Peculiarities of the magnetic phase transition in chromium chalcogenide spinels

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On the basis of a comprehensive investigation of the magnetic and nonmagnetic properties of the semiconducting chalcogenide spinels $CdCr_2(S_xSe_{1-x})_4$, a magnetoconcentration diagram of their magnetic phase transition has been constructed. It is shown that in the composition range $0.6 < x < 0.7$ the transition changes from the first to the second order. The presence of exchange striction may be the mechanism responsible for the occurrence of a magnetic phase transition of the first order in a number of these solid solutions.

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Investigation of the phenomena resulting from the existence of ferromagnetic ordering of the spins of the chromium ions, Cr^{3+}, in semiconducting spinels has not been motivated solely by the emerging possibilities for their practical use.[1] Among this class of compounds, as has recently been established for the spinels $CdCr_2S_4$[2] and $CuCr_2Se_4$,[3] there can be cases in which a process of spin disordering occurs and is accompanied by a magnetic phase transition of the first order (MPT-1). Among ferromagnets, the number of such examples is known to be very limited[4]; therefore the addition of new materials to this list is of interest both from the point of view of knowledge of the nature of this type of transition, and also for its technical application.

One of the known mechanisms of a magnetic phase transition of the first order for magnetic materials is the existence within the critical region of exchange striction, caused by the dependence of the exchange integral on the volume of the crystalline lattice.[5] The non-Heisenberg character of the exchange can be taken into account by adding to the Heisenberg Hamiltonian a term biquadratic in the spins.[6]

In the spinel $CuCr_2Se_4$, which possesses a metallic type of conductivity, and for which, along the 90-degree Kramers-Anderson superexchange, there occurs for the Cr^{3+} ions an exchange via the current carriers, a transition mechanism is evidently valid that is due to the existence of narrow conduction bands, genetically related to the *d* levels of the metal.[7] But in this case the isolation of either of the two mechanisms mentioned is difficult, because during the magnetic disordering of $CuCr_2Se_4$ there is also observed a discontinuous change of the specific volume of the elementary cell by about 0.5%.[3] Therefore it is of interest to study and discuss mechanisms that explain the nature and pecularities of the magnetic transition for a series of nonconducting ferromagnetic spinels, such as mutual solid solutions of the type $CdCr_2(S_xSe_{1-x})_4$. The modeling of this system can be clarified on the one hand by the observation of the existence of MPT-1 in the sulfide spinel and of MPT-2 in the selenide,[8] and on the other hand by the fact that here it is easy to trace the increase of the energy of 90-degree magnetic exchange between the chromium ions ($I_{exch} \sim T_c$) on increase of the crystal lattice parameter from the value $a = 10.244$ Å (for $CdCr_2S_4$) to $a = 10.755$ Å (for $CdCr_2Se_4$). For this series of solid solutions $CdCr_2(S_xSe_{1-x})_4$, the parameter a varies linearly (in accordance with Vegard's law), whereas the exchange parameter and the Curie temperature vary with composition nonlinearly, with a negative deviation from additivity.[9] The concentration range, for these solid solutions, within which there should be observed a change of the type of MPT from the first to the second order has not hitherto been established.

A change of T_c in the direction of a decrease on replacement of Se by S, in these solutions, is apparently equivalent to the influence of hydrostatic compression of the $CdCr_2Se_4$ lattice, which leads to a similar effect.[10] Here it should be mentioned that we can probably neglect the influence of nonstoichiometric chemical composition of the spinels on the peculiarities of their magnetic transition under discussion. This is a consequence both of the constancy of the parameter a on departure of the spinel composition from stoichiometry[11] and of the fact that, as is shown by the results of investigations of resonance phenomena and in particular of ferromagnetic resonance,[12] such departures of the composition of the spinel $CdCr_2S_{4-x}$ from stoichiometry affect only the linewidth of the signal. Nonstoichiometricity of the spinel $CdCr_2Se_{4-x}$ may also cause some broadening of the peak of the specific heat in the magnetic phase transition of the second order.[8]

METHODS AND RESULTS OF THE INVESTIGATION

In the present work, an attempt was made to trace the peculiarities of the transformation of the MPT in a series of mutual solid solutions of spinels, $CdCr_2(S_xSe_{1-x})_4$, by study of their magnetic and nonmagnetic parameters: the magnetization, the specific heat, and the magnetocaloric effect in the vicinity of their Curie point T_c. The first-mentioned characteristic of these solid solutions has already been communicated; see, for example,[13–15]. But it is quite difficult to judge, solely from the variations of the polytherms $\sigma(T)$ or $\chi(T)$, whether MPT-1 occurs, because in these cases the jump of magnetization at the Curie point may be "blurred" by possible im-

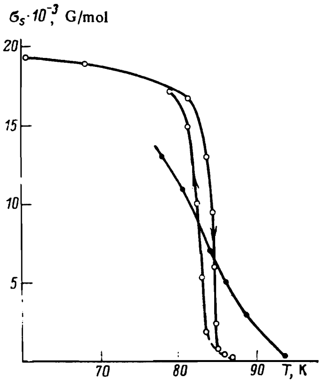

FIG. 1. Change of spontaneous magnetization of hardened (○) and annealed (●) specimens of the spinel $CdCr_2S_4$ near the Curie point.

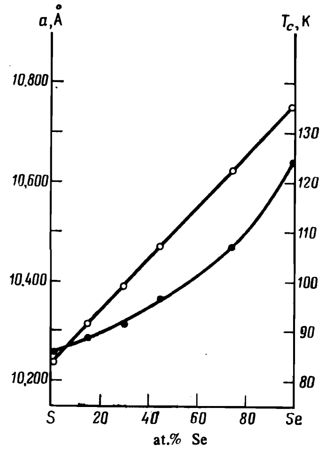

FIG. 2. Concentration dependence of lattice parameter (○) and Curie temperature (●) of solid solutions $CdCr_2(S_xSe_{1-x})_4$.

perfections of the crystal, and the type of phase transition according to these variations may not differ from MPT-2. This is seen from the example of the sulfide spinel, where we observed the occurrence of MPT-1 not only on the polytherm of the specific heat[2] but also by the 16-fold jump and temperature hysteresis of the magnetization in an interval of 2–3° adjoining its T_c (Fig. 1). Additional vacuum annealing of this specimen$^{1)}$ had practically no effect on the form of the specific-heat polytherms, but led to zero jumps of $\sigma(T_c)$.

For the further investigation, the method of solid-phase interaction of chalcogenides of cadmium with anhydrous chromium trichloride was used to synthesize polycrystalline specimens of mutual solid solutions $CdCr_2(S_xSe_{1-x})_4$, whose compositions were estimated by chemical analysis and x-ray diffraction. The characteristics of the specimens are given in Table I, and Fig. 2 shows their concentration dependences $a(x)$ and $T_c(x)$. The latter differs slightly from the data of[9]; this, in our opinion, can be explained by a difference in the experimental methods used for determination of the Curie points in the cited work and in ours.

The technical possibilities of the methods used by us were communicated earlier.[16] We add only that the investigation of the magnetocaloric effect was made in longitudinal magnetic fields of intensity up to 2.3 kOe, by means of an adiabatic vacuum calorimeter, which guarantees a high sensitivity of recording of the change of temperature (to ~ 10^{-4} K), and that the measurements of magnetization were made in fields of 4.2, 6.3, 8.3, and 10.1 kOe. The spontaneous magnetization $\sigma_s(T)$, shown in Figs. 1 and 3, were determined in these cases by extrapolation to $H = 0$.

As follows from the results presented here, the jump of magnetization at the Curie point could be observed only in the case of the spinel $CdCr_2S_4$; this corresponds to the existence in it of MPT-1, accompanied by a jump of enthalpy (~ 17.7 J/mol) and of entropy (~ 0.21 J/mol deg).[2] The present measurements did not reveal the presence in this spinel of a magnetocaloric effect in the vicinity of its T_c (at least in the fields mentioned above). In contrast to this, the magnetic and nonmagnetic parameters of the selenide spinel in the neighborhood of its Curie temperature behave in the manner characteristic of MPT-2. In particular, the magnetization near T_c undergoes a smooth variation, and the temperature of the maximum of the $\Delta T(H, T)$-effect agrees with the previously reported[8] maximum of the function $C_p(T)$ and is 124 K.

Thus on the basis of these limiting compositions for the solid solutions, it appeared that the magnetocaloric effect may be the most sensitive characteristic for determination of the type of MPT. The absolute value of the $\Delta T(H, T)$-effect in the solid solution, according to the results presented, increases with increase of the selenium concentration and is greatest for $CdCr_2Se_4$. But a similar concentration dependence, within quite broad temperature intervals including T_c, is characteristic also of the specific-heat polytherms of the spinels. Their values of $C_p(x)$ meanwhile increase, remaining within limits defined by the limiting ($x = 1$ and $x = 0$) compositions. We note, however, that at room temperature the differences between the values of C_p of these solid solutions is very small, and for $CdCr_2S$ and $CdCr_2Se$

TABLE I. Some characteristics of the specimens of mutual solid solutions of spinels $CdCr_2(S_xSe_{1-x})_4$.

Specimen number	x	a, Å (± 0.001)	T_c, K	T_0, K	Θ/T_K	$\Delta T(H, T)$-effect	$\frac{\Delta V}{V}(T_c)$, %	Order of MPT
1	1	10.243	85.1	65	1.72	Absent	0.3	1
2	0.85	10.317	88.5	74	1.76	»	–	1
3	0.70	10.387	91.5	84	1.80	»	0.1	1
4	0.55	10.471	96.8	–	1.80	Positive	0	2
5	0.25	10.624	107.6	–	1.80	»	–	2
6	0	10.755	124	–	1.74	»	0	2

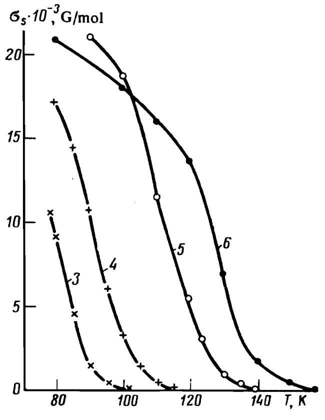

FIG. 3. Polytherms of the spontaneous magnetization of the solid-solution specimens investigated in the vicinity of their Curie points (the numbers on the curves correspond to the numbering in Table I).

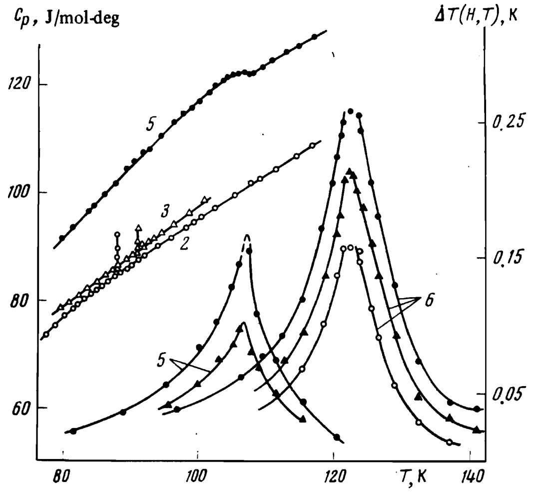

FIG. 4. Polytherms of the specific heat and of the magnetocaloric effect of the spinels: ●, $H=2.3$ kOe; ▲, $H=1.65$ kOe; o, $H=1.15$ kOe. The numbers on the curves correspond to the numbering in Table I.

amounts altogether to 6 J/mol deg.

Because the magnetocaloric effect cannot be used to determine the Curie temperature in the case of MPT-1, as is usual for MPT-2, the values of T_c given in the table for the solid solutions of spinels correspond either to the anomalies of their specific-heat polytherms alone (in the case of MPT-1 specimens) or to the peaks of the $\Delta T(H, T)$-effect as well (for specimens with MPT-2). As it turned out, especially for the second group of specimens, the values of their Curie points determined from magnetic data, for example on the basis of the maximum of the derivative $\partial\sigma_s/\partial T$, differ somewhat from the results of a determination of T_c from nonmagnetic investigations and are above them. The largest difference in these determinations of T_c was that for the spinel $CdCr_2Se_4$, where it amounted to ~6° (or a difference of ~5%). This situation is apparently systematic and is explained both by the polycrystallinity of our specimens and by the ordering effect of the external magnetic field in the determination of their $\sigma(T)$ polytherms.[17] Furthermore, study of the nonmagnetic characteristics of solid solutions has shown that they are less sensitive than is the magnetization to the previous history of the specimens, involving peculiarities of their synthesis. This is noticed, in the first place, in the behavior, characteristic of MPT-2, of the function $\sigma(T)$ in the T_c regions for all the synthesized compounds, including those characterized as MPT-1 on the $C_p(T)$ polytherms (Fig. 3). In these, apparently, occurrence of a jump of magnetization requires certain conditions of hardening of the specimens, which, however, we did not suceed in attaining in our work. Nevertheless, for specimens No. 2 and No. 3 the $C_p(T)$ polytherms show a high degree of localization of the magnetic transformation (Fig. 4), characterized by excess parameters significantly smaller than in $CdCr_2S_4$. Likewise, for them no magnetocaloric effect was observed.

On the contrary, for specimen No. 5 (similarly for specimen No. 4) a noticeable $\Delta T(H, T)$-effect is observed, whereas its specific-heat anomaly is to a significant degree "smeared out." This fact may indicate the existence of microscopic inhomogeneities of chemical composition in this specimen, which show up especially in the critical region because of possible differences in the magnetization fluctuations.

Thus it follows from the results presented that in the series of mutual solid solutions of spinels $CdCr_2(S_xSe_{1-x})$, at compositions from 30 to 40 atomic% Se, there is a change of the type of magnetic ferromagnet-paramagnet phase transition from the first to the second order. Figure 5 shows the magnetoconcentration diagram of these solid solutions according to the $\Delta T(H, T)$-effect data. From it it follows that in fields close to or larger than the saturation field of these spinels (~4.5 kOe), the boundary of transformation of the type of MPT is quite accurately determined.

DISCUSSION

The results of the present investigation indicate that the change of the type of MPT in this series of spinels is accompanied by a breakdown of the conditions necessary for transitions of the second order, adiabaticity ($\Delta S=0$) and constancy of volume ($\Delta V=0$). The occurrence of MPT-1 and the absence of a magnetocaloric effect are accompanied, as is well known,[18] by a breakdown of these conditions. For the composition range $0.6<x<1$, the existence of the condition $\Delta S\neq 0$ follows directly from an analysis of the specific-heat polytherms in the vicinity of T_c. Nonfulfillment of the second condition (that is, $\Delta V\neq 0$) has been so far suggested only by indirect data[19,20] on the temperature dependence of the lattice parameter of $CdCr_2S_4$: in the neighborhood of the Curie point, there was observed a departure of the $a(T)$ dependence from the predictions of Debye's theory.

For a quantitative estimate of the departure alluded to, we made measurements of the lattice parameters of the spinels at $T\leq T_c$; these enabled us to calculate the jump of the specific volume of the specimens that were characterized as MPT-1. It was found that for them, on transition to the spin-ordered state there occurs an increase of the parameter a by about 0.01 Å as compared with the values obtained at room temperature and given in the table. For the spinel $CdCr_2S_4$, this corresponds to a jump of volume, at $T<T_c$, of ~0.3%. But under these conditions, for specimens distinguished as MPT-2 no noticeable change of the parameter a and of the specific volume of the lattice was detected. Conse-

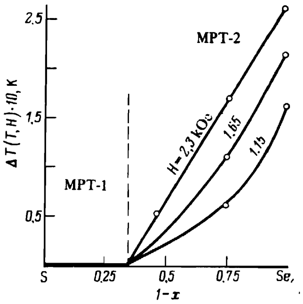

FIG. 5. Magnetoconcentration phase diagram of mutual solid solutions $CdCr_2(S_xSe_{1-x})_4$.

quently, the occurrence of MPT-1 in the series of spinels $CdCr_2(S_x Se_{1-x})_4$ with $0.6<x<1$ is accompanied by an increase of the specific volume of the lattice. This indicates the validity of using the thermodynamic theory of Bean and Rodbell[5] for discussion of the nature of MPT-1 in them.

In this case, as is well known, the measured Curie temperature T_c differs from the "true" Curie point T_0, corresponding to absence of exchange striction in a "rigid" lattice, and is connected with it by the relation

$$T_c=T_0[1+\beta\Delta V/V].$$

Here $\Delta V \equiv V - V_0$; V_0 is the volume of the "rigid" lattice; and β determines the value of the change of exchange energy on compression of the lattice. If we adopt this mechanism and suppose, in agreement with the present experimental data, that for the spinel composition range $x<0.6$, $\Delta V \to 0$, i.e., $T_c = T_0$, then from Fig. 2 and from the results of[9] we can draw a conclusion regarding a possible linear character of the concentration variation of the true Curie temperature. Then by extrapolating this dependence to the composition range $x>0.6$, we can estimate the values of $T_0(x)$ (see table) and of the parameter β, which within the framework of the assumptions made is independent of composition. Calculation gives $\beta \approx 10^2$.

Finally, it is interesting to explain the possible reasons for existence of the mechanism of exchange striction in spinels with $x>0.6$. For this purpose it is necessary to consider the peculiarities of the crystal chemistry of mixed spinels. We recall that in the spinel structure the Cr^{3+} ions, which occupy octahedral positions, produce an indirect 90-degree exchange with each other via the X^2-anions. Assuming that the maximum permissible volume of such an octahedron is bounded by dimensions determined by the selenium anions, one can easily show that in the case of a sulfide spinel the volume occupied by the octahedron is less by 25%. The difference between the Cr^{3+}–Cr^{3+} distance and the radii of the S^{2-} and Se^{2-} anions for such cases is 8.5%. Thus in spin ordering of the chromium ions in the spinel $CdCr_2S_4$, there is a potential possibility for occurrence of an increase of the Cr^{3+}–S^{2-} distance (a process similar to that caused by negative pressure), leading to an increase of the exchange integral and of the Curie point. The spatial indeterminacy produced during such a transition in the relative position of these ions is apparently the condition that transforms MPT-2 to MPT-1. In a solid solution, this indetermninacy decreases in proportion to the replacement of sulfur by selenium; and if we restrict ourselves to the first magnetic neighbors of the central Cr^{3+} cation, it vanishes at $x=0.5$. Allowance for the second coordination sphere already leads to 33.3-percent replacement. This last value, as is seen from Fig. 5, corresponds to the boundary established for the concentration range of the solid solution within which a transformation of the type of MPT occurs.

In conclusion, we remark that the facts discovered indicate the impossibility of determining the Debye temperature of such spinels for their low-temperature ($T < T_c$) specific heats, because such data will lead to overestimation of the values of Θ_D.

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[1] Here there occurs some change of the chemical composition of the specimen, in the direction of a decrease of the chalcogen content.

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