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ELECTRON SPIN RESONANCE IN THE COMPOUNDS $HgCr_{2-x}Al_xSe_4$ AND $HgCr_{2-x}Ga_xSe_4$

By A. Kasprzyk

Institute of Physics, Silesian University, Katowice*

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ESR measurements were made in the X-band for the temperature range 105–300 K for polycrystalline compounds $HgCr_{2-x}Al_xSe_4 (x = 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.4)$ and $HgCr_{2-x}Ga_xSe_4 (x = 0.1, 0.2, 0.3, 0.4, 1.0, 1.25)$. An analysis of the dependence on temperature of ESR line width $\Delta H_{pp} = f(T)$ has been made. It was shown that temperature changes of line width could be due to diffusion of defects near the structural octahedron occupied by the chromium ion Cr^{3+}.

1. *Introduction*

The compounds under investigations are magnetic semiconductors. These compounds were obtained from the normal spinel $HgCr_2Se_4$ by partially replacing the Cr^{3+} ion by Al^{3+} or Ga^{3+} ions.

ESR of chromium spinels $HgCr_2Se_4$, $HgCr_2S_4$, $CdCr_2S_4$ and $CdCr_2Se_4$ [1–4] indicates the temperature dependence of line width. This dependence cannot be explained on the basis of the chromium ion Cr^{3+}, weakly relaxing to the lattice.

2. *Results*

The measurements of ESR line width at the frequency of 9.25 GHz in the temperature range 105–300 K for the polycrystalline compounds $HgCr_{2-x}Al_xSe_4$, $x = 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.4$ and $HgCr_{2-x}Ga_xSe_4$, $x = 0.1, 0.2, 0.3, 0.4, 1.0, 1.25$ (Fig. 1, 2) were made. The line widths reported in this paper are peak-to-peak magnetic field separations in the absorption derivative. The investigated samples are mixed spinels: $(Hg^{2+}_{1-\lambda}Al^{3+}_{\lambda})[Hg^{2+}_{\lambda}Al^{3+}_{x-\lambda}Cr^{3+}_{2-x}]Se_4$ and $(Hg^{2+}_{1-x}Ga^{3+}_{x})[Hg^{2+}_{x}Cr^{3+}_{2-x}]Se_4 - x = \lambda$, ($\lambda$ is the parameter of inversion), for aluminium concentrations 0.1, 0.2, 0.4, 0.6 and gallium concentrations 0.1, 0.2, respectively [5, 6]. Apart from the magnetic spinel phases, for the concentrations $x(Al) > 0.6$ and $x(Ga) > 0.2$, there are diamagnetic tetragonal phases $HgAl_2Se_4$ and $HgGa_2Se_4$, respectively [6].

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* Address: Instytut Fizyki, Uniwersytet Śląski, Uniwersytecka 4, 40-007 Katowice, Poland.

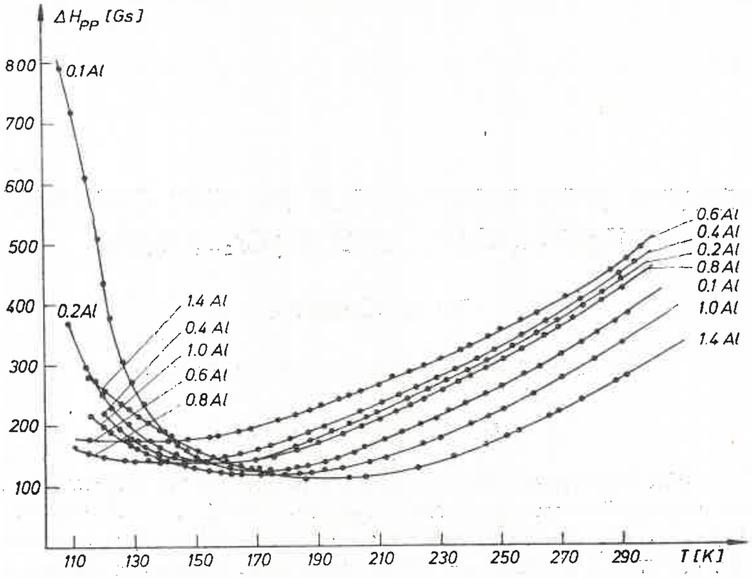

Fig. 1. Temperature dependence of ESR line width for $HgCr_{2-x}Al_xSe_4$

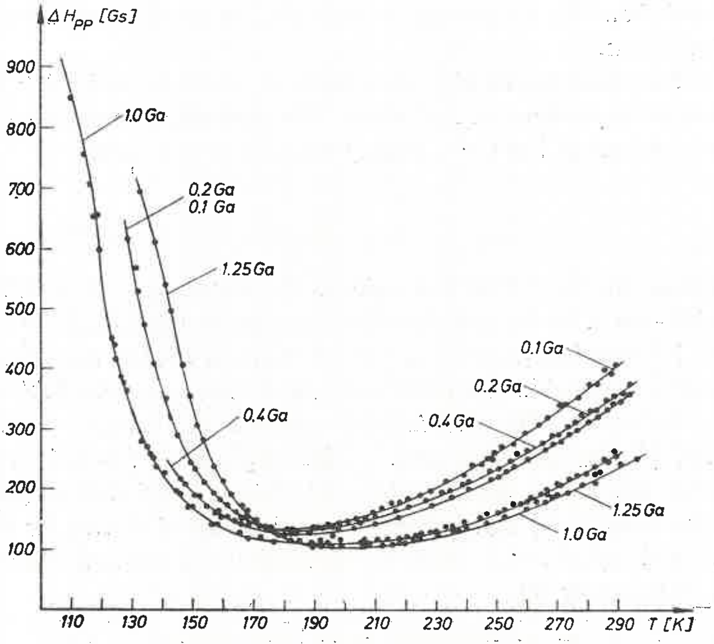

Fig. 2. Temperature dependence of ESR line width for $HgCr_{2-x}Ga_xSe_4$

3. Discussion

The temperature dependences of line width are similar for all the substances under investigations. The line widths decrease with decreasing temperature down to some temperature $T_{\min}$, where the line widths have their minimum values ($T > T_{\min}$ — paramagnetic region). For temperatures $T < T_{\min}$ the line widths increase. This is connected with the paramagnetic-ferromagnetic phase transition [3].

The line widths are of the order of 400 Gs at room temperature. This value corresponds to the relaxation time of the order of 10^{-9} sec. This time can be estimated on the basis of line width. The shape of an ESR line in the temperature range under investigation was determined from the ratio [7]:

$$\frac{I'(\frac{3}{2}\Delta H_{\mathrm{pp}})}{I'(\frac{1}{2}\Delta H_{\mathrm{pp}})} = f(T),$$

where $I'(3/2\Delta H_{\mathrm{pp}})$ is amplitude of absorption derivative at a distance of $3/2\Delta H_{\mathrm{pp}}$ from the centre of the line and $I'(1/2\Delta H_{\mathrm{pp}})$ is amplitude at distance $1/2\Delta H_{\mathrm{pp}}$. The theoretical values of this ratio are: 0.333 — for a Gaussian curve, 0.0549 — for a Lorentzian curve.

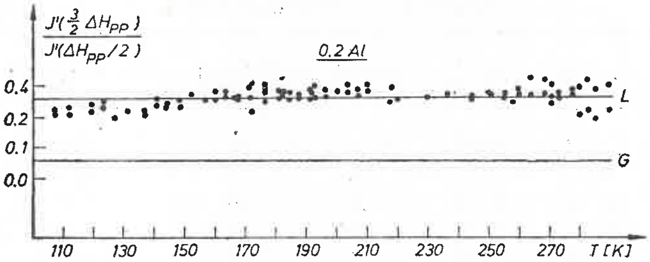

Fig. 3. Temperature dependence of the ratio for a typical ESR line

Typical dependence is seen in Fig. 3. The investigated samples demonstrate Lorentzian-type resonance lines.

Two types of function were used for the description of temperature dependence of the ESR line width [4]:

$$\Delta H(T) = \Delta H_0' + A'T^n \tag{1}$$

$$\Delta H(T) = \Delta H_0 + A\exp\left(-\frac{\theta}{T}\right). \tag{2}$$

Parameters $\Delta H_0'$, A' and n in Eq. (1) and parameters ΔH_0, A and θ in Eq. (2) were calculated using an ODRA 1204 computer. The error in fitting was determined using the following formula:

$$\delta H = \left[\sum_{i=1}^{N} \frac{(\Delta H_i - {}^t\Delta H_i)^2}{N}\right]^{1/2}.$$

where ΔH_i are the experimental values of the line width, $'\Delta H_i$ — the theoretical values of the line width calculated from Eqs (1) and (2), N — the number of experimental points The fitted parameters and the errors are given in Tables I and II.

TABLE I

Parameters for $HgCr_{2-x}Al_xSe_4$

x(Al)	ΔH_0[Gs]	A[Gs]	θ[K]	δH[Gs]	$\Delta H'_0$[Gs]	$A'[GsK^{-n}]\times 10^8$	n	$\delta H'$[Gs]
0.1	93	8920	989	8.1	46	1078	3.0	8.1
0.2	123	7755	919	8.3	70	3731	2.8	7.6
0.4	130	6964	893	9.5	79	5270	2.8	8.2
0.6	154	3972	746	8.1	110	35891	2.4	7.9
0.8	120	10796	1015	11.5	83	241	3.3	11.5
1.0	104	13787	1202	7.9	83	4	4.0	7.9
1.4	102	46296	1626	8.5	94	2×10^{-4}	5.7	8.6

TABLE II

Parameters for $HgCr_{2-x}Ga_xSe_4$

x(Ga)	ΔH_0[Gs]	A[Gs]	θ[K]	δH[Gs]	$\Delta H'_0$[Gs]	$A'[GsK^{-n}]\times 10^8$	n	$\delta H'$[Gs]
0.10	94	9171	1023	13.6	60	260	3.3	13.7
0.20	102	14613	1169	5.4	75	113	3.8	5.8
0.30	107	22763	1291	12.8	85	1	4.3	12.4
0.40	104	25441	1346	4.2	82	0.35	4.4	4.5
1.00	108	240135	2117	8.4	102	1.7×10^{-8}	7.3	8.0
1.25	92	74269	1790	6.9	85	8.3×10^{-6}	6.2	6.0

Changes in line width in the investigated temperature range are described very well by both functions. However, the n (function (1)) change their values within rather wide limits: 2.4–4 for $HgCr_{2-x}Al_xSe_4$ and 3.3–7.3 for $HgCr_{2-x}Ga_xSe_4$. For the temperature range under investigation the theory of spin-lattice relaxation predicts: $n = 1$ or $n = 2$ [8]. Then, the function (1) can be excluded from the following considerations (the value $n \approx 2$ for x(Al) $= 0.6$ is probably accidental).

4. *Conclusions*

The chromium ion Cr^{3+} is the only magnetic ion in the compounds $HgCr_{2-x}Al_xSe_4$ and $HgCr_{2-x}Ga_xSe_4$ and it occupies an octahedral position. The great separation between the ground state level $^4A_2$ (zero angular momentum) and the nearest level $^4T_2$ (with nonzero angular momentum) gives evidence of a weak bounding to the lattice. The concentration of magnetic ions is high in the investigated materials. Then, the main factor determining the ESR line width ought to be the spin-spin interactions: exchange and magnetic dipole-

-dipole (nearly independent of temperature). However, the exponential temperature dependence of ESR line width is observed.

The changes of parameter θ with respect to aluminium (gallium) concentration cannot be explained on the basis of present models (relaxation through local phonons localized on paramagnetic impurities [1, 2, 4]).

It seems, that the line broadening in $HgCr_{2+x}Al_xSe_4$ and $HgCr_{2-x}Ga_xSe_4$, at the investigated paramagnetic region, can be due to diffusive jumps of defects near an octahedron occupied by the ion Cr^{3+} [9]. If the diffusion of defects causes the observed temperature change of ESR line width, the line width (the part dependent on temperature) must be equal to the frequency of diffusive jumps. The equation, which coupled the frequency of the jumps ν_p and the diffusion barrier E_A (activation energy of diffusion) separating the two positions of a defect, before and after the jump, has the following form [10]:

$$\nu_p = \nu \exp\left(-\frac{E_A}{T}\right), \tag{3}$$

where the frequency ν is generally not known and is usually taken as the Debye frequency. The value of E_A can be estimated on the basis of Eq. (3). For compounds $HgCr_{2-x}Al_xSe_4$ and $HgCr_{2-x}Ga_xSe_4$ the Debay temperatures [6] are of the order of 200 K, which corresponds a Debay frequency of the order of 10^{12} Hz. The line widths, at the temperature of 200 K, are about 50 Gs, which corresponds to a frequency $\nu_p = 10^8$ Hz. Then, the activation energy of diffusion is of the order of 1000 K, according to parameters θ calculated from formula (2). The estimated values of activation energy of diffusion indicate that temperature changes of line width could be due to the diffusion of defects. It can explain the observed temperature changes of the ESR line width not only for compounds under discussion but also for other spinel structures (for example $HgCr_2S_4$, $HgCr_2Se_4$, $CdCr_2S_4$, $CdCr_2Se_4$) where similar values of the parameter θ were obtained [1, 2, 4].

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