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# The Influence of Cation Arrangement on the EPR Spectrum of $Mn^{2+}$ in the Spinel Compounds $CdB_2X_4$

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$CdB_2X_4$ spinels—$B$ = Sc, Y, Lu; $X$ = S, Se—were synthesized and their lattice constants were determined. After $Mn^{2+}$ doping they were investigated by the EPR method over the temperature range 4.2–330 K. The temperature dependence of the hyperfine structure constant, $A$, was described by the Šimanek–Orbach equation and its parameters were determined. Chemical bonds in the studied spinels were characterized in more detail to obtain a linear dependence of the $A$ constants on the modified covalency parameter.

## Introduction

Rare earth compounds of the spinel-type structure have been known since 1964 (*1*, *2*), but their properties have not been studied fully (*1*–*5*). Information is especially lacking regarding the chemical bond character and its influence on physicochemical properties of these compounds. In their crystal lattice the metal ions occupy two types of voids: tetrahedral and octahedral: i.e., they appear in environments of the most frequently discussed symmetries. We used $Mn^{2+}$ ions and the EPR method to obtain some information about the $CdB_2X_4$ spinels, where $B$ denotes scandium, yttrium, and lutetium, and $X$ denotes sulfur or selenium. The hyperfine structure constant of the manganese ion in the investigated compounds is related to the nature of the chemical bonds.

## Experimental

All compounds were prepared by direct synthesis from the elements in evacuated quartz ampoules at 950 to 1250 K. After synthesis the samples were powdered, doped with MnS or MnSe in the amounts of 5.0 to 10.0 × $10^{-2}$ mole%, pressed into pellets, and heated at 950–1100 K for 1 week. $CdSc_2S_4$, which was the most difficult to synthesize, was reground and reheated three times for complete reaction.

The compounds prepared were stable in air. They all occur in the spinel $MgAl_2O_4$ structure. Their structures and lattice constants were determined by X-ray method using a Guinier camera and Ni-filtered Cu$K\alpha$ radiation (Table I). The lattice constant of $CdSc_2Se_4$ is reported for the first time. The X-ray data of the other compounds prepared are in agreement with the previously reported data (*1*–*4*).

All the above-mentioned compounds are

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TABLE I

CHARACTERISTICS OF THE SPINEL $CdB_2X_4$ COMPOUNDS

| Compound | Color | Lattice constant (Å) | |
|---|---|---|---|
| | | Found | References |
| $CdSc_2S_4$ | Brownish yellow | 10.739 | 10.733(*1*) |
| $CdSc_2Se_4$ | Dark grey | 11.208 | — |
| $CdY_2S_4$ | Dark yellow | 11.197(*5*) | 11.196(*1, 2*) |
| $CdY_2Se_4$ | Brown-black | 11.660(*5*) | 11.654(*1*), 11.660(*2*) |
| $CdLu_2S_4$ | Greenish yellow | 11.048 | 10.945–11.045(*2–4*) |
| $CdLu_2Se_4$ | Cherry-black | 11.515 | 11.480(*2*) |

diamagnetic and have the nature of semiconductors with a broad (1.8–2.5 eV) forbidden gap (*3*).[1] Electron paramagnetic resonance (EPR) of the $Mn^{2+}$ ions in their crystal lattice was observed on powdered samples at the $X$ band. The spectra were recorded over the temperature range 4.2–330 K using a Bruker 418 S spectrometer.

## Results and Discussion

The manganese ion in the spinel lattice substitutes for the divalent cadmium ion. It may occupy tetrahedral voids in the case of a normal spinel or octahedral voids in the case of an inverse spinel. Each of these positions of the manganese ion is characterized by a different hyperfine structure constant in the EPR spectrum. Thus, the nature of the $Mn^{2+}$ spectrum in the spinel lattice provides information on its structure.

The EPR spectra of powdered $CdY_2S_4$ and $CdY_2Se_4$ samples doped with manganese (*5*) consisted of two groups of six lines each corresponding to octahedral and tetrahedral coordination of the $Mn^{2+}$ ions, respectively. This is evidence of partial inversion of the cationic lattice in both spinels. The intensity ratio of these lines indicates a higher degree of inversion in $CdY_2S_4$ than in $CdY_2Se_4$. This is also supported by crystallochemistry considerations. The $Y^{3+}$ ion is the largest of the rare earth ions forming thiospinels with cadmium and distorts the anionic lattice of the spinel to the largest extent. In the case of selenospinels the voids are larger and may be occupied by the yttrium ions in a more ordered manner, thus, the degree of inversion indicated by the EPR spectrum is lower. The ionic radii of scandium and lutetium are much smaller (*6*). Thus, inversion of the arrangement of cations in the spinels formed by them is less likely. This is confirmed by the EPR spectra of $Mn^{2+}$ in the scandium and lutetium compounds. These spectra consist of one group of six lines characteristic of one type of $Mn^{2+}$ ion environment and show normal cation distribution in the spinel lattice.

The hyperfine structure constant, $A$, and $g$ factors were determined from the spectra measured at various temperatures (Table II). The $A$ constants were found to vary with temperature according to the Šimanek–Orbach equation (*7*):

$$A(T) = A(0\text{ K})\left[1 - CT^4\int_0^{\Theta/T} \frac{x^3}{e^x - 1}\,dx\right]$$

($A$—hyperfine structure constant, $T$—temperature, $C$—constant, $\Theta$—Debye temperature, and $x = \Theta/T$). The parameters of this equation were fitted to the experimental

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[1] Unpublished results obtained from optical reflectance measurements made on cold-pressed powder compounds with $LiCO_3$. The observed absorption edges were not sharp and only approximate values of the bandgaps could be derived.

TABLE II

EPR PARAMETERS OF $Mn^{2+}$ IN THE SPINEL COMPOUNDS

| Compound | $g$ | $A(0\ K) \times 10^4$ ($cm^{-1}$) | $A(293\ K) \times 10^4$ ($cm^{-1}$) | $C \times 10^{12}$ ($K^{-4}$) | $\Theta$ (K) | References |
|---|---|---|---|---|---|---|
| $CdSc_2S_4$ | 2.002 | 66.43 | 65.90 | 0.969 | 559 | This work |
| $CdSc_2Se_4$ | 2.004 | 63.25 | 62.56 | 5.30 | 318 | This work |
| $CdY_2S_4$ | 2.002 | 68.92 | 68.24 | 11.7 | 270 | (5) |
| $CdY_2Se_4$ | 2.004 | 65.40 | 64.39 | 21.2 | 230 | (5) |
| $CdLu_2S_4$ | 2.001 | 68.39 | 67.56 | 22.0 | 187 | This work |
| $CdLu_2Se_4$ | 2.003 | 65.02 | 64.26 | 17.6 | 205 | This work |

results by a computer least-squares analysis. The best fitting parameters $A(0\ K)$, $C$, and $\Theta$ are summarized in Table II. The Debye temperatures obtained for the studied compounds should be considered approximate, although there is a lack of other data for comparison.

The EPR parameters of the manganese ions in various crystal lattices are related to the nature of chemical bond found in the host (*8*). Šimanek and Mueller (*9*) noted the dependence of the hyperfine structure constant on the ionicity of the chemical bonds and on the coordination number of the manganese ion. The covalency parameter $c/n$ applied by them has the following form:

$$\frac{c}{n} = \frac{1}{n}[1 - 0.16\,(x_{\mathrm{Mn}} - x) - 0.035\,(x_{\mathrm{Mn}} - x)^2],$$

where $x_{\mathrm{Mn}}$ and $x$ are the electronegativities of manganese and the anion (*10*), and $n$ is the coordination number. The disadvantage of this relationship is that it gives the same value of the covalency parameter for all compounds with the same anion and coordination number. In order to eliminate this defect we have allowed for the geometric factor, namely, the distance between the manganese and nonmetal ions in the covalency parameter. The best results were obtained by multiplying the Šimanek–Mueller parameter by $(r/d)^2$, where $r$ is the nonmetal ion radius and $d$ is the manganese–nonmetal distance in a given structure. Calculations were performed with the ionic radii of Shannon (*6*) and our crystallographic and EPR results. The same was done for $Mn^{2+}$-doped $CdIn_2S_4$, $MgAl_2O_4$, and $ZnAl_2O_4$ spinels which were investigated by the EPR method (*11–13*). The Mn–nonmetal distance in spinels depends considerably on the structure parameter, $u$. Where possible, it was taken into consideration for the spinels under investigation by analogy to similar lanthanide compounds (*4*): $u$ was assumed to be equal to 0.378. The results of the modified covalency parameter vs $A$, the hyperfine structure constants, are shown in Fig. 1. The deviation in

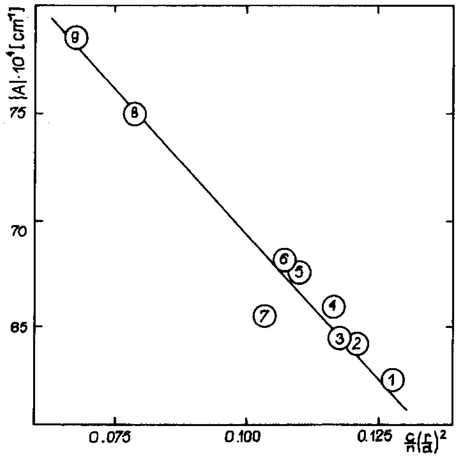

FIG. 1. The hyperfine structure constant, $A$, of $Mn^{2+}$ as a function of the modified covalency parameter: (1) $CdSc_2Se_4$, (2) $CdLu_2Se_4$, (3) $CdY_2Se_4$, (4) $CdSc_2S_4$, (5) $CdLu_2S_4$, (6) $CdY_2S_4$, (7) $CdIn_2S_4$, (8) $ZnAl_2O_4$, (9) $MgAl_2O_4$.

the case of $CdIn_2S_4$ might be related to the value of $u = 0.386$, which indicates considerable distortion of the anionic lattice with respect to the ideal spinel-type structure.

For a broad range of compounds (from ionic to covalent) the hyperfine structure constant varies linearly with the modified covalency parameter as in Ref. (*9*).

Figure 1 confirms that the covalency character of the $Me^{2+}$–anion bond increases from the oxide through sulfide to selenide spinels. This is correlated to the decrease of the hyperfine structure constant, *A*. Also, in the range of cadmium thio- and selenospinels the covalent character of the $Me^{2+}$–$S^{2-}(Se^{2-})$ bond varies depending on the trivalent metal and increases from yttrium through lutetium to scandium (Fig. 1).

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