Features of electric and magnetic hyperfine interactions of Fe$^{57}$ nuclei in chalcogenide spinels

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The electric and magnetic hyperfine interactions of Fe$^{57}$ nuclei in the system of chalcogenide spinels Fe$_{1-x}$Cd$_x$Cr$_2$S$_4$ (x = 0.0, 0.1, 0.25, 0.5, 0.75) are investigated by the Mössbauer technique. Introduction of cadmium leads to a resonance-line quadrupole splitting $\Delta E$ which increases with decreasing temperature. The widths of lines comprising the quadrupole doublets possess a temperature dependence similar to that of $\Delta E$. Two inequivalent positions of the iron atoms are found in the magnetically-ordered temperature region for the Fe$_{0.9}$Cd$_{0.1}$Cr$_2$S$_4$ spinel. The results are discussed on the basis of the Jahn-Teller effect.

1. INTRODUCTION

Much attention has been paid recently to chalcogenide compounds with spinel structure of the type $M^{2+}CV^{2+}X_4$, where $X = S, Se$, or Te and $M^{2+}$ is a divalent metal. In contrast to oxygen spinels, which as a rule are ferrimagnets and dielectrics, chalcogenide spinels can be ferri-, ferro-, or antiferromagnets, and their electric conductivity may vary in a wide range$^{[1,4]}$.

The compound FeCr$_2$S$_4$ is a normal spinel, has the magnetic structure of a collinear ferromagnet, and its crystal structure is cubic down to 4.2°K$^{[5,6]}$. This spinel was investigated many times both by macroscopic methods and with the aid of the Mössbauer effect, but its unexpected properties have not yet been uniquely interpreted so far. According to the magnetic-measurement data obtained by various authors$^{[7-10]}$, the Curie temperature of the spinel FeCr$_2$S$_4$ ranges from 170 to 195°K, and the magnetic moment at 0°K lies between 1.55 and 1.86 $\mu_B$.

The most interesting feature of the Mössbauer spectra is the appearance, below the Curie point, of a quadrupole splitting that increases with decreasing temperature. Above the ordering temperature, the spectrum is a narrow single line, thus evidencing a strictly cubic environment of the Fe$^{3+}$ in the tetrahedral sites.

At the present time there is no meeting of minds concerning the cause of the quadrupole splitting in the magnetically-ordered region. It is proposed in a number of papers$^{[11-13]}$ that the electric field gradient (EFG) at the Fe$^{3+}$ nucleus is magnetically induced, i.e., it is due to the joint action of the molecular field and the spin-orbit interaction on the energy levels of Fe$^{3+}$. The joint action of these two effects lifts the degeneracy of the energy levels of Fe$^{3+}$, which are not equally populated at low temperatures. It is noted in$^{[9]}$ that the presence of an electric field gradient, and also of a nonzero asymmetry parameter, can be due to the lattice distortion produced at low temperatures. At the same time, Spender and Morrish$^{[14,15]}$ believe that the electric field gradient is a result of Jahn-Teller distortions of the tetrahedral environment of the Fe$^{3+}$ ions.

The investigation of the system Fe$_{1-x}$Cd$_x$Cr$_2$S$_4$ has revealed a number of anomalies of the magnetic properties, which were explained by resorting to the Goodenough model of delocalized electrons$^{[16]}$.

In this paper we report the results of investigations of the system of chalcogenide spinels Fe$_{1-x}$Cd$_x$Cr$_2$S$_4$ with the aid of the Mössbauer effect. The observed singularities of the electric and magnetic hyperfine interactions of the Fe$^{3+}$ nuclei are explained on the basis of the dynamic Jahn-Teller effect.

EXPERIMENTAL PROCEDURE. SAMPLES

The samples of Fe$_{1-x}$Cd$_x$Cr$_2$S$_4$ (x = 0, 0.1, 0.25, 0.5, 0.75) were synthesized by annealing a mixture of initial elements taken in stoichiometric proportions, in quartz ampoules evacuated to $10^{-5} - 10^{-4}$ mm Hg and sealed. The annealing was carried out in several stages in a two-zone oven with a temperature gradient along the ampoule. During the first stage, the mixture of elements, located in the lower end of the ampoule, was maintained for several days at a temperature 400–500°C, whereas the temperature in the region of the upper edge of the ampoule was 250° C. During the succeeding annealing stages, the temperature in the reaction zone was raised to 800–900° C and maintained there for one to five days. To obtain a homogeneous phase, the reaction products were cooled in the intervals between the annealings and were thoroughly pulverized. The one-phase character of the samples was monitored by x-ray diffraction. X-ray patterns of the powder were obtained with a Toshiba diffractometer. The magnetization was measured by the vibration-magnetometer method. The Mössbauer spectra of the Fe$^{57}$ nuclei were measured in the temperature interval 78–300°K, with the source Co$^{57}$ in a platinum matrix maintained at room temperature.

RESULTS AND DISCUSSION

1. X-Ray Diffraction and Magnetic Measurements

The x-ray phase analysis of the samples confirmed the presence of a spinel structure in the absence of extraneous phases. It was found that the unit-cell parameter increases when the iron ions are replaced by the larger cadmium ions. The $a(x)$ dependence was in accord with Vegard’s law.

The sample magnetization curves plotted in magnetic fields up to 15 kOe indicate collinear ordering of the magnetic moments. The plots of the magnetization against the temperature were used to obtain the Curie points and to determine the dependence of $T_C$ on $x$. A
change of \( x \) from 0 to 0.75 caused a change of \( T_c \) from 170 to 128°K (± 5°K).

2. Investigation of Mössbauer Spectra

a) Paramagnetic temperature region. The spectrum of the spinels \( \text{FeCr}_x\text{S}_4 \) in the paramagnetic temperature region is a single line of width 0.28 ± 0.01 mm/sec practically independently of the temperature. The isomorphic shift \( \delta \) at room temperature is \((0.82 ± 0.02)\) mm/sec relative to sodium nitroprusside. These results agree with earlier investigations of the spinel \( \text{FeCr}_x\text{S}_4 \) and indicate that the iron ions \( \text{Fe}^{2+} \) are only in tetrahedral \( A \) sites in a strictly cubic environment. It should be noted that the isomeric shift is much smaller than for the analogous oxygen spinel \( \text{FeCr}_2\text{O}_4 \), this being due to the larger covalence of the bond of the \( \text{Fe}^{2+} \) ions in sulfur compounds.

The spectra of the samples with \( x = 0.1, 0.25, \) and 0.5 at room temperature take the form of single but noticeably broadened lines, and the broadening increases with increasing \( x \). With decreasing temperature, the line width increases, and at a definite temperature the spectra split into symmetrical doublets (Fig. 1).

A least-squares computer reduction of the spectra yielded quite accurate values of the quadrupole splitting \( \Delta E \) and also values of the isomeric shifts and the widths \( \Gamma \) of the lines making up the quadrupole doublet. The results are shown in Figs. 2–4. The presented data indicate that the quadrupole splitting \( \Delta E \) increases noticeably with decreasing temperature (see Fig. 2). In addition, the widths of the lines making up the doublets also increase with decreasing temperature (Fig. 3).

It follows from Fig. 4 that the temperature dependence of the isomeric shift is determined in the paramagnetic region mainly by the relativistic effect. On going over to the ferrimagnetic state, a kink appears on the \( \delta(T) \) curve, indicating that the density of the \( s \) electrons increases at \( T < T_c \). This is attributed to the increase of the \( d \)-electron mobility as a result of the decrease of their thermal scattering on going to the magnetically-order state\(^{[8]} \).

The results obtained by us for the \( \text{Fe}_{1-x}\text{Cd}_x\text{Cr}_2\text{S}_4 \) system can be explained on the basis of the dynamic Jahn-Teller effect, using for the relaxation processes the concepts developed by Spender and Morrish\(^{[9,11]} \).

According to the Jahn-Teller theorem, if there exist in the crystal degenerate orbital states of an ion of a transition metal with localized \( d \) electrons, then the structure of such a crystal is unstable to distortions that lower the symmetry of the surrounding of the ion and lift the degeneracy of the energy levels.

The ion \( \text{Fe}^{2+} (3d^6) \) is the so-called Jahn-Teller ion. In a cubic crystal field, the fivefold degenerate state \( \text{D} \) splits into two levels, a triplet \( \text{T}_2 \) and a doublet \( \text{E}_g \), separated by an energy \( 10D_q \) (see Fig. 2). For the tetrahedral environment, the ground state is \( \text{E}_g \). The Jahn-Teller distortions (usually tetragonal) lift the double degeneracy of the ground level, as a result of which the level \( \text{E}_g \) splits into two sublevels separated by an energy \( \Delta \). It is the unequal population of these sublevels which leads to the presence of the electric field gradient that manifests itself in the Mössbauer spectra.

However, inasmuch as all the investigated spinels are cubic, one should expect the Jahn-Teller effect to be dynamic. The main features of the dynamic effect consists in the following. For a site with cubic symmetry there exist several equivalent directions along which Jahn-Teller distortions can be produced. Owing to thermal excitations, these distortions will “hop” in disordered fashion from one equivalent direction to another. As a result of the fluctuations of the Jahn-Teller distortions in time relative to several (three) crystallographic directions, the time averaged electric field gradient is equal to zero (there are no static distortions).

![FIG. 2](image)

FIG. 2. Temperature dependence of the quadrupole splitting \( \Delta E \) in the chalcogenide spinel system \( \text{Fe}_{1-x}\text{Cd}_x\text{Cr}_2\text{S}_4 \): \( 1-x = 0.10; 2-x = 0.25; 3-x = 0.50 \). In the upper right corner is shown the splitting of the energy levels of the \( \text{Fe}^{2+} \) ion following tetragonal distortion of the tetrahedral surrounding.

![FIG. 3](image)

FIG. 3. Temperature dependence of the width \( \Gamma \) of the lines making up the quadrupole doublet: \( \circ-x = 0.10; \bullet-x = 0.25; \square-x = 0.50 \).

![FIG. 4](image)

FIG. 4. Dependence of the isomeric shift \( \delta \) on the temperature: \( \circ-x = 0.10 \) (at \( T < T_c \)), \( \circ-x = 0.10 \) (at \( T > T_c \)). \( \circ-x = 0.25; \square-x = 0.50 \). The solid line shows the temperature dependence of the relativistic shift in the Debye approximation.

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The influence of the dynamic Jahn-Teller effect on the quadrupole splitting of the Mössbauer spectra was considered in\textsuperscript{[14,15]}. The appearance or absence of quadrupole splitting in the Mössbauer spectra depends on the ratio of the fluctuation time $\tau_j$ of the Jahn-Teller distortions to the measurement time $\eta/\Delta E$ characteristic of the Mössbauer experiment, where $\Delta E$ is the quadrupole splitting. A nonzero quadrupole splitting will be observed under the condition

$$\tau_j > \eta/\Delta E \quad \text{and} \quad \tau_j > \tau_c,$$

where $\tau_\text{n}$ is the lifetime of the nucleus in the excited state and $\Delta E$ is the quadrupole splitting produced as a result of the Jahn-Teller distortions along one crystallographic axis. It is obvious that the time $\tau_j$ increases with decreasing temperature. This leads to an increase of the quadrupole splitting.

We have found that the width of the lines making up the quadrupole doublet also increases with decreasing temperature for samples with $x = 0.1$, 0.25, and 0.5 (see Fig. 3) and depends on the temperature approximately in the same manner as $\Delta E$. According to the theory\textsuperscript{[14,15]} this is a characteristic feature of the relaxation processes described above, and confirms the applicability of this representation for the system investigated by us.

If the condition (1) is satisfied, then the temperature dependence of the electric field gradient at the Fe\textsuperscript{57} nucleus, and consequently also of the quadratic splitting $\Delta E$, is determined by the expression

$$\Delta E(T) = \Delta E(0)\left[1 - \frac{T}{T_c} - Tight].$$

Formula (2) can be easily obtained from the general theory of Ingalls\textsuperscript{[15]}. Assuming the extrapolated value $\Delta E(0) = 2.7$ mm/sec obtained in\textsuperscript{[16]}, we have calculated the temperature dependence of $\Delta E$. From a comparison of the calculated $E(T)$ curves with the experimental data we obtained the values of $\Delta E$ for the investigated compounds (see Fig. 2). The values of $\Delta E$ for the samples with $x = 0.1$, 0.25, and 0.5 were 30, 40, and 50 K, respectively (accuracy $\pm 4$ K).

b) Ferrimagnetic temperature region. In the ferrimagnetic temperature region, the Mössbauer spectra were plotted for compositions with $x = 0.0$, 0.1, 0.25, and 0.5 in the interval $78^\circ K < T < T_c$. Figure 5 shows by way of example spectra of some of the spinels at $78^\circ K$.

The Mössbauer spectrum of the spinel Fe\textsubscript{3-x}Cd\textsubscript{x}Cr\textsubscript{2}S\textsubscript{4} has shown that in the best approximation the quadrupole splitting in the Mossbauer spectra depends on the ratio of the fluctuation time $\tau_j$ of the Jahn-Teller distortions along one crystallographic axis. It is obvious that the time $\tau_j$ increases with decreasing temperature. This leads to an increase of the quadrupole splitting.

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The Mössbauer spectra of samples with $x = 0.25$ and 0.5 are quite complicated and do not lend themselves to unique interpretation. It appears that in these samples there exist several nonequivalent positions, as the result of the statistical distribution of the iron and cadmium ions in the A-sublattice, and this makes the interpretation of the spectra quite difficult.

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1) Relative to sodium nitroprusside.


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