

SPIN-LATTICE RELAXATION IN CdCr_2Se_4 , CdCr_2S_4 , ZnCr_2Se_4
AND $\text{HgCr}_2\text{Se}_{4-x}\text{S}_x$

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The EPR line width in CdCr_2Se_4 , CdCr_2S_4 , ZnCr_2Se_4 , $\text{HgCr}_2\text{Se}_{4-x}\text{S}_x$ ($x = 0, 0.25, 0.5, 1.0, 3.0, 3.5, 3.75, 4.0$) was investigated in the range 100 K to 300 K (higher than the Curie temperature). Temperature broadening of the line width was observed. It was stated, that this broadening is connected with the presence of impurities (Cr^{2+} or Cr^{3+} ions). The broadening is also caused by the Raman relaxation process with phonons localized on impurities. The energies of local phonons were determined and compared with lattice constants obtained from X-ray investigations.

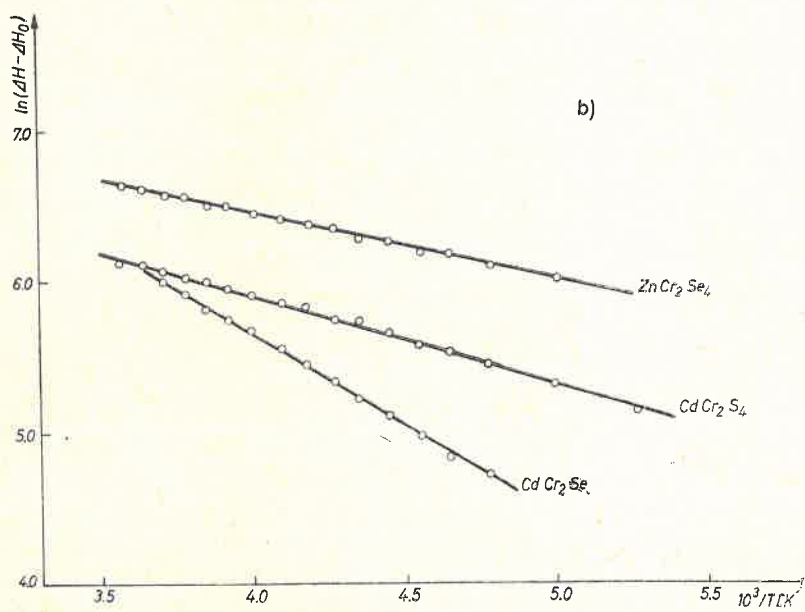
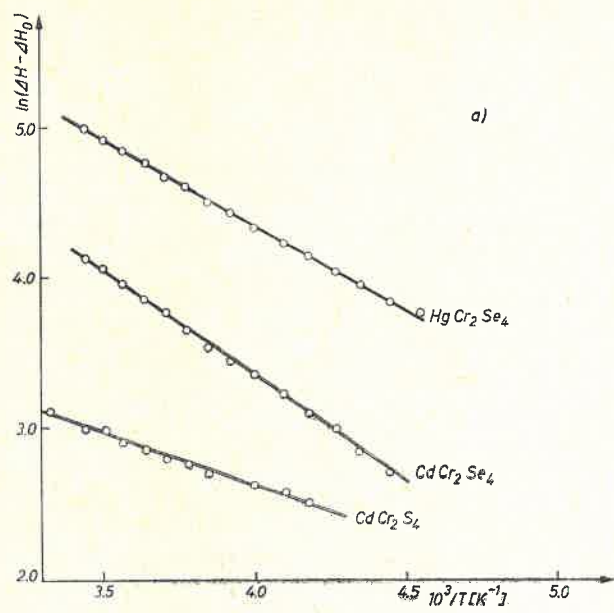
1. Introduction

The temperature broadening of the resonance line (in the paramagnetic region) was reported in the EPR investigation of a magnetic semiconductor of the ACr_2X_4 type [1-9]. The temperature broadening observed in CdCr_2Se_4 , CdCr_2S_4 and HgCr_2Se_4 was explained by means of a two-step model of relaxation with the participation of impurities fast relaxing to the lattice [4, 5]. The impurity is the Cr^{2+} ion in the octahedral site or the Cr^{3+} ion in the tetrahedral site [8]. The existence of the Cr^{2+} ions can explain the results of ferromagnetic resonance at 4.2 K [10, 11]. The authors of paper [9] have proposed for CdCr_2Se_4 and $\text{Co}_x\text{Cd}_{1-x}\text{Cr}_2\text{Se}_4$ a different, four-phonon mechanism of spin-lattice relaxation with the participation of optical phonons.

2. Results of measurements

The EPR line width were measured using the RE-1301 EPR spectrometer operating on the X-band. The measurements were carried out in the temperature range 100 K to 300 K (higher than the Curie temperature) for mono- and polycrystalline samples of CdCr_2Se_4 , CdCr_2S_4 , HgCr_2Se_4 and for polycrystalline samples of ZnCr_2Se_4 and

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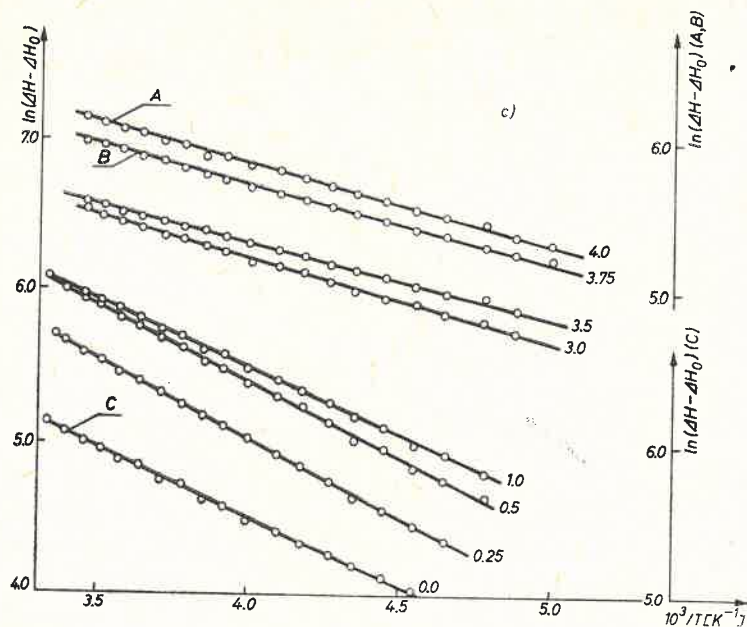


Fig. 1. Dependence of line width on temperature plotted in coordinates $\ln(\Delta H - \Delta H_0)$ versus $1/T$: (a) HgCr_2Se_4 , CdCr_2Se_4 , CdCr_2S_4 (monocrystals), (b) ZnCr_2Se_4 , CdCr_2Se_4 , CdCr_2S_4 (polycrystals), (c) $\text{HgCr}_2\text{Se}_{4-x}\text{S}_x$ (polycrystals)

$\text{HgCr}_2\text{Se}_{4-x}\text{S}_x$ ($x = 0, 0.25, 0.5, 1.0, 3.0, 3.5, 3.75, 4.0$). The EPR spectrum consisted of a single Lorentz shape resonance line. The temperature broadening of the line width was observed for all samples. The measured line width can be described by the formulas:

$$\Delta H = \Delta H_0 + A \exp\left[-\frac{\theta}{T}\right] \quad (1)$$

Experimental results

TABLE I

Sample	θ [K]	n
HgCr_2S_4	2100	2.5
$\text{HgCr}_2\text{Se}_{0.25}\text{S}_{3.75}$	1900	2.3
$\text{HgCr}_2\text{Se}_{0.5}\text{S}_{3.5}$	1800	2.2
$\text{HgCr}_2\text{Se}_1\text{S}_3$	1680	2.8
$\text{HgCr}_2\text{Se}_3\text{S}_1$	1200	3.5
$\text{HgCr}_2\text{Se}_{3.5}\text{S}_{0.5}$	1000	3.8
$\text{HgCr}_2\text{Se}_{3.75}\text{S}_{0.25}$	990	3.9
HgCr_3Se_4	1080	3.9
HgCr_2Se_4 mono	870	4.2
CdCr_2Se_4	820	5.3
CdCr_2Se_4 mono	720	5.9
CdCr_2S_4	1750	2.7
CdCr_2S_4 mono	1740	3.2
ZnCr_2Se_4	2200	1.9

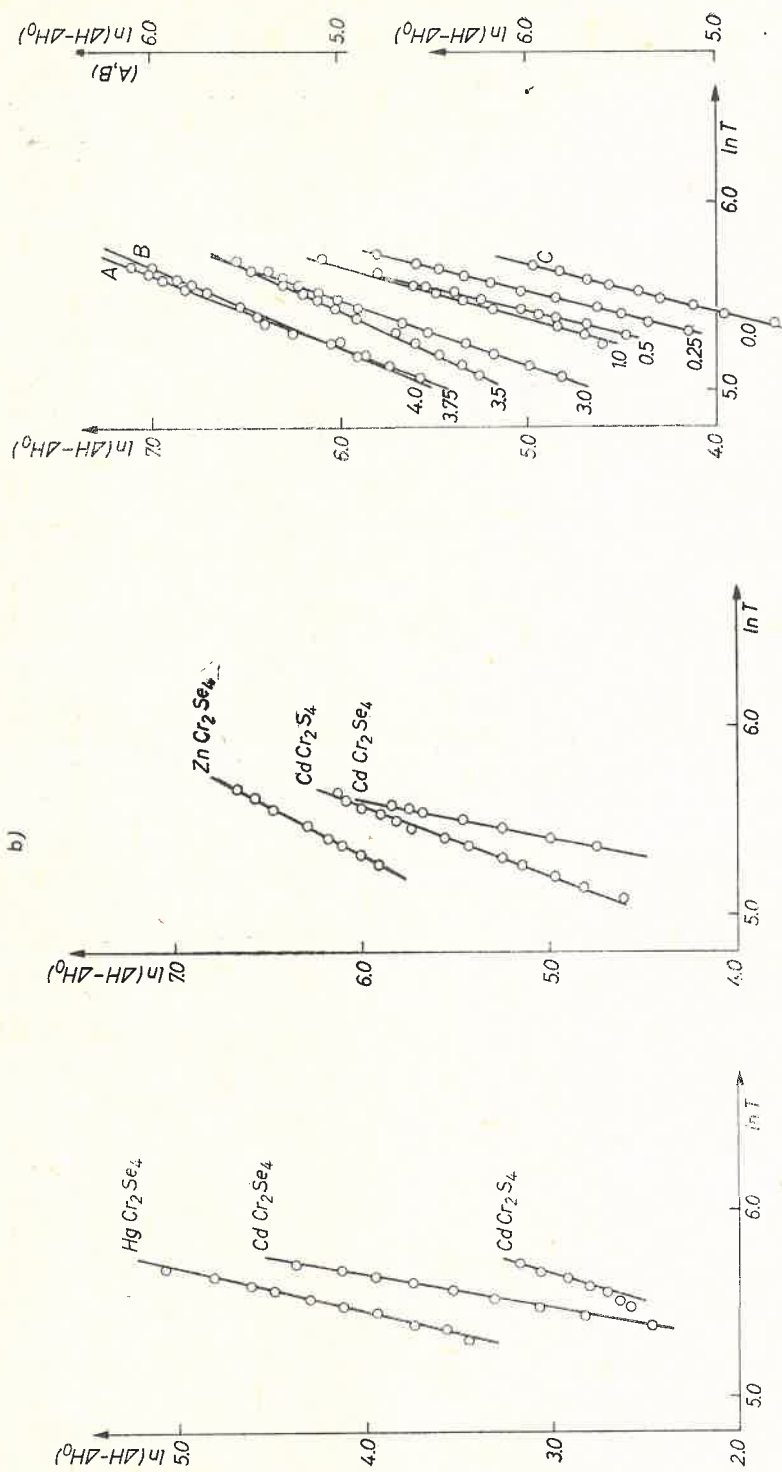


Fig. 2. Dependence of line width on temperature plotted in coordinates $\ln(\Delta H - \Delta H_0)$ versus $\ln T$: (a) HgCr_2Se_4 , CdCr_2Se_4 , CdCr_2S_4 (monocrystals), (b) ZnCr_2Se_4 , CdCr_2S_4 (polycrystals), (c) $\text{HgCr}_2\text{Se}_{4-x}\text{S}_x$ (polycrystals)

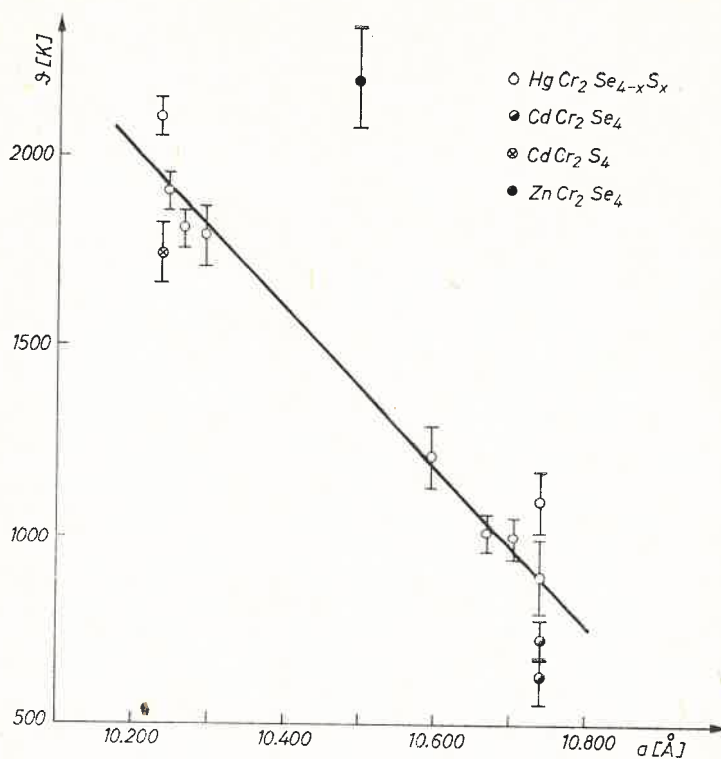


Fig. 3. Dependence of local phonon energy θ on lattice constant a

or

$$\Delta H = \Delta H_0 + aT^n. \quad (2)$$

The obtained values of θ and n are in Table I. The n and θ change from sample to sample. X-ray investigation of the same samples were carried out [12]. The dependence of θ on lattice constant a is presented (Fig. 3). Except for the ZnCr_2Se_4 , a distinct correlation between θ and a is seen.

3. Interpretation

The observed broadening of an EPR line cannot be explained by temperature changes of spin-spin and exchange interaction. The change in the lattice constant for the temperature range 100 K to 300 K [13] produces a relative change in line width of the order of 10^{-4} to 10^{-3} . Therefore this effect can be neglected.

Dependence (2) is predicted for a direct relaxation processes ($n = 1$) and Raman processes ($n = 7, 9$). Experimental values of n in the range 1.9 to 5.9 were obtained. Therefore these processes are improbable.

In the materials under investigation the Cr^{3+} ion placed in the octahedral site has a ground state corresponding to the orbital singlet. Then the Cr^{3+} ion is weakly bound

to the lattice and can only weakly effect spin-lattice relaxation. More effective is the two — step process involving the coupling of the Cr^{3+} ion system to the fast relaxing impurity, e.g. the Cr^{2+} ion in an octahedral site [4, 5], or Cr^{3+} ion in a tetrahedral site [8].

The exponential dependence (1) is predicted for the following relaxation processes:

- (a) the Orbach process
- (b) process involving relaxation by exchange-coupled clusters of neighbouring ions [19]
- (c) the Raman process involving optical phonons from the edge of the Brillouin zone [14]
- (d) the Raman process involving local phonons [15].

(a) The crystal field separation of Cr^{3+} or Cr^{2+} ion levels is $\Delta > 10^4 \text{ cm}^{-1}$ [16]. $\Delta > k\theta$, therefore the Orbach process is improbable.

(b) The characteristic energy of this process Δ' is the nearest-neighbour exchange constant, $\Delta' \approx 10 \text{ K}$ [20]. $\Delta' \ll \theta$, then this process can be excluded.

(c) The energy of optical phonons in CdCr_2Se_4 and CdCr_2S_4 were measured [17]. From experimental data follows (the values of $k\theta$ are from EPR measurements, Table I):

for CdCr_2Se_4 , $107 \text{ cm}^{-1} \leq E_{ph} \leq 412 \text{ cm}^{-1}$, $500 \text{ cm}^{-1} < k\theta < 570 \text{ cm}^{-1}$

for CdCr_2S_4 , $37 \text{ cm}^{-1} \leq E_{ph} \leq 543 \text{ cm}^{-1}$, $1145 \text{ cm}^{-1} < k\theta < 1280 \text{ cm}^{-1}$.

Then, $E_{ph} < k\theta$, and this process can be excluded.

In paper [9] the four-phonon Raman process was proposed for CdCr_2Se_4 based on the dependence $k\theta \approx 2E_{ph}$. This dependence was in agreement with the one phonon energy from the measured spectrum. In the case of CdCr_2S_4 , the dependence $k\theta \approx 2E_{ph}$ is not satisfied. Consequently, this process is rather improbable.

(d) The relaxation process involving local phonons [4, 5] is also confirmed for spinels $\text{HgCr}_2\text{Se}_{4-x}\text{S}_x$. The distinct correlation between θ and the lattice constant is stated. The increase in the lattice constant corresponds to a decrease of θ values (except for the ZnCr_2Se_4).

The masses of Cr^{2+} and Cr^{3+} ions are almost equal, but a difference in Coulomb interactions with anions surrounding the octahedral site exist. The vibrations of Cr^{2+} ions are described by different force constants, and so a localized vibration is created.

The Cr^{3+} ion in the tetrahedral site (for the case of normal spinel structure) is an impurity ion substituting a Hg or Cd ion (both have higher masses than Cr). Then, a localized vibration is also created.

The Cr^{2+} or Cr^{3+} ions are in the force field created essentially by surrounding anions. In the simplest case there is the Coulomb type interaction with point charges (like in the theory of crystal field). The correlation between θ and a has a simple interpretation. The Coulomb forces decrease with an increase in the size of a vacancy in an anion lattice. The energy of local phonons depends on the magnitude of Coulomb forces. The lower θ values for Cd spinels can be explained by the lower mass of the Cd anion with respect to Hg.

The deviation from θ — a correlation for ZnCr_2Se_4 is probably due to high electric conductivity [18] or an admixture of other kinds of impurities.

4. Conclusions

The EPR investigation of sulfo- and selenospinelns confirm the two-step spin-lattice relaxation mechanism with the participation of paramagnetic impurities [4, 5]. The correlation between the lattice constant and the energy of phonons localized on an impurity was stated. The impurity present in sulfo- and selenospinelns is probably: Cr^{2+} ion in an octahedral site or Cr^{3+} ion in a tetrahedral site.

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