

PARAMAGNETIC RESONANCE IN MONOCRYSTALS OF CdCr_2Se_4 AND CdCr_2S_4

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Paramagnetic resonance was studied in the magnetic semiconductors CdCr_2Se_4 and CdCr_2S_4 which possess a spinel structure. The measurements were carried out in the 3 cm band in a temperature range from the Curie temperature to 500°K. It was found that the temperature dependence of the resonance width is characterised by a broad minimum at a temperature T_{min} which is equal to 200°K for CdCr_2Se_4 and 240°K for CdCr_2S_4 . It was determined that the minimal width of the resonance curve is proportional the concentration of paramagnetic impurities. Further, it was proved that the broadening of the EPR curve for temperatures higher than T_{min} is caused by Raman relaxation processes in which local phonons take part. The energy of these was determined.

1. Introduction

Crystals of CdCr_2Se_4 and CdCr_2S_4 belong to a large group of so-called magnetic semiconductors with a spinel structure. The interest attaching to this type of compound arises from the possibility of a strong interdependence between the electric and magnetic properties in such crystals. This fact also augurs well for the feasibility of technical exploitation of semiconducting magnetics in electron devices with magnetically controlled parameters. Prospects of technical application are difficult to predict at this point.

Studies on the semiconducting properties of magnetic spinels have centered largely on CdCr_2Se_4 [1-3]. This crystal, in its undoped state, is a *p*-type semiconductor. Small admixtures of monovalent ions such as silver, gold, or copper, introduced in place of the cadmium ions, enhance the *p*-type conductivity. Doping with gallium or indium results in *n*-type conductivity. Studies on electric conductivity in undoped CdCr_2Se_4 crystals

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lead to the conclusion that the presence of Cr^{2+} ions plays a large part in the conduction mechanism. (In an ideal CdCr_2Se_4 crystal, the chromium ions appear only as trivalent ions Cr^{3+} .) Conductivity and photomagnetic effect studies in $\text{CdCr}_2\text{Se}_4:\text{Ga}$ lead to similar conclusions. The presence of Cr^{2+} ions also serves to explain the anomalous dependence of the resonant field and of the peak width in ferromagnetic resonance upon the direction of the magnetic field at 4.2°K [5–10]. The parameters cited vary from sample to sample and also depend, as was found in [9–10], upon the conditions of crystal formation (especially upon the temperature). Magnetocrystal anisotropy constants, determined from the angular dependence of the resonance field also indicate the presence of chromium Cr^{2+} ions, probably in octahedral sites.

The optical properties of doped and undoped crystals of CdCr_2Se_4 and CdCr_2S_4 were studied in Ref. [11]. The interpretation of experimental data, and especially of absorption spectra, carried out in [11] does not assume the presence of Cr^{2+} ions in these crystals. Although such an interpretation is possible, it does not exclude the presence of Cr^{2+} ions or of other paramagnetic impurities in the spinels under study. It is to be expected that the presence of Cr^{2+} ions (or of other impurities) will affect not only ferromagnetic resonance, but also the resonance in the paramagnetic region.

2. Objectives

The objective of the present work was to study paramagnetic resonance in monocrystals of CdCr_2Se_4 and CdCr_2S_4 . Both crystals are ferromagnetics with Curie temperatures T_c of 129.5–142°K for CdCr_2Se_4 and 84.5–97°K for CdCr_2S_4 , according to Ref. [12]. The uncertainty of T_c arises both from differences in definition and measurement of the Curie temperature, and also from the presence of impurities which likewise have a strong effect upon it [7].

Paramagnetic resonance in CdCr_2Se_4 was measured in Refs [5, 6, 9, 13] and in CdCr_2S_4 in Ref. [13], the experiments being carried out in polycrystals in the last case. The results of these experiments are, in the paramagnetic region, often contradictory and fragmented. For this reason studies were also conducted on monocrystals of CdCr_2Se_4 , in addition to experiments on paramagnetic resonance measurements in monocrystals of CdCr_2S_4 , hitherto unstudied. The technology of growing the above-mentioned crystals has a strong influence upon their magnetic properties. The crystals studied in this work were characterised by a relatively narrow paramagnetic resonance curve (generally narrower than in the other papers), so it is to be expected that the concentration of Cr^{2+} ions in them was also relatively low. For this reason the technology of obtaining these crystals will be described in detail below.

3. Technology of growing CdCr_2S_4 and CdCr_2Se_4 monocrystals

The initial ingredients in the technology of growing CdCr_2S_4 monocrystals were CdS and CrCl_3 [5, 14, 15]. Anhydrous CrCl_3 was amalgamated with a small amount of platinum and pressed into pellets of 2 cm diameter. The cadmium sulphide was also pressed

in a like manner after being subjected to double sublimation in vacuum [16] and to pulverisation. The pressed pellets (CdS and CrCl_3 in a weight ratio of 2:1) were partitioned with fused quartz and placed in a suitably prepared quartz capsule, which was fused at a vacuum of 5×10^{-5} Tr. After the capsule was placed in the kiln (Fig. 1) at room temperature, the heat was turned on and the maximum temperature reached within 5 hours. The insert was kept at this temperature for 3–5 days after which the whole

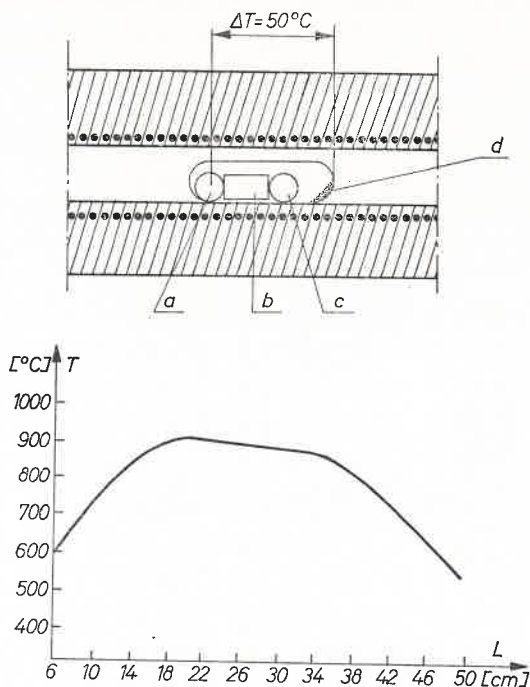


Fig. 1. Diagram of capsule arrangement with reagents for obtaining CdCr_2S_4 crystals and temperature characteristics of cylindrical resistance — element oven. *a* — CrCl_3 + Pt pellet, *b* — quartz cone, *c* — CdS pellet, *d* — condensed liquid with crystals

oven was cooled down. Under these conditions transport through the gas phase takes place and the condensed liquid gradually collects in the cooled part of the capsule. Inclination of the kiln at around 20° from the horizontal facilitates the gathering of the liquid in the cooler part of the capsule. The best crystallisation conditions were obtained at a maximum temperature $T_{\text{max}} = 900^\circ\text{C}$, at a processing time of 4.5 days, a platinum content of 4% mol in relation to the quantity of CrCl_3 , and a cooling rate of 27.4°C/hr . Under those conditions crystals were obtained not only in the condensed liquid but also at the site of the CdS pellet. The dimensions of the crystal were of the order of 1 mm. The efficiency of the process of obtaining CdCr_2S_4 crystals described above was assessed at 20% in relation to substratum weight.

CdCr_2Se_4 crystals were obtained by a method similar to one proposed by von Philipsborn [17, 18, 19]. The initial materials were pressed pellets of CdSe and CrCl_3 . The CdSe pellets were prepared using a powder obtained from the synthesis of cadmium and

selenium of spectral purity after twofold sublimation in vacuum [16]. The pellets, ordered in the sequence CrCl_3 - CdS - CrCl_3 , were placed in a quartz vessel in such a manner as to maintain contact between them, after wrapping them in thin platinum foil. The rest of the capsule was filled with quartz glass. The vessel and its contents were placed in the quartz capsule, which was fused in a vacuum of 5×10^{-5} Tr. The capsule was then placed in the kiln at room temperature, heated to a maximum temperature (700°C) within 3–5 hours, and maintained in these conditions for 3–5 days, after which the capsule was removed from the kiln and cooled in air to room temperature. The distribution of the capsule

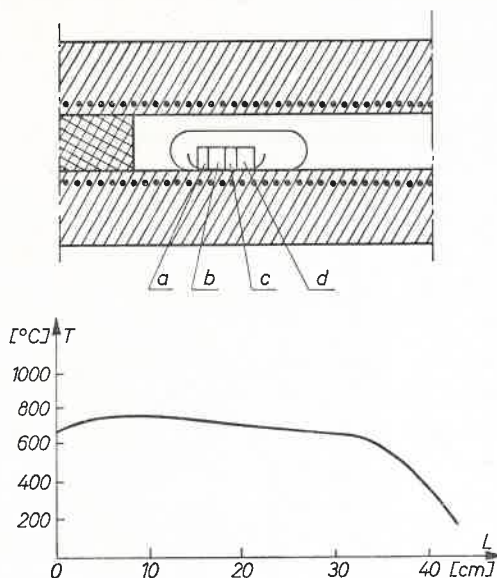


Fig. 2. Diagram of capsule arrangement for obtaining CdCr_2Se_4 crystals and temperature characteristics of cylindrical resistance — element oven. *a* — CrCl_3 , *b* — CdSe , *c* — CrCl_3 , *d* — quartz

elements in the oven and the temperature gradient over its length are depicted in Fig. 2. From this diagram it is evident that the crystallization process in CdCr_2Se_4 took place in the absence of a temperature gradient. Crystals formed mostly at the contact between the CdSe - CrCl_3 pellets in the CrCl_3 part, largely in the vicinity of the surface. The efficiency of the process varies in the range 20–22% in relation to the weight of the substrata. The crystals possess the form of well-developed octahedrons of dimensions around 2 mm.

4. Results of the experiment

The paramagnetic resonance was measured using an EPR spectrometer operating on the X-band. The spectrometer was equipped with an apparatus for stabilising and regulating the crystal temperature in a range from the Curie temperature to 500°K . The width of the resonance curve and the strength of the resonant field were measured by means of a proton magnetic-field intensity meter.

A single, symmetric resonance curve was observed over the whole range of temperatures investigated. The resonance curve had a shape similar to that of the Lorentz curve except for the region around T_c . No variation in the g -factor with temperature was observed. The measured g -value was close to 1.99, similarly as in isolator-spinels of the $\text{MgAl}_2\text{O}_4 + \text{Cr}^{3+}$ type.

Fig. 3 depicts changes in the resonance width for CdCr_2Se_4 and CdCr_2S_4 in the temperature range from T_c to 480°K. The width ΔH was measured between points of

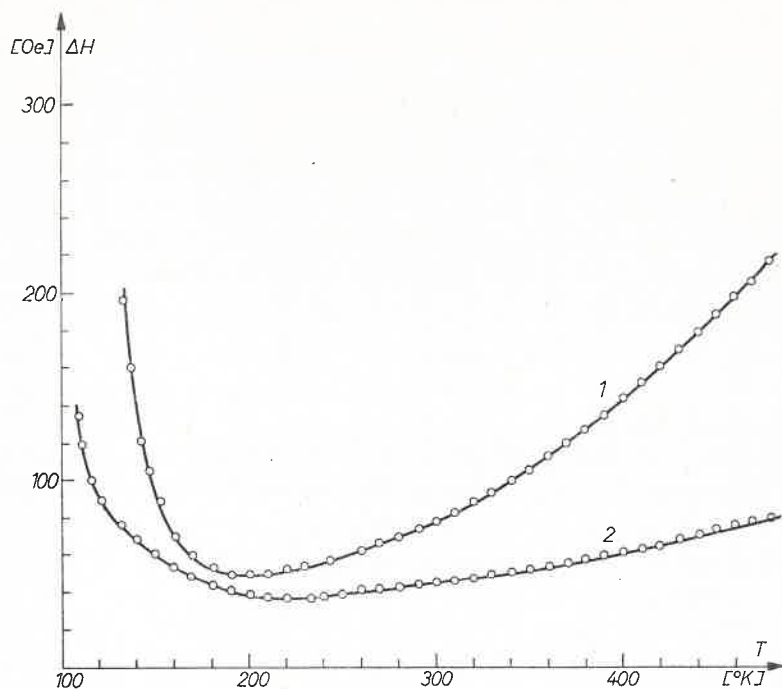


Fig. 3. Dependence of resonance width ΔH on temperature in monocrystals of CdCr_2Se_4 (1) and CdCr_2S_4 (2)

maximum slope on the resonance curve. The nature of the dependence $\Delta H = \Delta H(T)$ is similar in both crystals and is characterised by the presence of a broad minimum at around 200°K for CdCr_2Se_4 and around 240° for CdCr_2S_4 . The smallest line width, occurring at $T = T_{\text{max}}$ in 48 Oe for CdCr_2Se_4 and 38 Oe for CdCr_2S_4 .

5. Interpretation

Paramagnetic resonance in CdCr_2Se_4 was measured in Refs [5, 6, 9, 13]. On comparison of the findings of these experiments with the results presented in Fig. 3 it can be seen that in all cases the dependences $\Delta H = \Delta H(T)$ are similar in character. In every instance a minimum of the resonance width is observed at a specific temperature T_{min} (which is different in different sources). The smaller the resonance width the better defined is the minimum. In Ref. [6], where the curve at $T = T_{\text{min}}$ is the widest, the minimum is the least

clearly defined. The minimum appears most clearly in [13] where $\Delta H(T_{\min}) = 45$ Oe, that is, as in Fig. 3. This phenomenon can be explained assuming that the broadening of the resonance curve in the temperature range $T > T_{\min}$ is associated with the presence of impurities that are very strongly bound to the lattice. With an increased concentration of such impurities the width of the resonance curve increases and at the same time the minimum shifts toward T_c and becomes less pronounced.

Experimental results in CdCr_2S_4 are similar in form. They can be compared only with results of measurements on polycrystals in Ref. [13]. In [13] the width of the resonance curve is around twice that of the curve shown in Fig. 3 in the temperature range $T \geq T_{\min}$.

On the basis of the results in Fig. 3 it can be observed that the mechanism of broadening of the resonance curve is the same for both crystals. Here we must distinguish the two following temperature regions: $T_c < T < T_{\min}$ and $T > T_{\min}$. In the range $T_c < T < T_{\min}$ the broadening is associated with the occurrence of short-range ordering. The line width of the electron paramagnetic resonance in the vicinity of the Curie temperature was measured in many cases (see *e. g.* [20-23]). From these reports it appears that in the temperature range under discussion,

$$\Delta H \sim \chi^n \quad n > 0 \quad (1)$$

where χ = magnetic susceptibility.

The parameter n is equal to 3/4 under the assumption that the exchange interaction Hamiltonian is isotropic in character when effects due to the crystal field are not taken into account.

From (1) it appears that in the vicinity of the transition temperature the following temperature dependence is to be expected:

$$\Delta H \sim (T - T_c)^{-\gamma} \quad \gamma > 0. \quad (2)$$

In actual fact the following dependence is observed in the region $T_c < T < T_{\min}$:

$$\Delta H = C(T - T_c)^{-\gamma} + D \quad (3)$$

where C and D are constants.

The parameter γ has the same value for both crystals and is equal to 1.1 ± 0.1 .

Empirical formulas analogous to (3) were obtained also in other sources [23-27]. Although a detailed theory of EPR line width in vicinity of the critical point (taking into account exchange and dipole interactions, effects due to the crystal field, and Zeeman energy) has not as yet been elaborated, there is little doubt that the broadening of the curve in the region $T_c < T < T_{\min}$ is connected with the occurrence of short-range ordering.

The mechanism of EPR curve broadening in the range $T > T_{\min}$ is altogether different. The widening in this range is caused by the coupling of the spin to the crystal lattice. In the case when spin-lattice coupling is not taken into account, the width of the resonance curve does not depend on temperature and is determined by exchange and spin-spin interactions.

In that case the resonance line has the Lorentz-curve shape with a width:

$$\Delta H = \alpha M_2 \sqrt{\frac{M_2}{M_4}}, \quad (4)$$

where α — constant, M_2 and M_4 are the second and fourth moments of the curve, defined as follows:

$$M_n = h^n \int_{-\infty}^{+\infty} g(h) dh,$$

where $h = H - H_{\text{res}}$, and $g(h)$ is the normalised function describing the shape of the resonance curve.

The isotropic exchange interactions contribute to M_4 but not to M_2 , causing (in accordance with (4)) a narrowing of the resonance peak (so-called exchange narrowing). Since the fourth moment of the curve, M_4 , goes as J^2 (where J is the exchange integral in the exchange interaction Hamiltonian), then:

$$\Delta H \sim J^{-1}. \quad (5)$$

From (5) it follows that the width of the paramagnetic resonance curve depends in an essential way upon the strength of exchange interactions between the magnetic ions. Exchange interactions can take part in yet another mechanism of broadening the resonance curve, namely in the spin-lattice interaction mechanism. In the most general case the coupling can be of the single-ion type — when lattice vibrations modulate the crystal field acting on the magnetic ion — or of the multi-ion type (mostly two-ionic) when lattice vibrations modulate exchange or other interactions (*e. g.* dipole), between the magnetic ions. In the case of CdCr_2Se_4 and CdCr_2S_4 crystals the magnetic ions (chromium ions Cr^{3+}) have a ground state corresponding to the orbital singlet 4A_2 . For this reason it is to be expected that the single-ion mechanism will have a relatively weak effect on spin-lattice relaxation in these crystals. The multi-ionic mechanisms will have a much greater effect on spin-lattice relaxation in the case under study. It seems that the most relevant mechanism is one involving the coupling of the Cr^{3+} ions to paramagnetic impurities that quickly relax into the lattice. The fact which argues for the last of these mechanisms is that the resonance width in the crystals under study in the region $T > T_{\text{min}}$ differs in different sources (*i. e.* it depends on the technique of growing the crystals). The problem of the effect of fast-relaxing impurities on the EPR resonance width was studied in detail in [28]. Paramagnetic impurity is related to the array of magnetic moments through cross-relaxation mechanisms. The flattening of the paramagnetic resonance curve will then depend on the relationship of the time of spin-lattice impurity relaxation to the cross-relaxation time. When this ratio is high (this pertains to the case in which spin-lattice coupling is weak, considerably weaker than exchange interaction between magnetic ions), the increase in width is of the form:

$$\Delta H = \Delta H_0 + Cf T_1^{-1}, \quad (6)$$

where C — constant, f — impurity concentration, T_1 — spin-lattice paramagnetic impurity relaxation time, ΔH_0 — width of resonance curve in undoped crystals.

For very strong spin-lattice coupling the "bottle neck" effect can appear in the process of energy transfer from the spin array to the lattice, and then the broadening of the resonance line is limited by the finite probability of cross-relaxation transitions. The fact that the experimental results can to a high degree of accuracy be represented by the formula:

$$\Delta H(T) = \Delta H(T_{\min}) + Ae^{-\theta/T} \quad (7)$$

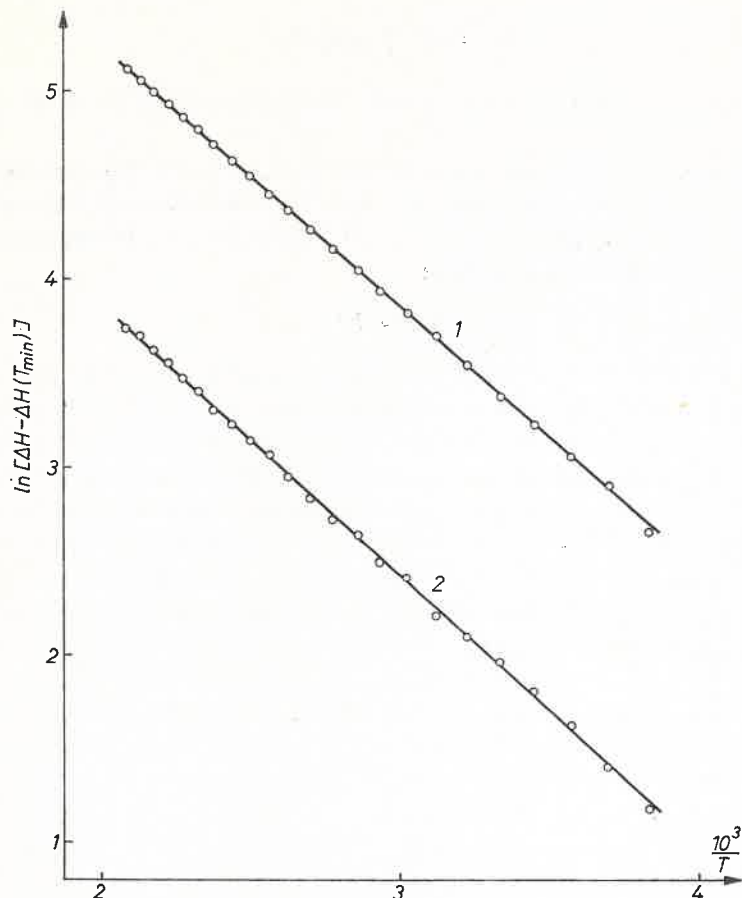


Fig. 4. Dependence of resonance width ΔH upon temperature in the region $T > T_{\min}$ plotted in coordinates $1/T$ vs $\ln [\Delta H - \Delta H(T_{\min})]$. 1 — CdCr_2Se_4 , 2 — CdCr_2S_4

is of essential relevance in explaining the widening of resonance curves with temperature.

Here, $\theta = 1400^\circ\text{K}$ $A = 3130$ Oe for CdCr_2Se_4
 $\theta = 1480^\circ\text{K}$ $A = 930$ Oe for CdCr_2S_4

This confirms the data in Fig. 4, wherein the experimental results in the region $T > T_{\min}$ are presented in a coordinate system $\ln [\Delta H - \Delta H(T_{\min})]$ and T^{-1} .

A dependence of type (7) is predicted by the spin-lattice relaxation theory for the following relaxation processes:

1. Orbach processes [29]. In this case θ represents the distance to the nearest excited level.

2. Raman processes (involving optical or acoustic phonons from the edges of the Brillouin zone) [30]. In this case $k\theta$ denotes phonon energy (optical or acoustic).

3. Raman processes involving local phonons [31]. In this case $k\theta$ denotes the energy of local phonons, localised on the impurities with $\theta > T_D$ (T_D = Debye temperature). Of the three relaxation processes mentioned above the first seems the least probable since the experimental values obtained for θ greatly exceed the Debye temperature T_D in the crystals under consideration.

The probability of occurrence of Raman processes involving optical phonons can be assessed on the basis of observation of the phonon spectrum near $k = 0$, given for CdCr_2Se_4 and CdCr_2S_4 [32, 33].

From the experimental data it follows that the energy of optical phonons in CdCr_2Se_4 is less than 300 cm^{-1} and in CdCr_2S_4 less than 400 cm^{-1} . From this it appears that the occurrence of this process is likewise improbable. There remains the conjecture that the widening described by formula (7) is due to Raman processes involving local phonons.

From this we conclude that the widening is connected with the presence of paramagnetic impurities, more importantly, impurities that are relatively tightly bound to the lattice. It is likely that the Cr^{2+} ions in octahedral sites play the role of highly relaxing centres. The ground state of such an ion is the 5E level, and such ions are tightly bound to the lattice, as it appears from [34]. At the same time one should expect the occurrence of a strong Jahn — Teller effect in such an ion. Lattice deformations produced by the Jahn-Teller effect also affect the crystal field acting on the chromium Cr^{3+} ions. Aside from the normal dipole interaction this effect causes the spreading of the EPR curve. In this way we can explain the fact that at a temperature $T = T_{\min}$ where the spreading due to spin-lattice interaction does not come into play, the width of the resonance peak is dependent on the technology of crystal growth. Both mechanisms of curve widening — the static and the dynamic — are proportional to the concentration of paramagnetic impurities and for this reason the parameter $\Delta H(T_{\min})$ can be used as its gauge.

6. Conclusions

The experiment confirmed the hypothesis that paramagnetic impurities present in crystals of CdCr_2Se_4 and CdCr_2S_4 are responsible for the characteristic dependence of paramagnetic resonance width upon temperature. It was found that the minimal curve width, $\Delta H(T_{\min})$, is proportional to impurity concentration. It was also shown that the flattening of the EPR curve at temperatures higher than T_{\min} is caused by Raman processes involving local phonons — and their energy was determined. The results show that the paramagnetic impurities present in the spinels under study could consist of chromium Cr^{2+} ions in octahedral sites.

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