In the following we call this the $[111]$ center. Its eigenvalues are given by

$$\begin{aligned} E(M) = & \mu_B g_{\parallel} B M + D[M^2 - \frac{1}{3}S(S+1)] \\ & - \frac{(a-F)}{180} \{35M^4 - [30S(S+1) - 25] \\ & \times M^2 + 3S^2(S+1)^2 - 6S(S+1)\}, \end{aligned} \quad (2)$$

$$M = -S, -S+1, \dots, S+1, S.$$

In this case the separation of the fine structure lines turns out to be at a maximum compared with other angles between the magnetic field and the center orientation. Equation (2) was therefore used for a fit of the well-separated lines (centers of gravity of the groups of hyperfine lines) in Fig. 2 to obtain the parameters of the Hamiltonian:

$$S = 11/2,$$

$$g_{\parallel} = 2.016 \pm 0.002,$$

$$g_{\perp} = 2.00 \pm 0.02,$$

$$|D| = 0.0420 \pm 0.0001 \text{ cm}^{-1},$$

$$|a-F| = 0.00030 \pm 0.00005 \text{ cm}^{-1},$$

$$\text{sgn}[D/(a-F)] \text{ is negative.}$$

No good fit could be obtained with a value of S different from $11/2$. Figure 6 shows the energy levels calculated with these parameters from Eq. (2) as a function of B . Allowed transitions of 9.41 GHz are indicated by vertical bars.

The levels and allowed transitions for $\mathbf{B} \parallel [111]$ of the other three center orientations, $[1\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$, and $[\bar{1}\bar{1}1]$,

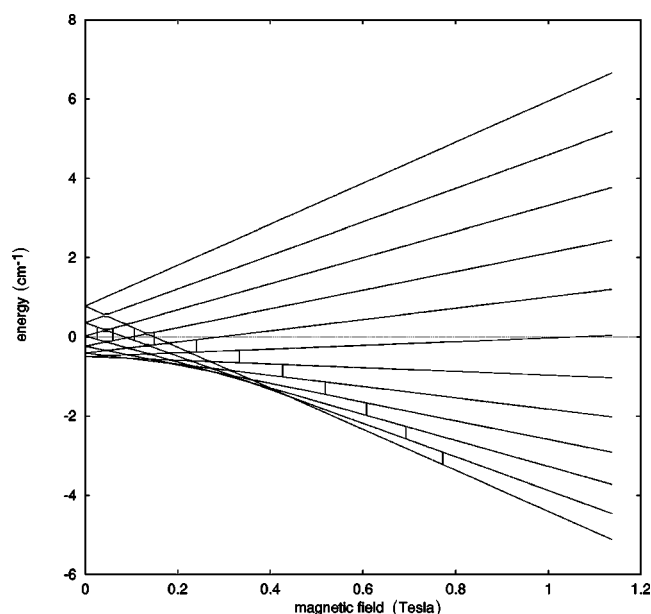


FIG. 6. Energy level diagram of the $[111]$ center of a Mn_{i3}^{2+} cluster for $\mathbf{B} \parallel [111]$. Allowed transitions for 9.41 GHz are represented by vertical bars.

are plotted in Fig. 7. All three are equivalent. One might expect at first sight that, because of this threefold degeneracy, resonance lines of the other orientations should have a far higher intensity than those of the $[111]$ center in Fig. 2. However, it turns out that most transition probabilities which were calculated together with the energy levels are much lower. Furthermore, the energies of the levels involved in the transitions are higher, so that their occupation at 4 K where the measurements were done is appreciably lower than for the $[111]$ center (compare Figs. 6 and 7). The results of a numerical diagonalization of Eq. (1) with these parameters are included in Fig. 4. The fine structure lines of the $[111]$

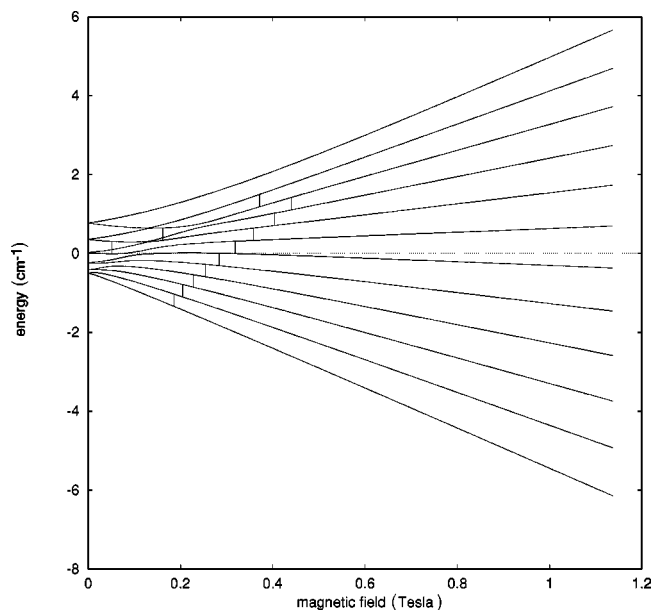


FIG. 7. Energy level diagram of the three other orientations of the Mn_{i3}^{2+} cluster for $\mathbf{B} \parallel [111]$.

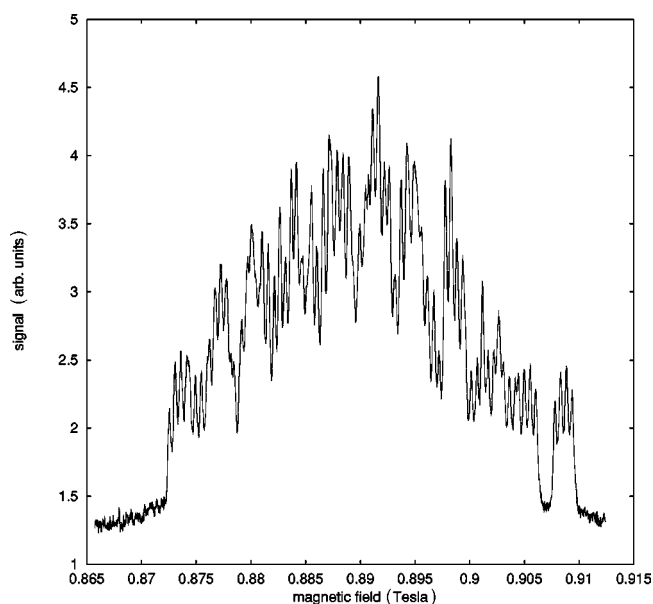


FIG. 8. Part of the spectrum of the Mn_2B center.

center are given by continuous lines, and those of the other centers by dashed lines. Not all the EPR lines that are predicted theoretically for all center orientations can actually be observed. Some are obscured by the strong Mn_{i4}^0 signal, and others cannot be resolved because of low intensity, superposition of different hyperfine groups, etc. But all observed lines fit the theoretical prediction with the accuracy to which their positions can be determined experimentally.

The spin $S=11/2$ can be explained by assuming that two of the three Mn_i have lost one electron and carry a positive charge. The spin of Mn_i^0 is $S=3/2$, the spin of a Mn_i^+ is $S=2$ because the d shell is more than half filled.

We therefore conclude that the new spectrum is due to a Mn_{i3}^{2+} center, where the Mn_i form an equilateral triangle. A strong exchange interaction couples the spins to a total value $S=11/2$.

In the spectra there are several groups of lines that do not belong to the new center and were consequently not included in Fig. 4. These are (1) the strong group at 330 ± 50 mT, which belongs to the Mn_{i4}^0 cluster, (2) a Mn_i^0 signal near 210 mT, (3) the group around 480 mT in Figs. 1 and 2, (4) the group around 840 mT in Fig. 2, (5) the weak extended group in Fig. 3 which is visible between 540 and 600 mT. Groups (3)–(5) were eliminated because these signals disappeared after 6 months, while the intensity of all other lines remained unchanged within the experimental accuracy. Furthermore, their intensity under illumination changes in a different way. Of these centers the group at 840 mT is the only one which does not overlap with other line groups and therefore allows for a more detailed analysis. In Fig. 8 the group is shown in higher resolution. It can be described as two overlapping fine structure lines that are each split into 11 hyperfine lines due to the nuclear spin of the manganese atoms (see above). In addition, each hyperfine line shows a small splitting into four lines. This second hyperfine splitting is characteristic of boron which has the two isotopes ^{11}B (abundance 81.2%, nuclear spin $I=3/2$) and ^{10}B (18.8%, $I=3$).⁹ Therefore we tentatively associate these lines with a

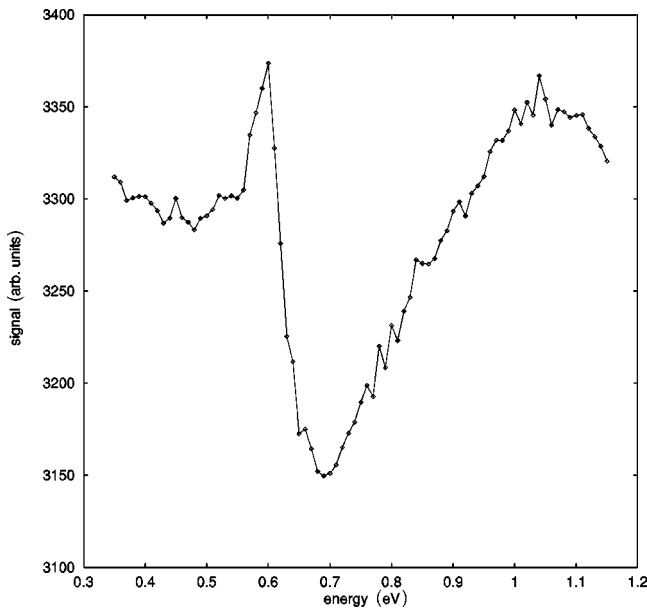


FIG. 9. Variation of the signal intensity of the Mn_{i3}^{2+} cluster with the photon energy of incident light.

Mn_2B center (Fig. 8). Unfortunately we could not prepare this center separately and a more detailed investigation of its angular dependence was not possible due to overlap with other spectra.

IV. PHOTO-EPR

The determination of the level of the new triangular cluster in the gap is complicated by the presence of other centers from which it could not be fully isolated. As mentioned before, MnB pairs have to be taken into account in samples prepared at room temperature. No EPR lines of the MnB^+ center¹⁰ could be detected without incident light. Therefore the level of the Mn_{i3}^{2+} cluster must lie above the known $\text{MnB}^{+/0}$ level at $E_C - 0.57$ eV.¹¹ Under illumination the MnB^+ lines appear, parallel to the decrease of the intensity of the Mn_{i3}^{2+} lines. Therefore we believe that electrons are excited from the MnB^0 pair to the conduction band and are captured by Mn_{i3}^{2+} centers which are transformed to Mn_{i3}^+ .

After annealing at 180 °C both the Mn_2B center and the MnB pairs disappear while the Mn_{i3}^{2+} and Mn_{i4}^0 are still present. Measuring again the photo-EPR in such an annealed sample we obtained the results in Fig. 9 which shows the dependence of the signal intensity on the energy of the inci-

dent photons for the hyperfine group of Fig. 5. The following interpretation of these results is straightforward:

In the dark the Fermi level coincides with the level of the $\text{Mn}_{i3}^{2+} \leftrightarrow \text{Mn}_{i3}^+$ transition. Above a photon energy of 0.55 eV, electrons from this partly occupied level are excited to the conduction band and the concentration of Mn_{i3}^{2+} increases. For photon energies higher than 0.6 eV a transition between the valence band and the center leads to an increase of Mn_{i3}^+ which is not EPR-active and to a decrease of the Mn_{i3}^{2+} signal. The sum of the onset energies of these transitions equals the gap energy which is expected if the two transitions are correlated in the described manner.

At energies higher than 0.69 eV a transition from the valence band to an unoccupied level of another, yet unknown, center takes place, creating holes that are captured by the Mn_{i3}^+ centers, which leads again to an increase of Mn_{i3}^{2+} signal intensity.

Besides the Mn_{i3}^0 and Mn_{i4}^0 cluster (the latter is not involved in the optical transitions) the annealed sample contains also other centers that are manifest by several so far unidentified EPR peaks which appear after the annealing process. It is also possible that additional clusters which are not EPR active are present. Since we cannot find an EPR-signal of isolated Mn_i centers which are released by the decay of the Mn-B centers and since the signal intensities of Mn_{i3}^{2+} and Mn_{i4}^0 are only slightly increased, it must be concluded that new centers besides the ones that we were able to identify are formed. Unfortunately this lends some residual uncertainty to our interpretation of the level at $E_C - 0.55$ eV which may not be directly associated with the transition Mn_{i3}^{+2} to Mn_{i3}^+ but with a transition from an unidentified center to the conduction band from which the electron is captured by the Mn_{i3}^{2+} center.

V. SUMMARY

We have extended the EPR investigations of Mn_i clusters to p -doped material. No signals of $\text{Mn}_{i3}\text{Mn}_i$ can be seen in p -type samples with more than 7×10^{14} B cm^{-3} indicating that the center which was previously observed by EPR is negatively charged. A new EPR spectrum could be observed which is identified as a Mn_{i3}^{2+} cluster. This center has most likely a $+/2+$ level at $E_C - 0.55$ eV. Another so far unknown center could be tentatively identified as Mn_2B .

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