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Electron paramagnetic resonance studies of magnetic interactions in $Hg_{1-x}Mn_xSe$

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Abstract. The EPR linewidth has been studied in four samples of $Hg_{1-x}Mn_xSe$ with $x = 0.09$, 0.11, 0.15 and 0.18 as a function of temperature in the range $19 \leq T \leq 290$ K, and as a function of dose of ^{60}Co gamma radiation up to 550 kGy. It was found that the EPR linewidth depends on temperature as $1/T$ in the range $50 \leq T \leq 290$ K for the samples with $x = 0.15$ and 0.18, and in the range $25 \leq T \leq 290$ K for the samples with $x = 0.09$ and 0.11. Using Anderson's model for the exchange-narrowed high-temperature EPR line, the exchange integral between the nearest-neighbour Mn^{2+} ions was found to be $J/k \simeq 0.1$ K in the sample with $x = 0.18$. The observed tendency of the EPR linewidth to decrease with increasing dose of gamma radiation is discussed in terms of a cluster model.

1. Introduction

In the past ten years semimagnetic semiconductors (SMSC) have been intensively studied. The most interesting problems in the physics of SMSC appear to be the problem of impurity states in these materials and the mechanism of exchange interaction between magnetic ions. The impurity states have been most extensively studied in $Hg_{1-x}Mn_xTe$ (Brandt *et al* 1983, Brandt and Moshchalkov 1984) where, like in HgTe and $Hg_{1-x}Cd_xTe$, mercury vacancies form the acceptor resonant states in the conduction band. On the contrary, crystals of $Hg_{1-x}Mn_xSe$, like HgSe, grow with a large number of native defects, usually attributed to Se vacancies (Mauger and Friedel 1975) which act as donors and have the dominant influence on the electrical transport properties of this semiconductor at low temperatures (Babić Stojić and Stojić 1989). Magnetic interactions have been also mostly studied in $Hg_{1-x}Mn_xTe$ (Brandt *et al* 1983, Brandt and Moshchalkov 1984). It was established that in the region where this SMSC is a zero-gap semiconductor ($0 < x \leq 0.075$) the existence of the spin-glass state is due to the long-range indirect exchange interaction between Mn^{2+} ions on account of virtual transitions from the valence band to the conduction band. However, in the recent study of the magnetic susceptibility data in $Cd_xHg_yMn_zTe$ (Manhas *et al* 1987) it was concluded that in alloys with energy gap $E_g > 1.5$ eV exchange interaction occurs through the mechanism of superexchange, whereas in the samples with $E_g \leq 1.5$ eV a Bloembergen–Rowland type of interaction should be included. Similar conclusions, that the superexchange is the dominant mechanism of d–d coupling in wide-gap SMSC like $Cd_{1-x}Mn_xTe$, $Zn_{1-x}Mn_xSe$ and $Hg_{1-x-y}Cd_yMn_xTe$ (Lewicki *et al* 1988) have been deduced from the magnetic susceptibility data of these alloys.

Since the magnetic properties of SMSC intimately depend on the interaction between spins localised on Mn^{2+} ions, the study of the EPR linewidth should significantly contribute

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to the understanding of magnetism of these materials. However, a relatively small number of EPR experiments has been done so far on SMSC, on $Cd_{1-x}Mn_xTe$ (Oseroff *et al* 1980, Webb *et al* 1984, Sayad and Ghagat 1985), on $Hg_{1-x}Mn_xSe$ (Mullin *et al* 1981), on some mercury based SMSC (Leibler *et al* 1977), and on some wide-gap SMSC (Kremer and Furdyna 1985). The common property of all these SMSC is a pronounced increase of the EPR linewidth with decreasing temperature and with increasing manganese concentration. Although a microscopic theory of the EPR effects in SMSC does not exist, experimental investigation can help to formulate the theory and to understand the EPR line broadening in these materials.

In the present work the EPR linewidth was measured in crystals of $Hg_{1-x}Mn_xSe$ with $x = 0.09, 0.11, 0.15$ and 0.18 as a function of temperature in the range $19 \leq T \leq 290$ K and as a function of gamma radiation dose up to 550 kGy.

2. Experimental details

The samples of $Hg_{1-x}Mn_xSe$ were prepared at the Institute of Physics of the Polish Academy of Sciences. The manganese concentration was checked by atomic absorption analysis and crystal structure tested by an x-ray diffraction technique. The EPR measurements were performed on a Varian spectrometer at microwave frequency $\nu = 9.4$ GHz. The samples were cooled in an open-cycle cryogenic refrigerator using flowing hydrogen gas. The temperature was measured by an iron-doped gold/chromel thermocouple. The first derivative of the absorption line was recorded, where the resonance field is defined as the zero of the derivative curve. No shift of the resonance field with temperature and with gamma radiation dose was observed. Lattice parameters were determined by x-ray powder diffraction using Mo Kα radiation.

3. Results and discussion

$Hg_{1-x}Mn_xSe$ is a semimagnetic semiconductor with the zincblende structure and with energy gap depending on the manganese concentration at $T = 10$ K (Takeyama and Galazka 1979) as:

$$E_g = (-0.27 + 4.4x)\ \text{eV}. \tag{1}$$

Therefore, the presence of manganese modifies the semiconducting properties of this material, particularly the energy gap value, and produces interesting magnetic properties such as the formation of the spin-glass state at low temperatures (Khattak *et al* 1981).

3.1. Temperature dependence of the EPR linewidth

The temperature dependence of the EPR linewidth in $Hg_{1-x}Mn_xSe$ crystals with manganese concentration $x = 0.09, 0.11, 0.15$ and 0.18 is presented in figure 1. A significant increase of the linewidth is observed with decreasing temperature, particularly for higher manganese concentrations. Although the manganese concentration and the crystal lattice structure were checked in all the samples and all the samples exhibit the same temperature dependence of the EPR linewidth, a reversed order of curves for $x \times 0.09$ and $x = 0.11$ was found (figure 1) which might be the consequence of some inhomogeneity of the composition in the sample with $x = 0.11$. Very pronounced temperature dependence of the EPR linewidth was also observed in mercury-based alloys $Hg_{1-x}Mn_xTe$ (Se, S) for higher manganese concentrations, $x \geq 0.20$ (Leibler *et al* 1977). Such behaviour was described by the expression $\Delta H = A[T_0/(T - T_0)]^P + B$, derived for the critical region

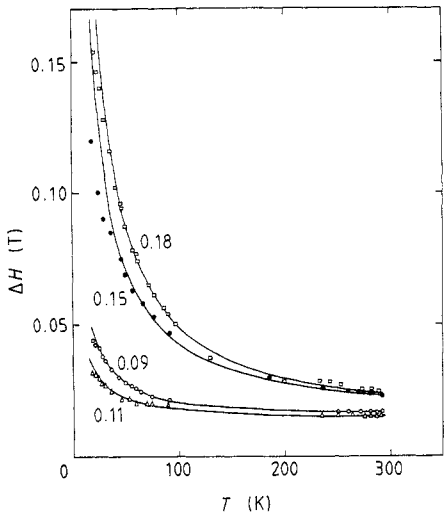

Figure 1. Temperature dependence of the EPR linewidth in $Hg_{1-x}Mn_xSe$ with $x = 0.09, 0.11, 0.15$ and 0.18.

Table 1. Linewidth parameters (equation (2)) for $Hg_{1-x}Mn_xSe$.

x	a (T)	b (T K)
0.09	1.46×10^{-2}	0.6620
0.11	1.44×10^{-2}	0.3882
0.15	1.42×10^{-2}	2.8451
0.18	1.05×10^{-2}	3.9106

in antiferromagnets above the Néel point (Huber 1972). A theory of the EPR line broadening in spin–glasses near the freezing temperature also predicts that the linewidth diverges as a power law in $(T - T_F)/T_F$ (Salamon 1979). However, in our experiment, temperatures above 19 K are far from the critical region of the spin–glass transition in the sample of $Hg_{1-x}Mn_xSe$ with $x = 0.18$ which is about 2 K (Khattak *et al* 1981) and for lower manganese concentrations in $Hg_{1-x}Mn_xSe$ the transition to the spin–glass state has not been observed so far.

In the present work we have found that the temperature dependence of the EPR linewidth in $Hg_{1-x}Mn_xSe$ can be well approximated by a formula

$$\Delta H = a + b/T \tag{2}$$

in the temperature range $50 \leqslant T \leqslant 290$ K for the samples with $x = 0.15$ and 0.18, and in the temperature range $25 \leqslant T \leqslant 290$ K for $x = 0.09$ and 0.11. The full curves in figure 1 represent a least-squares fit of the above formula to the experimental data. The values of the fitting parameters are shown in table 1. In the paper by Aliev and Tagirov (1985) the temperature dependence of the EPR linewidth in $Hg_{1-x}Mn_xSe$ with $x = 0.06$ was analysed. It was concluded that above 40 K the EPR linewidth can be fitted to a formula ΔH (T) $= a + bT + c/T$, where the dominant temperature-dependent term is c/T, which is in accordance with our result. In the paper by Oseroff *et al* (1980) the high-temperature EPR linewidth in $Cd_{1-x}Mn_xTe$ was also fitted to an expression $B(\theta/T + 1)$. Starting from the Huber approach to the EPR linewidth in the paramagnetic phase of an antiferromagnet well above the critical temperature Dormann and Jaccarino (1974) have evaluated an expression for the linewidth:

$$1/T_2 = g\mu_B \Delta H/\hbar = (kT\chi_T)^{-1}[g^2\mu_B^2\hbar^{-1}S(S+1)/3]^2 F(\boldsymbol{q}) \tag{3}$$

where $F(\boldsymbol{q})$ contains the correlation function, a function related to the $\boldsymbol{q}$ transform of the dipole–dipole interaction and $\boldsymbol{q}$-dependent magnetic susceptibility with $\chi_T \equiv \chi(\boldsymbol{q} = 0)$. It was pointed out that at temperatures well above the critical temperature, nearly all of the T dependence of ΔH is contained in the factor $(kT\chi_T)^{-1}$. In the mean-field approximation $\chi_T = C/T + \theta$, where θ is the Curie–Weiss temperature, and the expression (3) can be written as:

$$\Delta H = B(1 + \theta/T) \tag{3'}$$

which is essentially the same expression which was used by Oseroff *et al* (1980).

However, at temperatures below 50 K for the samples with $x = 0.15$ and 0.18, and below 25 K for $x = 0.09$ and 0.11, formula (2) for the temperature dependence of the EPR linewidth is no longer valid. An analysis of our experimental data has shown that the temperature variation of the linewidth in the samples with $x = 0.15$ and 0.18 and in the range $19 \leqslant T < 50$ K can be approximately described by a dependence

$$\Delta H = a + ce^{-T/T_0} \tag{4}$$

where the values of the fitting parameters are $c = 13.48 \times 10^{-2}$ T and $T_0 = 57.3$ K for $x = 0.15$ and $c = 22.22 \times 10^{-2}$ T, $T_0 = 47.4$ K for $x = 0.18$ and the values of parameter a are in table 1.

It should be mentioned that the same temperature dependence of the EPR linewidth as expression (4) has been reported for $Cd_{1-x}Mn_xTe$ by Webb *et al* (1984) and by Sayad and Bhagat (1985) in a wide temperature range but well above any spin–glass transition temperature for these compounds. The behaviour of the EPR line in $Cd_{1-x}Mn_xTe$ (Webb *et al* 1984, Sayad and Bhagat 1985) was interpreted phenomenologically in terms of random internal fields. The observed temperature dependence of the EPR linewidth (expression (4)) probably reflects the spin–glass dynamics in these magnetic systems. However, it is only empirical and requires an explanation on the basis of microscopic theory.

The width of the exchange-narrowed high-temperature EPR line in Anderson's model (Anderson and Weiss 1953) is given by:

$$\Delta H_{pp} = \frac{1}{2\sqrt{3}} \frac{(\Delta H_{pp})_{dip}^2}{\omega_e/\gamma} \tag{5}$$

where ΔH_{pp} is the peak-to-peak width of the derivative of the absorption line in field units which is observed in an experiment, $(\Delta H_{pp})_{dip}$ is the peak-to-peak linewidth originating from the dipole–dipole interaction, ω_e is a part of the fourth moment of the absorption frequency which depends on the exchange interaction and $\gamma = g\mu_B/\hbar$. Using Van Vleck's expression for the second moment of absorption frequency (Van Vleck 1948) we have obtained $(\Delta H_{pp})_{dip}$ for a polycrystalline sample in the nearest-neighbours approximation, where all the nearest-neighbour ions are assumed to be magnetic:

$$(\Delta H_{pp})_{dip} = (6/5)^{1/2} g\mu_B z^{1/2}[S(S+1)]^{1/2} x^{1/2} r_0^{-3} \tag{6}$$

where S is the spin of magnetic ion, z is the number of nearest neighbours, x is the magnetic ion concentration and r_0 is the distance between the two nearest-neighbour magnetic ions. Applying the above expression to the $Hg_{1-x}Mn_xSe$ sample with $x = 0.18$, where $S = \frac{5}{2}$, $z = 12$ in the FCC lattice of manganese ions, and taking room temperature as the high-temperature regime in this compound, so that $r_0 = a\sqrt{2}/2 = 0.4279$ nm at room temperature (figure 5), one obtains $(\Delta H_{pp})_{dip} = 0.1127$ T. The observed linewidth at room temperature is $\Delta H_{pp} = 0.0240$ T which suggests considerable exchange narrowing. From expression (5) one can obtain ω_e/γ, and in our case it is 0.1528 T. Since

$\omega_e/\gamma \simeq H_0$, where H_0 is the resonance field, ω_e/γ has to be multiplied by $\frac{10}{3}$ (Anderson and Weiss 1953). Therefore, $\omega_e/\gamma = 0.5093$ T and $\omega_e = 8.959 \times 10^{10}\ s^{-1}$. Then, the part of the fourth moment proportional to exchange coupling was calculated (Van Vleck 1948) for an FCC lattice of magnetic ions and taking the nearest-neighbour interactions only:

$$\langle \Delta\omega^4 \rangle' = \tfrac{1}{2}\pi \times \omega_d^2 \omega_e^2 = 12\omega_d^2\{[\tfrac{4}{5}S(S+1) - \tfrac{3}{5}] + \tfrac{7}{9}S(S+1)\}J^2/\hbar^2 \qquad (7)$$

where $\omega_d^2 = \gamma^2(\Delta H_{pp})_{dip}^2/4$ is the second moment of absorption frequency and J is the exchange integral between the nearest-neighbour magnetic ions. Using the above value of ω_e for the sample of $Hg_{1-x}Mn_xSe$ with $x = 0.18$ and for spin $S = \frac{5}{2}$ we have obtained $J/k \simeq 0.1$ K. This value is considerably lower than the values of exchange integral obtained for $Hg_{1-x}Mn_xSe$ in magnetisation measurements, 5.8 K for $x = 0.04$ in the paper by Dobrowolski *et al* (1982), and 5 K for $x = 0.05$ in the paper by Lascary and Bruno (1988). Calculating the second and fourth moment of the absorption frequency we have assumed that all the nearest neighbours of one Mn^{2+} ion in its sublattice are also manganese ions. Although the sample of $Hg_{1-x}Mn_xSe$ with $x = 0.18$ is very near the percolation threshold for the FCC lattice, $x_c \simeq 0.17$–0.20 (Brandt and Moshchalkov 1984), it seems that the above approximation is not quite satisfactory and that the manganese ions are distributed in magnetic clusters of finite size. In the calculation of the fourth moment such a distribution of magnetic ions should give rise to a higher value of the exchange integral.

From expression (5) one can see that the EPR linewidth depends on temperature in principle through the two quantities, ω_e (exchange interaction) and $(\Delta H_{pp})_{dip}$ (dipole–dipole interaction). In order to estimate how much the EPR linewidth due to dipole–dipole interaction only changes with temperature in the measured temperature range, the temperature dependence of the distance r_0 between the nearest-neighbour manganese ions should be found.

The linear coefficient of thermal expansion α was measured on several semiconducting compounds of the zinc blende structure (Novikova and Abrikosov 1963). We have used the values of α for HgTe which changes from $-4 \times 10^{-6}\ K^{-1}$ at $T = 20$ K, becomes zero at about 60 K and reaches the positive value of $4.8 \times 10^{-6}\ K^{-1}$ at 300 K. However, the coefficient α of other semiconductors of the zinc blende structure changes in a similar way with similar values in the temperature range 20–300 K. With the above values of the coefficient α, the interionic distance r_0 in the sample of $Hg_{1-x}Mn_xSe$ with $x = 0.18$ was estimated to increase from 0.4275 nm at 20 K to 0.4279 nm at 300 K. Such an increase of the interionic distance r_0 would reduce the linewidth due to dipole–dipole interaction (expression (6)) from 0.1130 T at 20 K to 0.1127 T at 300 K. However, such small variation of the linewidth cannot be measured. It follows that the dipole–dipole interaction is not responsible for the observed temperature dependence of the EPR linewidth in $Hg_{1-x}Mn_xSe$ (figure 1). In addition, the Mn^{2+} ion in $Hg_{1-x}Mn_xSe$ is in an S state, so that the spin–lattice coupling in this system is weak and spin–lattice relaxation also does not have any appreciable influence on the temperature dependence of the EPR linewidth (Huber and Seehra 1975). Moreover, $Hg_{1-x}Mn_xSe$ has an energy gap depending on the manganese concentration (expression (1)), so that for the sample with $x = 0.18$, $E_g = 0.52$ eV and for $x = 0.09$, 0.11 and 0.15 the energy gap is 0.13, 0.21 and 0.39 eV at 10 K respectively. At higher temperatures these energy gap values should be somewhat higher if one takes $dE_g/dT = 8 \times 10^{-4}$ eV K^{-1} as in HgSe (Takeyama and Galazka 1979). According to Manhas *et al* (1987), in a semimagnetic semiconductor with $E_g \simeq 0.5$ eV one can expect that the exchange interaction between magnetic ions occurs predominantly through the mechanism of superexchange, and in another three samples with smaller energy gaps superexchanges should play an important role.

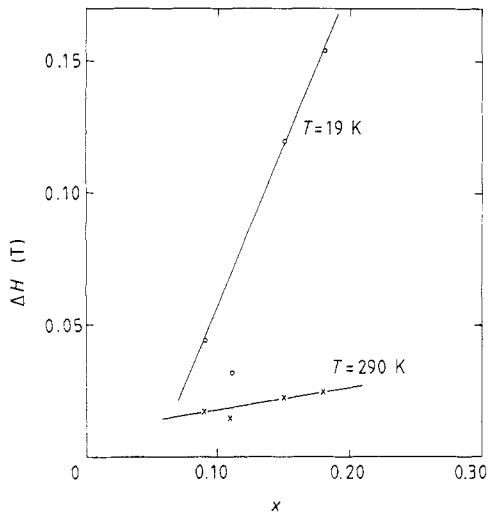

Figure 2. EPR linewidth in $Hg_{1-x}Mn_xSe$ as a function of manganese concentration at $T = 19$ and 290 K.

Taking into account all the above arguments, as well as the observed temperature dependence of the EPR linewidth in $Hg_{1-x}Mn_xSe$ (expression (2)), which is also predicted theoretically in Huber's theory (expressions (3) and (3′)), we have concluded that such a temperature dependence arises from the antiferromagnetic exchange interaction between Mn^{2+} ions which occurs mostly through the mechanism of superexchange like in magnetic insulators.

3.2. Concentration dependence of the EPR linewidth

In figure 2 the EPR linewidth in $Hg_{1-x}Mn_xSe$ is presented as a function of manganese concentration at two temperatures, 19 and 290 K. As can be seen, the linewidth has a linear dependence on manganese concentration with a significant deviation for $x = 0.11$ which has been discussed above. The slope of this linear function is about 0.0123 T/% Mn at 19 K and about 0.0009 T/% Mn at 290 K. A linear dependence of the linewidth on manganese concentration was also observed in $Hg_{1-x}Mn_xTe$ in the composition range $0.05 \leqslant x \leqslant 0.40$ (Leibler *et al* 1977) and in $Cd_{1-x}Mn_xTe$ for manganese concentrations $x \leqslant 0.20$ (Sayad and Bhagat 1985).

According to Van Vleck's model (Van Vleck 1948), in the concentrated system of magnetic ions in which all the lattice sites are equally populated, the second moment of the paramagnetic resonance depends on the dipole–dipole interaction and in the case of the polycrystalline sample we have obtained:

$$\langle \Delta\omega^2 \rangle = \omega_d^2 = \tfrac{3}{10} g^4 \mu_B^4 \hbar^{-2} z S(S+1) x r_0^{-6} \qquad (6')$$

which is proportional to $(\Delta H_{pp})^2_{dip}$. Starting from Van Vleck's general expression for the second moment and assuming a random distribution of paramagnetic ions Kittel and Abrahams (1953) have found that for paramagnetic ion concentrations $x > 0.1$ the dipolar linewidth should be Gaussian with the linewidth proportional to $x^{1/2}$. Since in Anderson's model of exchange-narrowed EPR line the linewidth is proportional to the square of the dipolar linewidth, it follows that $(\Delta H_{pp})^2_{dip} \sim x$ which is in fact the same result as (6′). Therefore, it seems that the observed linear dependence of the EPR linewidth on manganese concentration in $Hg_{1-x}Mn_xSe$ arises from the dipole–dipole interaction which is the main source of anisotropy in this system. However, with increasing manganese concentration the mean cluster size of Mn^{2+} ions also increases. In a

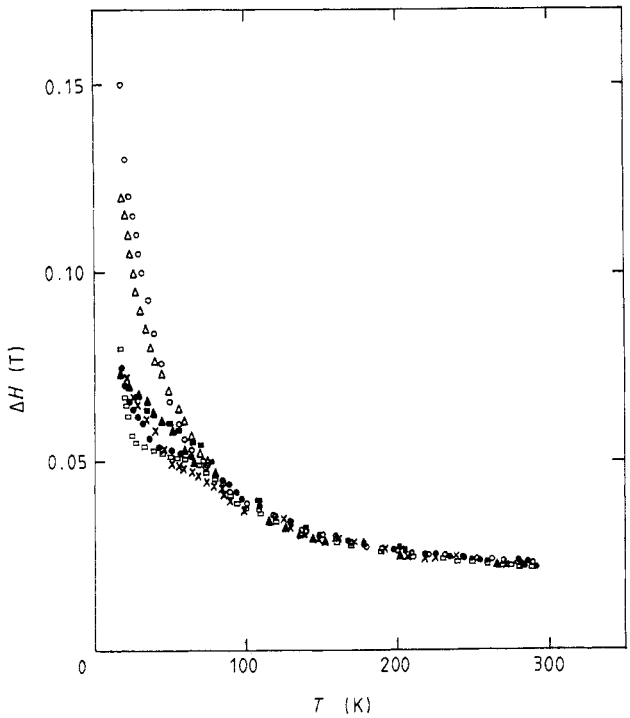

Figure 3. EPR linewidth in the sample of $Hg_{1-x}Mn_xSe$ with $x = 0.18$ plotted against temperature for several applied doses of gamma radiation: ○, 0 kGy; △, 50 kGy; □, 100 kGy; ×, 150 kGy; ●, 200 kGy; ▲, 300 kGy; ■, 550 kGy.

detailed study of the EPR linewidth dependence on manganese concentration, the influence of cluster structure changes on EPR spectra should be also examined.

3.3. Dependence of the EPR linewidth on the dose of ^{60}Co gamma radiation

The samples of $Hg_{1-x}Mn_xSe$ were irradiated at room temperature by ^{60}Co gamma rays. After each dose of gamma radiation, the EPR resonance spectrum of the samples with $x = 0.09$ and 0.18 was measured in the temperature range 19–290 K. The resonance spectrum remains single line without shift of the position of the line. The main effect of irradiation observed in this experiment is the variation of the linewidth with the radiation dose which becomes very pronounced at low temperatures. In figure 3 the linewidth of the sample $x = 0.18$ is plotted against temperature for several applied doses of gamma radiation from 50 kGy to 550 kGy. In figure 4 the EPR linewidth of the samples $x = 0.09$ and 0.18 is presented as a function of gamma radiation dose at $T = 19$ K. As can be seen, there is a common tendency of the linewidth to decrease with increasing dose, but in the sample with $x = 0.09$ a maximum of the linewidth was observed around 100 kGy.

The energy of gamma rays used in this experiment was $E_\gamma = 1.3$ MeV. It is known (Kelly 1970) that for energies of gamma rays below $10\,m_0c^2 = 5.1$ MeV the dominant process in the interaction of gamma rays with a material is the Compton effect. The Compton electron takes a large part of the energy E_γ and on its way through the material may interact with atomic nuclei and lead to a displacement of atoms. From the relation $AT_{max}(\text{eV}) = 560.8\,(2 + E/m_0c^2)\,E/m_0c^2$ (Kelly 1970) it was found that for the Compton electron energy $E = E_{max} = 1.1$ MeV the maximum energy T_{max} which can be transferred

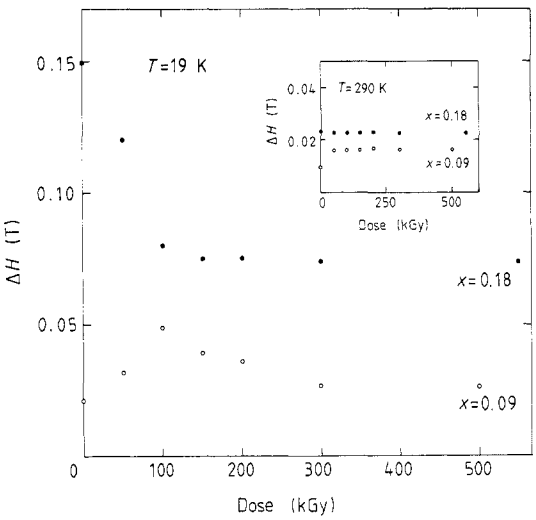

Figure 4. EPR linewidth in the samples $Hg_{1-x}Mn_xSe$ with $x = 0.09$ and 0.18 as a function of gamma radiation dose at $T = 19$ K. Inset: EPR linewidth in the same samples as a function of gamma radiation dose at $T = 290$ K.

to the atom of atomic mass A is: for mercury $T_{max} = 24.6$ eV, for manganese $T_{max} = 89.4$ eV and for selenium $T_{max} = 62.2$ eV. Since the minimum energy necessary to remove the atom from its lattice position is about $E_d \simeq 25$ eV, it is immediately seen that the energy of gamma rays used in this experiment is large enough to dislocate the atoms of manganese and selenium, but the probability of removing the heavy atoms of mercury from the lattice positions is so small that it can be neglected.

The quantity $n_d = E_{abs}/E_d$ was used as a measure of the number of defects (i.e. the number of dislocated manganese and selenium atoms) produced during irradiation. For the absorbed dose of 100 kGy in the sample with $x = 0.18$, $E_{abs} = 100 \times 10^3$ J kg^{-1} = 4.7×10^{21} eV cm^{-3} and $n_d \simeq 1.9 \times 10^{20}$ cm^{-3}. In the sample with $x = 0.18$ the number of atoms in unit volume is $N = 3.6 \times 10^{22}$ cm^{-3} and $N/n_d \simeq 190$, i.e. one defect is produced in a volume containing about 190 atoms.

For an absorbed dose of 500 kGy, $E_{abs} = 500 \times 10^3$ J kg^{-1} = 2.4×10^{22} eV cm^{-3} and $n_d \simeq 9.5 \times 10^{20}$ cm^{-3}, or $N/n_d \simeq 38$, i.e. one defect is produced in a volume containing about 38 atoms.

Two samples of $Hg_{1-x}Mn_xSe$, with $x = 0.11$ and 0.18, were irradiated with gamma rays and then put on a powder x-ray diffractometer. It was found (figure 5) that the crystal lattice parameter a in the sample with $x = 0.11$ remains practically unchanged as the applied dose increases up to 120 kGy, whereas in the sample with $x = 0.18$ there is a slight decrease of this parameter from $a = 0.6051$ nm in the unirradiated sample to $a = 0.6033$ nm for the applied dose of 120 kGy. Such a small change of the crystal lattice parameter is not surprising if only one defect is produced in about 190 atoms in the crystal for the gamma radiation dose of 100 kGy, as estimated above. However, the applied gamma radiation doses produce significant variation of the EPR linewidth at low T (figure 4).

The change of interionic distance between the nearest-neighbour Mn^{2+} ions induced by irradiation $\Delta r_0 = \Delta a\sqrt{2}/2$ is very small, so that the corresponding variation of the EPR linewidth due to the change of dipole–dipole and exchange interaction is also very small. For example, the decrease of interionic distance at room temperature in the sample with $x = 0.18$ induced by a gamma radiation dose of 120 kGy is $\Delta r_0 = r_0^{irr} - r_0 = -0.0013$ nm (figure 5). Such a decrease of interionic distance would increase the EPR

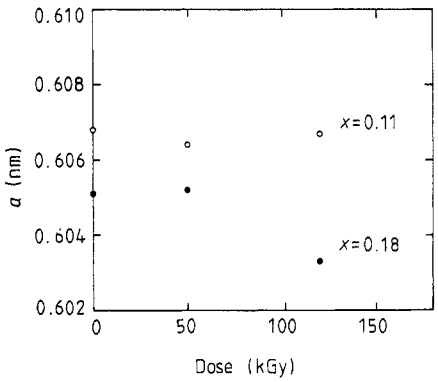

Figure 5. Crystal lattice parameter in unirradiated samples of $Hg_{1-x}Mn_xSe$ with $x = 0.11$ and 0.18, and for two doses of gamma radiation, 50 kGy and 120 kGy at room temperature.

linewidth due to dipole–dipole interaction (expression (6)) from 0.1127 T to 0.1137 T, i.e. by 0.9%.

The exchange integral also changes with the change of interionic distance. According to Manhas *et al* (1987) the dominant mechanism of exchange interaction in $Hg_{1-x}Mn_xSe$ with $x = 0.18$, which has the energy gap $E_g = 0.52$ eV, should be the superexchange. In that case (Manhas *et al* 1987), $J(r) = I_0 r^{-2} e^{-\alpha r}$. If one takes for α in the zinc blende structure $\alpha \simeq 6\ (\text{nm})^{-1}$, the relative increase of exchange integral, due to the radiation-induced decrease of interionic distance $\Delta r_0 = -0.0013$ nm, is $(J_{\text{irr}} - J)/J = r_0^2 (r_0 + \Delta r_0)^{-2} \exp(-\alpha \Delta r_0) - 1 \simeq 0.014 \simeq 1.4\%$. Such an increase of the exchange integral would decrease the EPR linewidth (expression (5)) by about $(\Delta H_{\text{pp}}^{\text{irr}} - \Delta H_{\text{pp}})/\Delta H_{\text{pp}} = (J - J_{\text{irr}})/J_{\text{irr}} = r_0^{-2} (r_0 + \Delta r_0)^2 \exp(\alpha \Delta r_0) - 1 \simeq -0.014 \simeq -1.4\%$. However, the variations of the linewidth of about 1% are less than the error in the measurements and cannot be detected. The inset in figure 4 shows that at room temperature there is no variation of the EPR linewidth with the applied gamma radiation dose (except the jump of the linewidth at 50 kGy in the sample $x = 0.09$).

We expect that the gamma-radiation-induced change of interionic distance at low temperatures is not very different from that observed at room temperature. In this case the corresponding variation of the EPR linewidth should also be very small. It seems that the real distribution of manganese ions in clusters has a considerable influence on the observed linewidth dependence on the gamma radiation dose at low T (figure 4). The integral absorption line around $g = 2$ is the superposition of spectra of all clusters, and the spectrum of each cluster can be considered as a superposition of contributions from many multiplets (Korteweg and van Reijen 1981). If some manganese ions are removed from the clusters during irradiation, the number of multiplets, i.e. the number of individual lines from these clusters, should be reduced, which may lead to a narrowing of the integral absorption line, as observed at low T. This effect is absent at room temperature (inset in figure 4) which might be connected with a distribution of manganese ions which is 'more random'. The rapid initial increase of the EPR linewidth in the sample with $x = 0.09$ as the gamma radiation dose increases up to 100 kGy at $T = 19$ K and up to 50 kGy at room temperature (figure 4) remains a puzzle. It may be connected with a decrease of the effective exchange integral of manganese ions in clusters from which some manganese ions are removed, and this effect should be more pronounced in clusters of smaller sizes. We believe that a cluster model of EPR spectra should be developed for a diluted magnetic semiconductor such as $Hg_{1-x}Mn_xSe$ in order to explain the observed effects of gamma radiation on these spectra and also to examine in detail the temperature and concentration dependence of the EPR linewidth.

4. Conclusions

The analysis of the EPR linewidth measured in $Hg_{1-x}Mn_xSe$ crystals with $x = 0.09, 0.11, 0.15$ and 0.18 as a function of temperature in the range $19 \leqslant T \leqslant 290$ K and as a function of gamma radiation dose up to 550 kGy suggests that:

(i) the temperature dependence of the linewidth arises from the antiferromagnetic exchange interaction between manganese ions which occurs mostly through the mechanism of superexchange;

(ii) the dependence of the linewidth on manganese concentration seems to arise from the dipole–dipole interaction; however, in a detailed study of the EPR linewidth dependence on manganese concentration, the influence of cluster structure changes on EPR spectra should be also examined;

(iii) the gamma-radiation-induced change of interionic distance and corresponding changes of dipole–dipole interaction and exchange integral are so small that they cannot account for the observed dependence of the EPR linewidth on the gamma radiation dose at low T; it seems that a cluster model of EPR spectra, including the radiation-induced lattice defects, should be developed for $Hg_{1-x}Mn_xSe$ in order to explain the observed effects of gamma radiation on these spectra.

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