

Superhyperfine structure in the EPR spectra of Mn^{2+} ions in PbTe

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(Received 30 June 1986)

The electron paramagnetic resonance of Mn^{2+} ions in powders and single crystals of PbTe and gadolinium-doped PbTe is reported. Resolved hyperfine and superhyperfine lines were measured from 4.2 to 120 K. The superhyperfine structure is attributed to the interaction between manganese ions and the tellurium ligands. At 4.2 K and 3330 G we obtain $g=1.994\pm 0.001$, $a_{Mn}=65.7\pm 0.1$ G or $(61.4\pm 0.1)\times 10^{-4}$ cm⁻¹ and $a_{Te}=15.5\pm 1.0$ G or $(14.5\pm 0.9)\times 10^{-4}$ cm⁻¹. The superhyperfine constant is temperature independent within experimental error.

I. INTRODUCTION

The EPR of Mn^{2+} ions in cubic semiconductors has been studied by various workers.¹⁻¹⁰ The spin Hamiltonian parameters of wide-band-gap materials have been determined including the g value, the fine-structure, and the hyperfine and superhyperfine coupling constants. In narrow-gap semiconductors, particularly IV-VI compounds, the native defects and free carriers can complicate the Mn^{2+} spectrum. For low manganese and free-carrier concentrations one would expect a Mn^{2+} spectrum similar to that in wide-gap materials. However, Pifer⁵ found that each hyperfine line has a complex structure, which follows the conductivity changes in PbTe or PbSe. Furthermore, this additional structure was not observed in PbS. These results are still unexplained.

On the other hand, in the work of Toth, Leloup, and Rodot,⁶ where the interaction between manganese and free holes was investigated, no additional structure on the hyperfine lines is reported, although linewidths as small as 7 G were observed.

It is the aim of the present paper to study the structure of the hyperfine lines of Mn^{2+} ions in PbTe reported by Pifer. The samples used are n -type PbTe crystals with a trace of manganese.

II. EXPERIMENTAL

X-band EPR measurements were performed on powders and single crystals of the semiconductor manganese-doped PbTe. The powders were size selected by liquid sedimentation, imbedded in insulating wax, and placed in quartz capillaries with diameter less than 3 mm. The single crystals were mounted in a two-circle goniometer as described in Ref. 11. The angular variation of the Mn^{2+} spectrum in the (110) crystallographic plane was measured in a PbTe crystal which also contained a small amount of Gd^{3+} . The fine structure of the Gd^{3+} ions was used to orient the crystals as described in Ref. 11.

An Apple II+ type of microcomputer controlled the EPR spectrometer and collected the resulting data. The spectrum and magnetic field intensities were digitized and recorded simultaneously, thus allowing precise determination of the line shapes and positions. The external magnetic field was measured by a self-locked proton resonance gaussmeter.

The measurements were carried out in a helium-gas-flow type of Dewar from 4.2 to 120 K. A conventional temperature controller with a Ge resistor and a Pt thermocouple as sensors was used to regulate the temperature. The sample temperature was measured by a gold-Chromel thermocouple placed 1 cm below the sample. For weak lines at higher temperatures a signal-averaging technique was used.

The PbTe and gadolinium-doped PbTe crystals with traces of manganese were prepared as described in Ref. 12. All the samples showed n -type conductivity as determined by thermoelectric hot-probe tests at room temperature.

A Gauss-Newton nonlinear least-squares program was written in BASIC and was used to fit the digitized spectra to determine line positions, intensities, shapes, etc.

III. RESULTS

Each of the six principal Mn hyperfine lines showed a fivefold structure as shown in Fig. 1, both in the powder and in the single crystal, although the outer lines were very weak in the latter case. These features were found to be isotropic under rotation in the (110) plane within the ex-

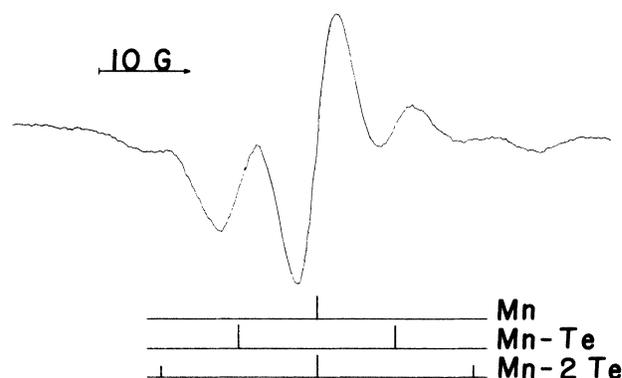


FIG. 1. Spectrum showing the lowest-field Mn hyperfine line and its superhyperfine structure. The stick plot shows the lines expected from the three dominant component spectra, i.e., those of Mn interacting with 0, 1, or 2 ¹²⁵Te nuclei. Powder sample 4.2 K, modulation frequency 10 kHz, microwave power 0.05 mW.

perimental error of about 0.1 G.

Fine-structure splitting can easily be eliminated as the source of the observed structure. Such a splitting, whether arising from higher-order hyperfine interactions, or cubic field or axial field perturbations, should yield five lines of intensities approximately 8:5:9:5:8 with a spacing varying with the Mn m_l value.^{13,14} Anisotropy would be expected for the two field perturbations. None of these features is observed.

The spectra can be explained in terms of superhyperfine interactions with the nearest-neighbor tellurium sites occupied by the isotopes¹⁵ ^{125}Te of abundance 7.1% and spin $I = \frac{1}{2}$, and ^{123}Te , 0.9% and $I = \frac{1}{2}$. The latter isotope has a nuclear moment 17% smaller than the former, but its principal lines overlap those of the former within their linewidth. Hence, for present purposes they may be considered as a single isotope of abundance 8.0%. Since Mn has six tellurium nearest neighbors in the NaCl structure of PbTe the fraction of Mn sites with n magnetic tellurium nuclei is given by the $(n+1)$ th term of the binomial expansion $(0.92+0.08)^6$. If these n nuclei are equivalent, as the isotropy indicates, they will give $2n+1$ equally spaced lines, with intensities given by the terms of the binomial expansion $(1+1)^n$. Summing over all n , i.e., 0–6, gives the predicted spectrum. A total of 13 lines is predicted, but only the central five have significant intensity. The relative intensities starting at the center are 1:0.25:0.027:0.0016. These are in reasonable agreement with our experiments, where the first satellite has intensities of 0.31, 0.26, and 0.25 at 4.3, 15.4, and 32.8 K, while the second satellite has an intensity 0.04 at 4.3 K. Each number is an average over a pair of lines.

At higher microwave power levels a third pair of lines can be detected outside these five but they are too weak to permit useful intensity measurements. The satellite lines were observed both in single crystals and in powders. In the crystal the line shape, in first-derivative mode, was a symmetric peak with a full width at half maximum of 4 G. The shape is partially explained by the classical skin-depth effect which yields¹⁶ a line shape which is a mixture of absorption and dispersion. Other effects may also be involved. Direct measurement of the peak positions gives a coupling constant at 4.2 K of $a_{\text{Te}} = 16.4 \pm 0.1$ G. Rotation in a (110) plane indicated that the anisotropy is less than 0.05 G.

Measurements were also made on powdered samples with particle sizes of a few micrometers where the lines had a more typical centrosymmetric line shape with a peak-to-peak width of about 7 G. A nonlinear least-squares fit of a single Mn line with a pair of Te lines gives $a_{\text{Te}} = 14.5$ G for an assumed Gaussian line shape and $a_{\text{Te}} = 15.8$ G for a Lorentzian one. Below 45 K the Gaussian gives the better fit. The discrepancy between the single crystal and the powder results is greater than the standard deviations which are typically 0.1 G or less. Since neither the discrepancy nor the detailed line shape can be explained at this time, we report the coupling constant as 15.5 ± 1.0 G at 4.2 K.

The manganese hyperfine coupling constant is $a_{\text{Mn}} = 65.7 \pm 0.1$ G at 4.2 K and 3300 G. In energy units $a = 61.4 \times 10^{-4} \text{ cm}^{-1}$. This value is in good agreement

with that of Pifer,⁵ $61.2 \times 10^{-4} \text{ cm}^{-1}$, and is consistent with the higher-temperature results of Inoue, Yagi, Muratani, and Tatsukawa⁷ and of Hejrowski and Subotowicz.¹⁰ It differs significantly from Tatsukawa's⁹ V -band value of 68.5 G.

IV. DISCUSSION

The Mn hyperfine coupling is comparable to that of some other semiconductors, e.g., ZnS and appreciably smaller than that in insulators such as MgO and NaCl.¹⁷ If this reduction is attributed to covalency with the tellurium and if $81 \times 10^{-4} \text{ cm}^{-1}$ is taken as the coupling constant in such ionic crystals as MgO, CaO, SrO, and NaCl (Refs. 17 and 18), then our value in PbTe implies $(81 - 61)/(6 \times 81)$ or 4% as the spin density on each tellurium. Presumably that density is in the tellurium p orbitals. Unfortunately, we do not have a direct measure of the tellurium p -orbital density. The absence of anisotropy seems to imply that as a result of σ and π bonding the p orbitals are all occupied to a similar extent with some allowance for direct dipolar contributions from the d electrons on the manganese.

The isotropic tellurium hyperfine coupling of 15.5 G or 44 MHz together with the free-atom s -electron coupling¹⁹ of 55 600 MHz indicates an s -electron density on the tellurium of about 0.08%. This density may arise from spin polarization by the p -orbital spin density. Another source, however, could be s - p hybridization on the tellurium since the manganese will destroy the center of symmetry on the neighboring ligands.

It is significant to note that within the resolution of our EPR spectra there is no splitting from ^{207}Pb . This situation contrasts with that in ZnS,^{3,8} CdS,¹ CdSe,³ and CdTe,^{1,2,4} where a distinct splitting arises from the cations, but none is seen from either Se or Te. A splitting from ^{33}S , if present, would have been difficult to detect at the low abundance¹⁵ of 0.79%.

The spectra published by Pifer⁵ for Mn in n -type PbSe show some lines which are similar to the superhyperfine lines we report here. The isotope ^{77}Se with spin $\frac{1}{2}$ and abundance 7.5%, would produce spectra qualitatively similar to those from ^{125}Te . Pifer notes that he sees similar structures from PbTe but not from PbS. As above, a superhyperfine interaction from ^{33}S would not be seen easily. Thus, it seems likely that Pifer was seeing an anion superhyperfine structure.

His spectra show other complex features which are not as readily explained. We have noticed an unusual sensitivity of our spectra to the microwave power level and are presently studying the matter. The mild asymmetry of the dominant pair of superhyperfine lines in Fig. 1, which decreases at lower microwave power, is one example of such effects.

ACKNOWLEDGMENTS

We offer our thanks to Dr. D. F. Williams for his support of this work, to Dr. Takako Amano for her assistance in developing spectrometer-control and data-acquisition programs in 6502 assembler language, to J. Bartkowska for her assistance in spectrum fitting, and to Dr. J. M. Park for helpful discussions.

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