

Magnetic properties and electron paramagnetic resonance spectra of CdGd_2Se_4

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 5339

(<http://iopscience.iop.org/0953-8984/4/23/010>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 11/05/2010 at 00:16

Please note that [terms and conditions apply](#).

Magnetic properties and electron paramagnetic resonance spectra of CdGd_2Se_4

E Machowska†, S Pokrzywnicki‡ and M Duczmał§

† Institute of Physics, Polish Academy of Science, Aleja Lotników 32/46, 02-668 Warsaw, Poland

‡ Institute of Mathematics and Physics, Technical University of Opole, ulica Luboszycka 3, 45-036 Opole, Poland

§ Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

Received 8 May 1991, in final form 24 February 1992

Abstract. The magnetic susceptibility and the magnetization of polycrystalline CdGd_2Se_4 were investigated. The data indicate that this compound exhibits an antiferromagnetic transition at 9.5 K. The effect of the dipolar interactions and the exchange coupling between the gadolinium ions in the crystal lattice were studied by analysis of the temperature dependence of the EPR linewidth.

1. Introduction

CdGd_2Se_4 is a magnetic semiconductor. It crystallizes in the cubic structure of the Th_3P_4 type ($I\bar{4}3d T_d^6$). The divalent cadmium atoms are randomly distributed among the metallic 12a positions. The unit cell contains four chemical molecules. More detailed data concerning the Th_3P_4 structure may be found in the literature (Kripyakevich 1963, Methfessel 1964–5).

The magnetic properties of CdGd_2Se_4 originate from the $^8S_{7/2}$ ground multiplet of Gd^{3+} . We studied the magnetic susceptibility and magnetization of CdGd_2Se_4 in order to determine the character of the magnetic ordering as well as to estimate the exchange coupling between the Gd^{3+} ions. These data were used further in the analysis of the EPR spectra. The discussion is referred to the earlier studies of Gd_2Se_3 (Pokrzywnicki and Solik 1985) which has the same type but a cation-deficient structure.

2. Experimental details

In the first step of the synthesis, binary CdSe and Gd_2Se_3 were obtained. The reactions were performed in evacuated quartz ampoules at 700 °C and 900 °C, respectively. The stoichiometric mixture of these two materials was pressed into pellets in a dry box and heated to 760 °C. X-ray analysis showed the pure Th_3P_4 -type structure with the lattice parameter $a = 0.8860$ nm. Because no additional lines were observed, we have excluded the occurrence of a superstructure. It means that the cadmium ions are distributed randomly among the 12a sites.

The measurements of magnetization were performed in an extracting sample magnetometer in magnetic fields up to 14 T at different temperatures. These measurements were made at the Institute for Low Temperatures and Structure Research, Polish Academy of Science in Wrocław. Magnetic susceptibility measurements were carried out over the temperature range 4.2–300 K by a Faraday method using a Cahn RH electrobalance.

The EPR spectra have been measured using an X-band spectrometer (9.26 GHz) in the temperature range 4.2–300 K.

3. Results and discussion

The plot of the inverse magnetic susceptibility of CdGd_2Se_4 is presented in figure 1. In the paramagnetic region it obeys the Curie–Weiss law. The values of the paramagnetic Curie temperature Θ_p and the effective magnetic moment are 11.5 K and $8.03 \mu_B$, respectively (the theoretical value of the Gd^{3+} moment is $7.94 \mu_B$). At the temperature $T_N = 9.5 \pm 0.5$ K the compound shows an antiferromagnetic transition. The close values of Θ_p and T_N indicate that the material is a Néel-type antiferromagnet.

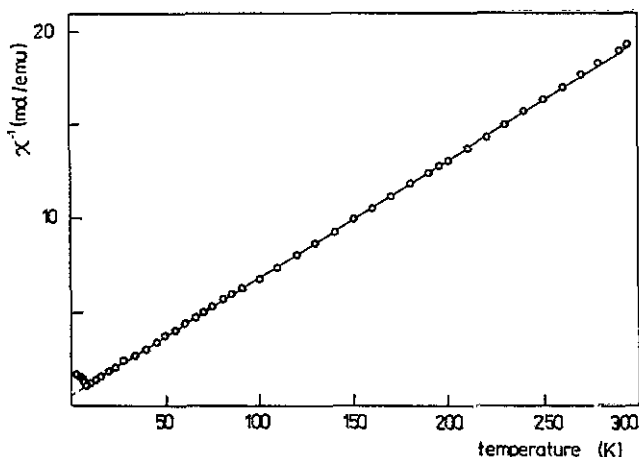


Figure 1. Magnetic susceptibility of CdGd_2Se_4 : O, experimental points.

The magnetizations at 4.21, 20 and 40 K are presented in figure 2. The magnetization at 4.2 K in the strongest magnetic field (14 T) is equal to $6.23 \mu_B$ per Gd atom; it is somewhat lower than the value in the completely saturated state ($7 \mu_B$).

Asymmetric EPR lines arising from the $^8\text{S}_{7/2}$ manifold of the Gd^{3+} ions were obtained. The value of the g -factor, the EPR lineshape and linewidth were examined as functions of temperature which gave information on the spin interaction mechanisms in the system. Two EPR spectra taken at room temperature and 30 K are presented in figure 3 as first derivatives of the absorbed power versus magnetic field. Both positive and negative frequency components of the dynamic susceptibility should be taken into account in the analysis of the lineshape since linewidths comparable with

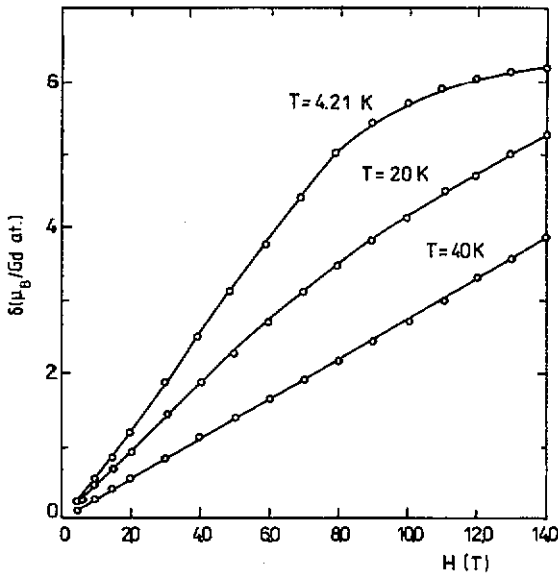


Figure 2. Magnetization of CdGd_2Se_4 at different temperatures: O, experimental points.

the resonant field were observed. Thus the average power absorbed in a sample is

$$\begin{aligned}
 P(H) \sim & \left[\frac{H/\Delta H}{1 + [(H - H_r)/\Delta H]^2} \right. \\
 & + \frac{H/\Delta H}{1 + [(H + H_r)/\Delta H]^2} \left. \right] \\
 & + b_0 \left[\frac{(H - H_r)/\Delta H}{1 + [(H - H_r)/\Delta H]^2} \right] \\
 & + \left[\frac{(H + H_r)/\Delta H}{1 + [(H + H_r)/\Delta H]^2} \right] \quad (1)
 \end{aligned}$$

where H_r is the resonant field, ΔH the half-width and b_0 a factor determining the admixture of the absorptive and dispersive parts of the dynamic susceptibility.

The evaluations of ΔH , H_r and g at different temperatures were made following the method described by Sugawara *et al* (1983).

Figure 4 shows the EPR linewidth versus temperature. It is seen that the linewidth increases rapidly when the temperature approaches T_N while at higher temperatures the dependence becomes less significant. The g -factor is equal to 2.02 ± 0.01 in the temperature range studied.

The EPR linewidth above the ordering temperature depends on the relaxation rate of the system of interacting magnetic ions (Kawasaki 1968, Huber 1972). In ferromagnets the main contributions to the relaxation function come from wavevectors near the centre of the Brillouin zone. In antiferromagnets an important role is played by wavevectors near the superlattice vector for the ordered state. This contribution is usually strongly temperature dependent and is responsible for the line broadening near T_N . It is useful (Huber 1972) to separate the critical and non-critical parts of the relaxation rate:

$$1/T_2(T) \simeq \Delta(1/T_2) + 1/T_2(\infty) \quad (2)$$

where $T_2(\infty)$ is the high-temperature limit of the relaxation time. A similar equation may be written for EPR linewidth:

$$\Delta H(T) \simeq \Delta H_c(T) + \Delta H_\infty \quad (3)$$

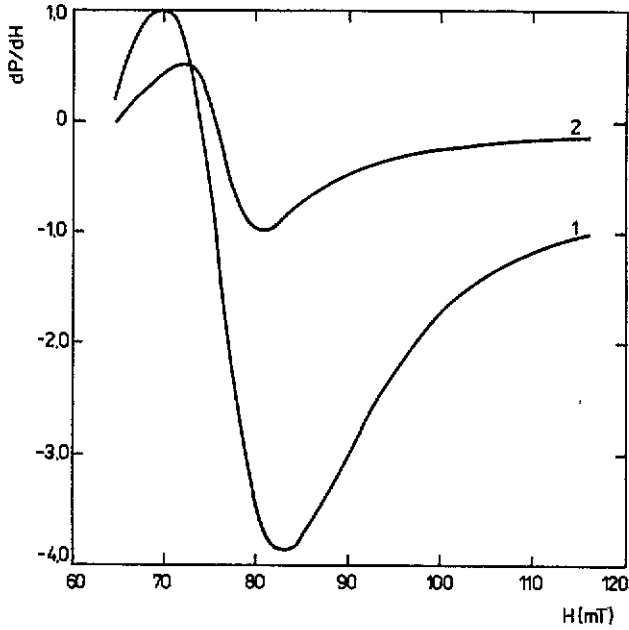


Figure 3. First derivatives of EPR spectra: curve 1, room temperature; curve 2, 30 K.

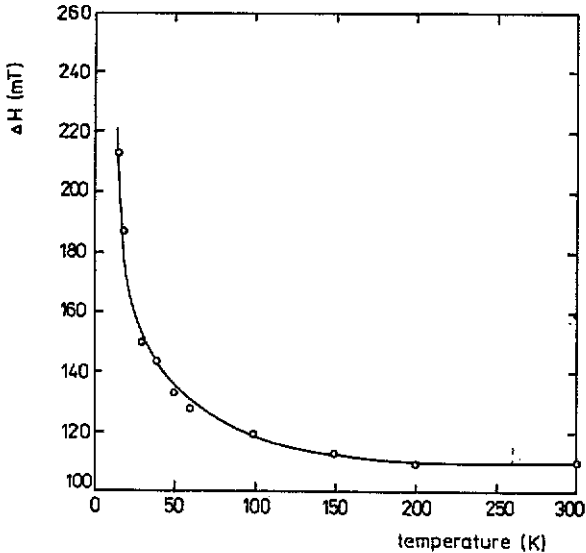


Figure 4. The EPR linewidth versus temperature for CdGd_2Se_4 : \circ , experimental results; —, result of the fitting.

where ΔH_∞ is the high-temperature limit of the linewidth. $\Delta_c(H)$ arises from the critical part of the relaxation rate $\Delta(1/T_2)$ and reflects a line broadening near the ordering temperature.

For a system with Néel temperature T_N the linewidth versus temperature is ex-

pressed as

$$\Delta H(T) \simeq \Delta H_\infty + A(T/T_N - 1)^{-p} \quad (4)$$

where ΔH_∞ is the high-temperature limit of ΔH . ΔH_∞ , A and p were fitted to the experimental $\Delta H(T)$ plot and the result is presented in figure 4 as the full curve. The parameters calculated for CdGd_2Se_4 are given in table 1 and compared with parameters for Gd_2Se_3 (Pokrzywnicki and Solik 1985).

Table 1. Best-fit parameters of equation (4).

Compound	ΔH_∞ (mT)	A (mT)	p
CdGd_2Se_4	83.6	151.6	0.517
Gd_2Se_3	92.1	127.3	0.480

No significant differences have been found between the parameters obtained for the two selenides. This indicates a similarity of the gadolinium-selenium chemical bond. Gd_2Se_3 crystallizes in the metal-deficient Th_3P_4 structure. The molecule may be described as $\text{Gd}_{8/3}\square_{1/3}\text{Se}_4$, where \square stands for a void. The unit cell contains 10.67 cations randomly distributed between 12 possible metal positions. The absolute values of the Néel temperature and the Curie temperature for Gd_2Se_3 (6 K and -10 K, respectively) are lower than the corresponding quantities for CdGd_2Se_4 (9.5 K and -11.5 K).

The main factors influencing the behaviour of the observed EPR linewidth are dipolar interactions and the exchange coupling between the gadolinium ions. A rough estimate of $\Delta H(\infty)$ may be achieved using the moment method (Abragam 1961):

$$\Delta H_\infty = \sqrt{\pi/2} M_2^{3/2} / M_4^{1/2} \quad (5)$$

where M_2 denotes the second moment of the dipolar interaction and M_4 is the fourth moment which contains both dipolar and exchange interactions.

We have estimated ΔH_∞ taking into account the interactions with ions from the first and second coordination spheres only. The corresponding exchange integrals $J_1 = -0.03$ K and $J_2 = -0.34$ K were calculated in the molecular-field approximation (Smart 1966). The estimated value of $\Delta H_\infty = 86$ mT is close to the value obtained by the fitting of equation (2) to the experimental $\Delta H(T)$ plot. The values of two remaining parameters of that equation, namely A and p , do not differ significantly for either CdGd_2Se_4 or Gd_2Se_3 . The absolute value of the p exponent is lower than that predicted by the RPA calculation ($\frac{3}{2}$). Similar deviations were reported in other work (Baran *et al* 1980, Kuriata *et al* 1988).

The magnetic dipolar interaction in CdGd_2Se_4 is weaker than that in Gd_2Se_3 because of the lower concentration of the gadolinium ions. The broadening of the linewidth for CdGd_2Se_4 may come from weaker exchange interactions with the nearest neighbours of a magnetic atom and stronger antiferromagnetic interactions with the next neighbours, in comparison with Gd_2Se_3 .

A more distinct change in the exchange mechanism is expected when a magnetic metal (e.g. manganese and iron) replaces the cadmium.

References

- Abraham A 1961 *The Principles of Nuclear Magnetism* (Oxford: Clarendon)
- Baran M, Novotorsev V M and Szymczak H 1980 *Acta Phys. Pol. A* **57** 43
- Huber D L 1972 *Phys. Rev. B* **6** 3180
- Kawasaki K 1968 *Prog. Theor. Phys.* **39** 285
- Kripyakevich P I 1963 *Sov. Phys.-Crystallogr.* **7** 556
- Kuriata J, Sadłowski L, Bojanowski B, Walczak L, Kurzawa M and Pichot J 1988 *Phys. Status Solidi a* **109** K139
- Methfessel S 1964–5 *Z. Angew. Phys.* **18** 414
- Pokrzywnicki S and Solik E 1985 *Phys. Status Solidi a* **88** 619
- Smart J S 1966 *Effective Field Theories of Magnetism* (Philadelphia, PA: Saunders) ch 8
- Sugawara K, Huang C Y and Cooper B R 1983 *Phys. Rev. B* **28** 4955