experiment with any of the variants of the Landau expansion is, strictly speaking, invalid. Within the framework of this expansion, for example, it is generally impossible to explain the large amplitude of the anomaly of the specific heat in the isotropic phase. For a quantitative comparison with the results of theoretical researches[2,3] new, more accurate experimental data are necessary.

If the tricritical point behavior near the transition isotropic liquid–liquid crystal is confirmed, then this will be by showing the important role of the interaction of the tensor order parameter with other power methods.

In conclusion, we thank V. M. Malyshev for help in setting up the experiment, E. E. Gorodetskiĭ and V. M. Zaprudskiĭ for useful discussion.

[1)]Naturally, this does not mean that there exists a tricritical point on the line $T_t(P)$, in the same way as the smallness of the constant B does not require the necessary existence of an isolated critical point on this line.

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Singularities of magnetic properties of doped $CdCr_2Se_4$ single crystals in the region of the Curie point

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The dependence of the magnetization σ on the temperature T and on the magnetic field H was investigated in $CdCr_2Se_4$ single crystals doped with indium or copper and also having a selenium deficiency, in the region of the Curie point T_c and somewhat above it. The (H) curves at temperatures slightly exceeding T_c have a critical field in whose vicinity the magnetization increases jumpwise by 80%. In the same temperature region, a temperature hysteresis of σ was also observed. Annealing of a selenium-deficient sample in a selenium atmosphere decreases greatly the jump on the σ(H) curves and narrows down the temperature hysteresis. The indicated experimental facts can be attributed to the production of ferrons under the influence of the magnetic field at temperatures above T_c. The field-induced transition from the paramagnetic state to the ferron-containing state is an analog of a first-order phase transition.

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In magnetic semiconductors, particularly $CdCr_2Se_4$, a strong exchange interaction exists between the carriers and the localized magnetic moments ($s-d$ exchange). This exchange interaction leads to a number of singularities of the magnetic and electric properties of these semiconductors. It is presently customary to attribute the greater part of these singularities to the presence of special magnetic microregions characterized by an increased degree of ferromagnetic order—ferrons. For pure magnetic semiconductors, these microregions were theoretically predicted by Nagaev[1,2] and by von Molnar and Methfessel.[3] They have shown that owing to the $s-d$ exchange it is energywise more convenient for the carriers to become autolocalized and

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to maintain a ferromagnetic order in the magnetoactive ions that surround them.

The formation of ferrons in ferromagnetic semiconductors is most probable near the magnetic-ordering point T_c and is impossible at $T=0$. The ferron radius depends on temperature and can reach several lattice constants. Yanase[4] calculated with a computer the probability of formation of such free ferrons, and showed that in practice they can occur in a magnetic semiconductor having a magnetic-ordering temperature not higher than 10 K. In impurity magnetic semiconductors, however, ferron production around donor (or acceptor) centers takes place practically always, since the electron is localized near the defect by Coulomb forces and the degree of ferromagnetic order in the region of localization increases because of the indirect exchange via the defect. Localized impurity ferrons were theoretically predicted by Yanase and Kasuya.[5,6]

We have shown earlier[7–9] that impurity ferron exist possibly in the compounds $CdCr_2Se_4$: Ga, $CdCr_2Se_4$: Cu and $CdCr_2S_4$: Cu. The indirect proofs of the presence of ferrons were the minimum of the photoconductivity in the region of T_c in the compound $CdCr_2Se_4$ weakly doped with gallium[7] and the increase of the paramagnetic Curie temperature with increasing doping level without a change in the ferromagnetic Curie point in $CdCr_2Se_4$: Cu and $CdCr_2S_4$: Cu,[8,9] as well as the maximum of the coercive force above T_c in the last two materials. We cite in the present paper new effects that confirm the existence of impurity ferrons in these materials in the region of T_c, namely the presence of critical fields on the magnetization curves $\sigma(H)$ above T_c, temperature hysteresis of the magnetization, and positive magnetoresistance in the region of T_c.

The investigated objects were $CdCr_2Se_4$ single crystals doped with indium and copper and also somewhat deficient in selenium (~1.5%). The characteristics of all the investigated compositions are listed in Table I which gives also the data for a $CdCr_2Se_4$ single crystal of stoichiometric composition (sample I) and for single crystals with a selenium deficiency of ~1.5% (samples II and III). The single crystals were grown by two methods, by spontaneous crystallization from the solution in the melt and by the method of liquid-transport reactions. The samples were regular octahedra with edge dimensions 1–3 mm. The chemical analysis was performed

TABLE. I.

Samples	T_c', K		$\Delta T_c'$, K
	$H=0.9$ kOe	$H=12.7$ kOe	($\Delta H=11.8$ kOe)
Gd'	287	290	3
$Cd'Cr_2Se_4$ (I)	140	144	4
$Cd'Cr_2Se_4$ (II)	138	161	23
$Cd'Cr_2Se_4$ (III)	140	175	35
III after annealing in Se	140	152	12
$Cd_{0,96}Cu_{0,04}Cr_2Se_4$	136.6	162	25.4
$Cd_{0,93}Cu_{0,07}Cr_2Se_4$	138.8	167	28.2
$Cd_{0,86}Cu_{0,14}Cr_2Se_4$	132	168	36
$Cd_{0,999}In_{0,001}Cr_2Se_4$	133.5	154.5	21
$Cd_{0,994}In_{0,006}Cr_2Se_4$	137	158	21
$Cd_{0,993}In_{0,007}Cr_2Se_4$	139.5	151	11.5
$Cd_{0,987}In_{0,013}Sr_2Se_4$	139.5	150.5	11
$Cd_{0,98}In_{0,02}Cr_2Se_4$	137.5	155	17.5

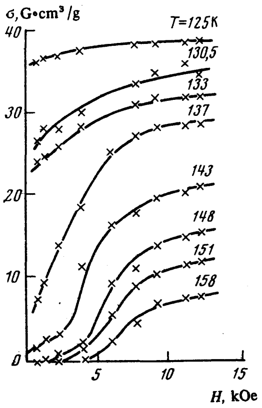

FIG. 1. Dependence of the specific magnetization σ on the magnetic field at $T \gg T_c$ for the sample $CdCr_2Se_4$ (II) with a ~1.5% selenium deficiency.

by the method of atomic absorption, using a Perkin-Elmer 303 spectrometer. To carry out the analysis, the $CdCr_2Se_4$ crystals were dissolved in nitric acid and the optical density of the prepared solutions was measured. The accuracy with which the optical density was measured was 0.5%. An x-ray phase analysis has demonstrated the absence of a second phase in these materials.

The sample magnetization σ was measured with a vibration magnetometer, while the resistivity was measured by the voltmeter–ammeter method, in which, owing to the high sample resistance (up to 10^9 ohm), an electrostatic voltmeter and a highly sensitive TR-1452 current indicator were used. The measurements were made in a vacuum in fields up to 14 kOe. The temperature in the measurement process was maintained with accuracy 0.2. In the measurement of the resistivity the ohmic contacts were made by fusing indium into an evacuated sealed ampoule in an atmosphere of spectrally pure argon.[10] The contact resistance was less than 10% of the sample resistance.

The $\sigma(H)$ curves of all the investigated compositions, with the exception of sample I, revealed in a certain temperature region above T_c a jumplike growth of σ at the critical value of H. This is clearly seen in Fig. 1, which shows the $\sigma(H)$ curves for sample II. Thus, for the temperature region 143–158 K, the jump of the magnetization at a critical field in the 5 kOe region reaches 80%. No such jump is observed at lower temperatures.

After annealing sample III in a selenium atmosphere for 72 hours at 730 °C and at a selenium vapor pressure 40 Torr, the jump of σ at the critical field value decreased by approximately 30%, and the temperature interval in which this jump was observed also decreased. Thus, the (H) curves no longer have a critical field at $T>145$ K.

A temperature hysteresis of the magnetization was observed in the region of T_c for all the investigated single crystals, with the exception of sample I. Figure 2 shows this hysteresis for sample III before and after annealing in the selenium atmosphere. Measurement of the temperature hysteresis were made in a magnetic field exceeding the critical field on the $\sigma(H)$ curves. It is seen from the figure that the annealing decreased the hysteresis width by an approximate factor of two.

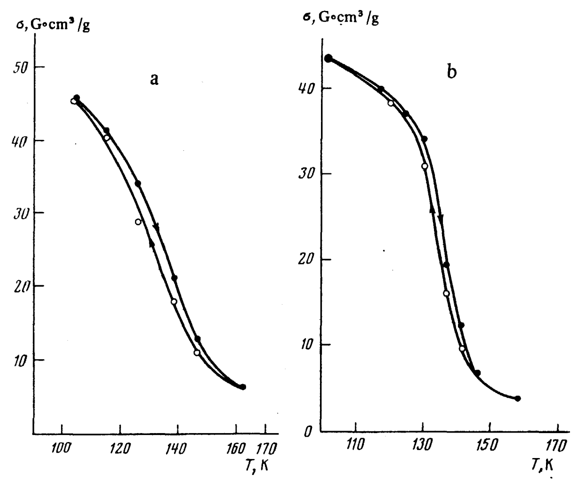

FIG. 2. Single crystal $CdCr_2Se_4$ with ~1.5% selenium deficiency (sample III). Temperature hysteresis of the magnetization: a) prior to annealing in a selenium atmosphere (H –4.15 kOe), b) after annealing (H =8 kOe).

We have previously observed[11,12] positive magnetoresistance in indium-doped $CdCr_2Se_4$ single crystals, and also in crystals deficient in selenium at temperatures above 140 K. It was shown that in the region of the Curie point the negative magnetoresistance first exhibits a maximum absolute value, and then reverses sign with rising temperature, becoming positive in a certain field interval, after which it passes through a maximum. An external magnetic field maintains long-range order in the region of T_c and by the same token decreases the magnetization fluctuations, meaning also the scattering of the carriers by these fluctuations as a result of s-d exchange. This is why the negative magnetoresistance was in fact observed in the region of T_c. However, for reasons similar to those indicated by Nagaev Kashin, [13,14] in the paramagnetic region, where the long-range magnetic order is already destroyed, the magnetic field near an unionized donor increases the degree of magnetic order to a greater degree than on the average over the crystal. The reason is that the donor electron increases the intensity of the effective exchange between the magnetic atoms in the vicinity of the donor and increases, as it were, the local Curie temperature. But the magnetic susceptibility at a given temperature is higher the higher T_c. On the other hand, the s-electron energy is lower the larger the amgenetization. The magnetic field therefore decreases more strongly the energy of the localized electron than the energy of the free one, so that the carrier density decreases with increasing H, and this leads to positive magnetoresistance.

The arguments advanced above pertain to donors whose electrons have a nonzero spin. In the case of singly charged donors this condition is satisfied automatically. In the $CdCr_2Se_4$ crystals under consideration, which are deficient in selenium, the donors are doubly charged, since their role is assumed by the selenium vacancies. If the crystal were nonmagnetic, the spins of both electrons would be antiparallel to each other (a state of the $(1s)^2$ type in the helium-like model). But if the magnetization differs from zero, then s-d exchange can make energywise more favored a state of the type $(1s)(2s)$, in which the electron spins are parallel to each other. [15] In this state the local magnetization near the donor is higher than on the average over the crystal.

The above-described experimental data, both on the dependence of the resistivity and of the magnetization on H, can be explained in the following manner. When the sample is heated above T_c, the parallel orientation of the paired spins is replaced by antiparallel orientation. Application of a magnetic field at $T \geq T_c$ can change the antiparallel spin disposition of the defect into a parallel one accompanied by ferron formation, as was apparently observed by us in $CdCr_2Se_4$ with a selenium deficiency.

The critical fields observed by us and the $\sigma(H)$ curves above T_c and the temperature hysteresis of the magnetization in the region of T_c both indicate that a magnetic field produces in the investigated materials a transition from the paramagnetic state into a ferron-containing state, an analog of a first-order phase transition.

In practice one frequently determines the Curie point by simple extrapolation of the steepest part of the $\sigma(T)$ to the temperature axis, although generally speaking this yields not the Curie point but a certain characteristic temperature T_c' close to the Curie point. Using this method, we have determined T_c' for all the investigated compositions in different magnetic fields. It turned out that the Curie point, determined from extrapolation of the steepest part of $\sigma(T)$ to the temperature axis, depends strongly on the field at which the curve was measured. This effect takes place for $CdCr_2Se_4$ single crystals with ~1.5% selenium deficiency, and also for crystals doped with copper and indium. By way of example Fig. 3 shows the dependence of $\sigma(T)$ in different magnetic fields for the sample $Cd_{0.93}Cu_{0.07}Cr_2Se_4$. It is seen that when H changes from 0.9 to 12.7 kOe the value of T_c' changes by an amount $\Delta T_c' = 28.2°$.

The table lists the values of $\Delta T_c'$ for all the investigated samples when the magnetic field is varied from 0.9 to 12.7 kOe. It is seen from the table that $\Delta T_c'$ depends monotonically on the doping level for the copper-doped compositions. The table gives also the values of

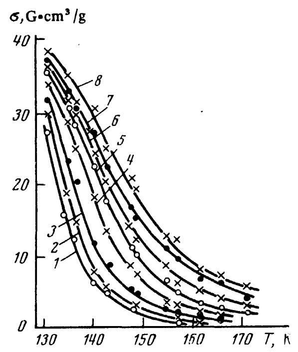

FIG. 3. Temperature dependence of the specific magnetization of single-crystal $Cd_{0.93}Cu_{0.07}Cr_2Se_4$ in the following magnetic fields (kOe): 1—0.9, 2—1.3, 3—2.25, 4—4.15, 5—6.2, 6—8, 7—9.6, 8—12.7.

$\Delta T'$ for single-crystal $CdCr_2Se_4$ (sample I), in which no selenium deficiency is detected, and for single-crystal gadolinium; both values are close to 4°. A similar investigation was made of two $CdCr_2Se_4$ single crystals having a selenium deficiency up to 1.5%. It turned out that $\Delta T_c' = 26°$ for one of them (sample II) and $\Delta T_c = 35°$ for the other (sample III). After the described annealing of sample III in the selenium atmosphere, the value of $\Delta T_c'$ decreased to 12°. We conclude therefore that the shift $\Delta T_c'$ is due to the selenium deficiency of the sample and to the impurity.

The foregoing examples show clearly that the Curie point of magnetic semiconductors must be determined by methods that exclude the external magnetic field, since the error can be quite large.

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Bound states of a large number of magnons in a ferromagnet with a single-ion anisotropy

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The conditions for the formation of a magnon bound state in one- and three-dimensional ferromagnets with the "easy axis" type of anisotropy are investigated. Explicit expressions are obtained in the one-dimensional case for the energies and wave functions of the bound states of an arbitrary number of magnons under the natural assumption that the magnetic anisotropy energy is small compared to the exchange energy. The binding energy per magnon increases monotonically with increasing number of magnons. For large numbers of magnons ($N \gg 1$) the solution to the quantum problem goes over into the specific self-localized solution to the Landau-Lifshitz equation for the magnetization vector. It is shown that, if there do not exist in a three-dimensional ferromagnet bound states of two magnons with a low quasimomentum, then there can arise in this ferromagnet bound states of a large number, N, of magnons (in the case when $N \geq N_*$, where the quantity N_* is determined by the ratio of the exchange energy to the anisotropy energy). The form of the self-localized solution is obtained by means of a numerical solution of the nonlinear equation of motion for the magnetization vector, and the dependence of the parameters of this solution on N is determined. An interpretation is given of the physical meaning of the bound state of a large number of magnons.

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INTRODUCTION

The physical properties of magnetically ordered crystals at low temperatures are determined to a considerable extent by the properties of the gas of elementary excitations of the magnetic substance—the magnons. The weakly excited states of a magnetic substance are usually described in terms of an ideal quasiparticle gas, i.e., in the approximation of noninteracting magnons. It is, however, clear that the interaction of the magnons

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