Model of $FeCr_2S_4$ as a true semiconductor in a strong Weiss field

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We propose the simple model for the colossal magnetoresistance in $FeCr_2S_4$. The material is considered a classical semiconductor with parabolic density of states that is affected by both the external magnetic field and the strong Weiss exchange field that arises from the magnetic order in the substance. The resulting effective field shifts the conducting bands and hence causes the change in the number of thermoactivated carriers. This change is presumed to be responsible for the magnetoresistance. Surprisingly this apparently oversimplified model describes well both the temperature and magnetic-field dependences of the resistivity in this material employing the minimal set of the adjusted parameters. The role of the critical phenomena above Curie temperature appears to be important.

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I. INTRODUCTION

Magnetic semiconductors with a spinel structure and general formula ACr_2X_4 (A=Fe, Mn, Co, Cu, Cd, Zn, Hg; X=S, Se) has attracted special interest because of the strong correlation of magnetic and transport properties. As a result these compounds exhibit the variety of physical effects such as colossal magnetoresistance (CMR),[1] "giant" red shift of the absorption edge,[2,3] and some others.[4–6]

$FeCr_2S_4$ is a ferrimagnetic semiconductor exhibiting CMR effect which amounts up to 20 percent near the Curie temperature T_C=174 K in the magnetic field of several teslas. There are a lot of the experimental studies concerning this compound.[1,7–12]

The main features obtained on the single-crystalline and ceramic $FeCr_2S_4$ samples may be listed as follows: (i) activationlike temperature dependence of the resistivity $R(T)$ both above and well below magnetic ordering temperature, with different activation energies; (ii) the broad maximum on $R(T)$ dependence near T_C and the broad minimum below this temperature; (iii) strong negative magnetoresistance in the vicinity of T_C, both below and above it. The magnetoresistance value typically reaches narrow maximum at $T_m \approx 0.97T_C$, i.e., below T_C; (iv) the magnetic-field dependence of the resistivity $R(H)$ is quadratic above T_C, linear below it, and sublinear in the close vicinity of T_m; (v) almost no field hysteresis on both the resistivity and magnetization dependencies on the magnetic field down to $T_C/2$; (vi) coercitive force is always less than 0.1 T and magnetic anisotropy can be considered negligible down to $T_C/2$; and (vii) there are additional magnetic phenomena below $T_C/2$ such as spin-glass-like transition and increase in magnetic anisotropy that we do not consider here.

Several physical phenomena were proposed as an explanation of the CMR effect in $FeCr_2S_4$: magnetic polaron conductivity,[10] magnetic nanoclusters,[13] half-metallic behavior,[14] and some others.[15,16] Most of them suggest that the anomalous behavior of the resistivity is mainly due to the change in the charge carriers' mobility with the variation of the temperature, magnetic ordering, and magnetic-field application.

There is, however, another contribution: magnetoresistance may arise from a change in the density of the charge carriers, caused by evolution of the band structure under magnetic ordering formation and/or magnetic-field application. This possibility was taken into consideration in the years 1960–70,[8,17–19] but, as far as we know, never attracted special attention in later decades. We are going to propose a simple model within this approach that is consistent with most of the properties listed above.

II. MODEL

We consider the simplest semiconductor with parabolic density of states in the conducting band and activation energy Δ, see Fig. 1(a). The local electrons responsible for the magnetic ordering form the local magnetic levels (depicted by inscription) that define the Fermi energy ϵ_F. The magnetic and conducting electrons are considered separately and assumed to be tied only by magnetic exchange between them. It means that the occurrence of the magnetic order, both spontaneous and/or induced by external magnetic field H_0, results in the nonzero Weiss field H_W applied to the conducting electrons, depicted by the bold arrow at Fig. 1(b). The external magnetic field H_0, expected to be much smaller in magnitude, in addition to the Weiss field H_W, forms the resulting effective field H_{eff}. This effective field causes the shift of the spin-up and spin-down conducting bands by $\mu_B H_{\text{eff}}$ down and up, respectively. The Fermi energy ϵ_F and activation energy Δ are assumed independent on temperature and magnetic field.

The expression for the density of thermoactivated carriers in this model is simply obtained. In the absence of magnetization and H_{eff} equal to zero [Fig. 1(a)] the density of carriers $n(T)$ is described by classical expression[20]

$$n(T) = A\int_0^\infty \frac{\epsilon^{1/2}d\epsilon}{\exp\dfrac{\epsilon+\Delta}{kT}+1},$$

and under occurrence of the effective field H_{eff} [Fig. 1(b)] this expression converts to

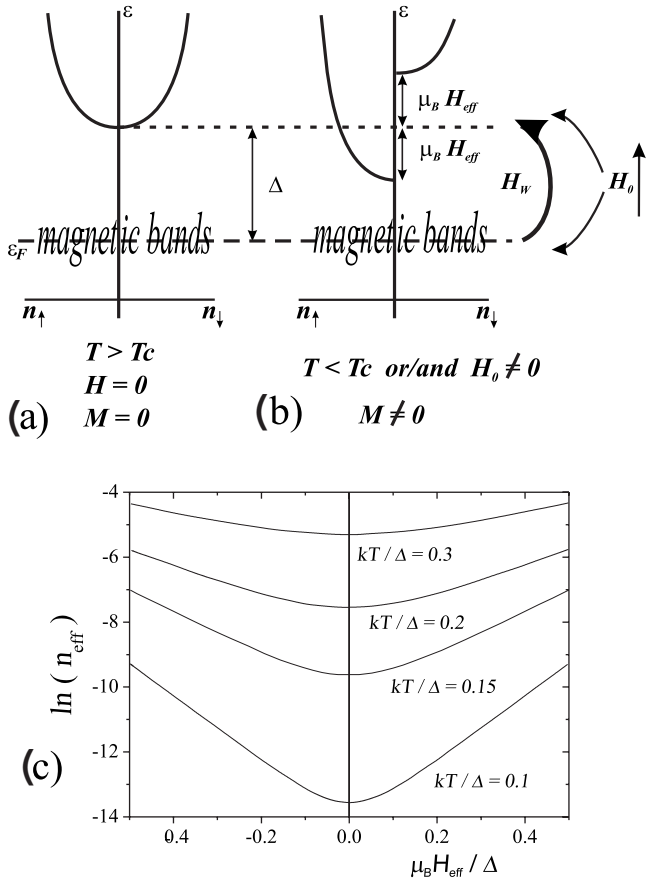

FIG. 1. (a) The basic model in the absence of the magnetic field and magnetic order: the density of spin-up and spin-down states as a function of a carrier energy $n(\epsilon)$. Δ is the activation energy; the conducting band (at the top) is assumed parabolic. Magnetic bands, depicted by inscription, are responsible for the magnetic order. They also define the Fermi energy ϵ_F (dashed horizontal line). (b) The model after occurrence of the spontaneous magnetization and/or external field H_0. A strong Weiss field H_W (depicted by bold arrow) arises from the magnetic order. In addition with the applied field H_0 it forms the effective field H_{eff} that shifts the conducting bands by $\mu_B H_{\text{eff}}$ down and up, respectively. The shift in the magnetic bands associated with the magnetic ordering not presented Δ and ϵ_F are assumed independent on temperature. (c) The density of carriers n_{eff} as a function of the effective field H_{eff} at different temperatures (arbitrary units, semilogarithmic scale).

$$n_{\text{eff}}(T,H_{\text{eff}}) = \frac{A}{2}\left(\int_0^\infty \frac{\epsilon^{1/2}d\epsilon}{\exp\dfrac{\epsilon+\Delta-\mu_B H_{\text{eff}}}{kT}+1} + \int_0^\infty \frac{\epsilon^{1/2}d\epsilon}{\exp\dfrac{\epsilon+\Delta+\mu_B H_{\text{eff}}}{kT}+1}\right), \quad (1)$$

where n_{eff} is a density of carriers under effective field, A a numerical coefficient, first integral corresponds to spin-up band, and second to the spin-down one. The typical dependences of n_{eff} on H_{eff} are presented in Fig. 1(c).

The number of experimental data on resistivity and magnetoresistance in $FeCr_2S_4$ is huge, see Sec. I. All these results agree well with each other. We choose for analysis the data[12] obtained on the single crystal under both the magnetic field up to 7 T and the hydrostatic pressure up to 12 kbar.

We assume the dominating scattering to be phononic and therefore the carriers' mobility to depend only on temperature by ordinary $T^{-3/2}$ law[20] that is typical for single-crystalline semiconductors at these temperatures. Hence scattering makes no contribution to the magnetoresistance and we suppose this phenomenon to be due solely to the change in the density of thermoactivated electrons caused by zones shifting under magnetic-field application. Therefore the expression used for the analysis was

$$R(T,H_{\text{eff}}) = BT^{3/2}/n_{\text{eff}}(T,H_{\text{eff}}), \quad (2)$$

where B is numerical coefficient and H_{eff} the effective field.

As a first approach we consider the external field equal to zero and assume Weiss field H_W to be directly proportional to the spontaneous magnetization $M(T)$. We even ignore here the ferrimagnetic structure in $FeCr_2S_4$, considering magnetization to be the only parameter that governs H_W. Hence we assume the simplest linear expression for the effective field

$$H_{\text{eff}}(T) = H_W^0 M(T)/M(0), \quad (3)$$

where parameter H_W^0 describes exchange between magnetic and conducting electrons and $M(0)$ is spontaneous magnetization at $T=0$.

As a first approach the expression (2) with H_{eff} defined as Eq. (3) was fitted to the experimental $R(T)$ dependences from Ref. 12 at zero magnetic field $H_0=0$ and pressures 0, 6, and 12 kbar as follows: first the Δ and B parameters were obtained from the high-temperature part of the $R(T)$ dependence at the ambient pressure. Next the H_W^0 parameter was obtained from the low-temperature part of the same dependence. This value used hereafter was $\mu_B H_W^0 = 490$ K. These H_W^0 value and numerical coefficient B were used for the dependences at all the three pressures and the only parameter Δ was obtained separately for each pressure. Finally the whole $R(T)$ curve was restored using the temperature dependence of spontaneous magnetization from Ref. 1 (see below) rescaled in T to match the Curie temperature T_C for each dependence.

The resulting curves are presented in Fig. 2. We see that the only area of disagreement is the vicinity of the Curie temperature while both the high-temperature and low-temperature branches are fitted good enough. Note that the numerical coefficient B is the same for all the three dependences. It means that at least above T_C the change in the resistivity under pressure may be attributed completely to the change in the activation energy Δ caused by pressure, i.e., to the perfect semiconductive behavior. Pressure dependence of Δ is linear, see inset Fig. 2.

If the measured resistivity in the vicinity of T_C was higher than the calculated value this difference could be attributed to the additional critical scattering. Actually it is significantly lower and hence needs another explanation. The next step is to reverse the problem and to obtain the "true" effective field H_{eff} as a function of temperature from experimental $R(T)$ curves using expression (1) when the rest parameters are already known. The result employing the same values for B

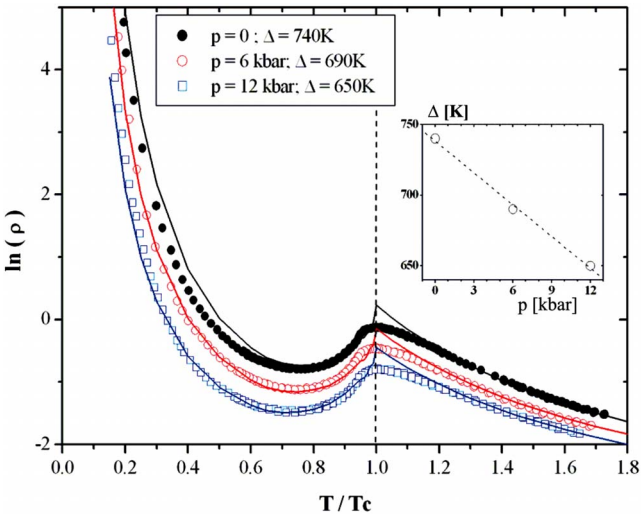

FIG. 2. (Color online) Temperature dependences of the resistivity of single crystalline $FeCr_2S_4$ at different pressures and zero magnetic field as a function of the reduced temperature (calculated from data of Ref. 12). Closed circles—ambient pressure, open circles—6 kbar, and squares—12 kbar. Lines are the results of calculation by Eq. (2). Inset: the pressure dependence of the activation energy Δ. The rest fitting parameters are the same for all the three curves (see text).

and Δ as before is presented in Fig. 3. The temperature dependence of the spontaneous magnetization $M(T)$ from Ref. 1 is presented for comparison (dashed line, right scale).

Below T_C the effective field H_{eff} follows nicely the temperature behavior of $M(T)$, showing the similar curves for all the three pressures studied. The discrepancy below T_C may be due to the spin-glass-like transitions at T_{sg}, marked by up

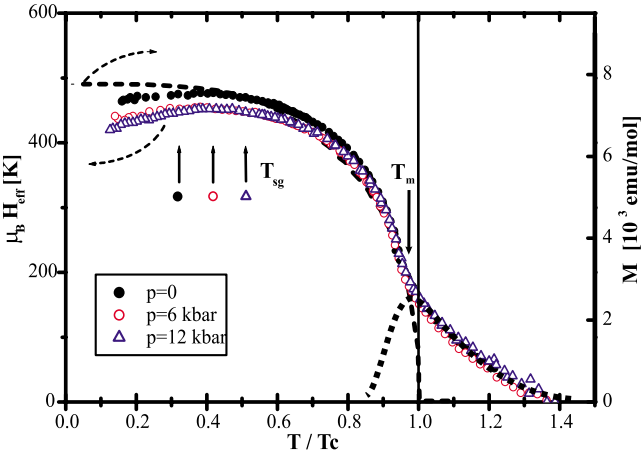

FIG. 3. (Color online) Left scale: dependences of the effective field on the reduced temperature $H_{\text{eff}}(T/T_C)$ obtained with Eq. (2) from experimental dependences Fig. 2 (from Ref. 12) employing the same fitting parameters. Closed circles—ambient pressure, open circles—6 kbar, and triangles—12 kbar. Dotted line (a guide to the eye) depicts the expected behavior of Weiss field caused by critical fluctuations. Arrows mark the spin-glass transition temperatures for the respective curves. Right scale: dependence of the spontaneous magnetization on the reduced temperature $M(T/T_C)$ (dashed line, from Ref. 1).

arrows. Near T_C the $H_{\text{eff}}(T)$ dependence demonstrates a clear contrary flexure and tends to zero with temperature increase. Such a behavior may be attributed to the critical phenomena above T_C. The reason is as follows: the random critical magnetic fluctuations provide the random Weiss field that shall affect the band structure in the same way as the uniform Weiss field does. The dependence of n_{eff} on the effective field is an even function hence the random field with mean value equal to zero can nevertheless produce nonzero effect on the density of carriers. The exact calculation of this random-field effect requires accurate treatment of the characteristic length and time both for the magnetic critical fluctuations and for carriers affected by these fluctuations. However it is legal to assume that the effect of critical fluctuations reaches maximum at T_C and tends to zero both above and below T_C, see dotted curve on Fig. 3. Note that the specific-heat study[21] confirms the critical behavior at least up to 1.2 T_C.

Next we are going to obtain the effect of the external magnetic field H_0 on the effective field H_{eff}. For this purpose we obtained the temperature dependences of H_{eff} with the technique described above both for $H_0=0$ T and $H_0=7$ T at all the three pressures over all the temperature ranges available. The result is presented in Fig. 4(a). To refine the effect we plotted the difference $H_{\text{eff}}(T,H_0=7\ \text{T})-H_{\text{eff}}(T,0)$ as a function of the reduced temperature T/T_C in Fig. 4(b). The first result is that all the three curves for the different pressures coincide nicely. Near T_C application of the magnetic field of 7 T causes increase in the effective field about 90 T. Such an amplification seems reasonable because near T_C the external field produces the greatest effect on the magnetic order and hence on the Weiss field. Note that maximum corresponds not to T_C but to ≈ 0.97 T_C that coincides with magnetoresistance maximum T_m (marked by arrow) as could be expected (see above). This unbalance is discussed below.

There is another important agreement. Well below T_C the available external magnetic field cannot affect the Weiss field any more because it almost reached its maximum value. Therefore the external field H_0 is simply added to the constant H_W when applied. It means that well below T_C the application of the external magnetic field $H_0=7$ T will just add 7 T to the effective field H_{eff}. On Fig. 4 we see that with the temperature decrease this addition to the effective field really tends to 7 T (dashed horizontal line) within the experimental accuracy. It suggests that our calculated field H_{eff} is a real physical parameter.

Now we shall discuss the field dependences of resistivity at different temperatures. In Fig. 5 we present a set of dependences $H_{\text{eff}}(H_0)$ below T_C at several temperatures and ambient pressure calculated by the same technique using data in Fig. 8 from Ref. 12. At 165 K, i.e., just below T_C it follows a power law $H_{\text{eff}}(H_0)-H_{\text{eff}}(0)\propto H_0^{0.58}$ while at lower temperatures this dependence tends to be linear.

In our model the increase in the effective field H_{eff} always causes the increase in the density of carriers [see Fig. 1(c)] hence magnetoresistance is always negative in agreement with the experiment. Over all the temperature ranges where magnetoresistance is observable even the strong magnetic field $H_0=7$ T causes only a small addition to the nonzero effective field H_{eff}, see Fig. 4(a). Following the dependence Fig. 1(c) the resulting density of carriers and hence magne-

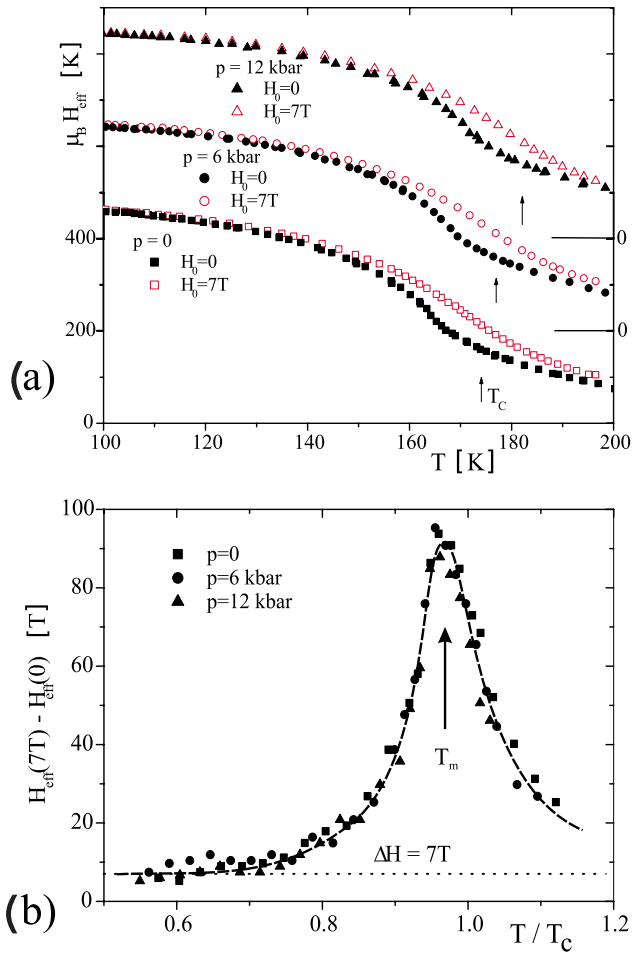

FIG. 4. (Color online) (a) Temperature dependences of the effective field H_{eff} with and without external magnetic field H_0 at different pressures. Closed points—$H_0=0$, open points—$H_0=7$ T, squares—ambient pressure, circles (shifted 200 K up)—6 kbar, and triangles (shifted 400 K up)—12 kbar. Arrows mark Curie temperatures T_C. (b) Change in the effective field H_{eff} caused by the applied magnetic field $H_0=7$ T as a function of the reduced temperature at different pressures [calculated from Fig. 4(a)]. Squares—ambient pressure, circles—6 kbar, and triangles—12 kbar. Dashed line is a guide to the eye. Dotted horizontal line marks the change in the effective field equal to the applied field 7 T (see text.)

toresistance are almost linear in this addition while its dependence on H_0 may vary with temperature. Note that the effect of the applied field always occurs on the basis of the strong nonzero Weiss field. Likely it is the main reason for the strong magnetoresistance. In the absence of this spontaneous Weiss field, such as at $T \gg T_C$, even the same change in the H_{eff} would have much smaller effect on the resistivity in accordance with Fig. 1(c).

Above T_C the applied magnetic field H_0 causes the magnetization $M(H_0)$ that in turn produces uniform Weiss field $H_W^u(M)$. This uniform field is added to the random Weiss field H_W^r that arises from critical fluctuations and is expected to be much stronger. When uniform field is added with the independent random one the resulting effective field H_{eff} behaves as follows: $H_{\text{eff}}^2 = H_W^u(M)^2 + \langle (H_W^r)^2 \rangle$, where angle brackets mean proper averaging in space and time (see

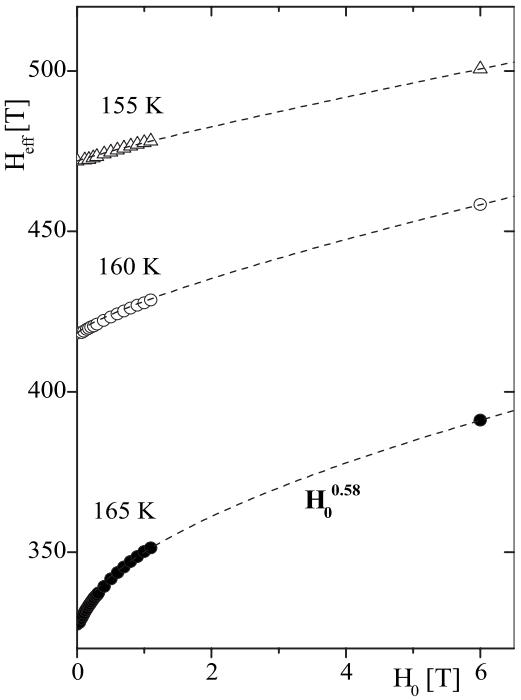

FIG. 5. Magnetic-field dependences of the effective field $H_{\text{eff}}(H_0)$ below Curie temperature at ambient pressure. Closed circles—$T=165$ K (dashed line is a power fit with critical index of 0.58), open circles—$T=160$ K (dashed line is a guide to the eye), and triangles—$T=155$ K (dashed line is a guide to the eye).

above). Assuming $|H_W^u(M)| \ll \langle (H_W^r)^2 \rangle^{1/2}$ we obtain $H_{\text{eff}} = \langle (H_W^r)^2 \rangle^{1/2} + H_W^u(M)^2 / (2\langle (H_W^r)^2 \rangle^{1/2})$. Well above T_C the random field H_W^r is independent on H_0, hence the resulting change in the effective field $H_{\text{eff}}(H_0) - H_{\text{eff}}(0) \propto [H_W^u(M)]^2$, assumedly proportional to $M(H_0)^2$. In this temperature range magnetization is straightly proportional to H_0 and hence $H_{\text{eff}}(H_0) - H_{\text{eff}}(0) \propto H_0^2$ in agreement with the experiment. In the vicinity of T_C situation becomes more complicated because applied field simultaneously suppresses critical fluctuations and supports uniform field thus producing counteracting contributions to the resulting effective field. Unexpectedly the experimental magnetoresistance exactly at $T=T_C$ is fairly quadratic in H_0 instead of the critical power-like dependence; such a power dependence $H_{\text{eff}} \propto H_0^{0.58}$ occurs only in the close vicinity (literally several kelvin) of T_m (see Fig. 5).

Hence both the linear field dependence of resistivity below T_C and quadratic above T_C are consistent with the model, while the vicinity of T_C requires separate treatment.

Another important feature is that the experimental temperature of the magnetoresistance maximum T_m does not coincide with T_C (see above). When temperature T_m was plotted on Fig. 3 (marked by down arrow) its association becomes clear: T_m corresponds to the intersection of the dashed and dotted curves that depict H_W^u and $\langle (H_W^r)^2 \rangle^{1/2}$, respectively (the latter curve is a guide to the eye). It means that at T_m the uniform spontaneous Weiss field H_W^u begins to dominate over the random Weiss field $\langle (H_W^r)^2 \rangle^{1/2}$ caused by critical fluctuations. The temperature defined this way is definitely below T_C and corresponds nicely to the experimental value 0.97 T_C.

III. DISCUSSION

The obvious conclusion from our model is that the magnetoresistance does not depend on the external field direction. The study[7] devoted to this anisotropy reveals that the magnetoresistance is really almost independent on the field direction apart from the initial magnetization effects in low fields.

The verification of the model can be done by Hall measurements that directly provide the density of carriers as well as the carrier's mobility. The studies we know[8,9,22] were carried out only in the magnetic field up to 1.5 T and hence provide poor accuracy. Nevertheless these results agree qualitatively with our model: the obtained density of carriers decreases with temperature decrease. It would be interesting to perform Hall measurements on the high-quality samples in high magnetic fields to obtain accurate results.

The obtained results can be easily associated with the well-known "redshift" phenomenon characteristic for the relative magnetic semiconductors such as $CdCr_2Se_4$ and $HgCr_2S_4$. The strong decline of the optical-absorption edge that coincides with the onset of the magnetic ordering was observed in these materials.[2,3] Approaching T_C the edge shifts strongly toward lower energies and an application of magnetic field in the magnetically ordered state results in a further shift. The optical study of our model Fig. 2(b) will reveal the same redshift behavior. With the onset of the magnetic ordering the bottom of the spin-up band Fig. 2(b) downshifts, that hence results in the decline of the optical-absorption edge. Application of the external magnetic field causes the additional downshift of the bottom of the spin-up band and therefore results in the further redshift. As far as we know, there is lack of the data concerning optical properties of $FeCr_2S_4$ in this energy range, but the redshift of the absorption edge can be expected by analogy with the related magnetic semiconductors.

The role of the magnetic polarons in our model shall be discussed. The thermoelectric power measurements[10] reveal that at least well above T_C there is evidence of the presence of polarons that are likely to be magnetic. A strong anomaly in thermoelectric power occurs between some 1.15 T_C and T_C, and below T_C its temperature behavior is regular. The dependences obtained in Refs. 16 and 21 reveal similar features. We propose a qualitative sketch of this behavior. Indeed, well above T_C the thermoactivated carrier is surrounded by short-range magnetically polarized area due to strong exchange between conducting and magnetic electrons. It means the formation of the magnetic polaron.[23] When approaching T_C the magnetic correlation length increases and random magnetic clusters begin to occur. The total exchange energy within such a cluster will somewhere become larger than the carriers' activation energy. It may mean the crossover from the "thermoactivated carrier that polarizes neighboring spins" to the "random magnetic clusters that affect thermoactivated carrier" behavior. In the other words, when magnetic correlation length exceeds several lattice periods the magnetic polaron behavior converts to our model Fig. 1(b). This crossover occurs definitely above T_C. Formation of permanent magnetic structure with further decrease in temperature below T_C does not change the situation qualitatively. This sketch agrees with the thermoelectric power dependence on temperature obtained in Ref. 10: magnetic polarons above 1.15 T_C, crossover in the range 1.15 $T_C > T > T_C$ reflected by anomaly in the temperature dependence, and regular behavior down to the low temperatures. It suggests that while magnetic polarons do likely exist in $FeCr_2S_4$ above T_C they are not responsible for the CMR.

IV. CONCLUSIONS

In conclusion, we considered a classical semiconductor affected by both the external magnetic field and the Weiss exchange field that arises from the magnetic order. This is likely the simplest approach to the rearrangement of the band structure with the onset of magnetic ordering. The results obtained in this phenomenological model give a credible description of the resistive and magnetoresistive properties of $FeCr_2S_4$, including fine features. The introduced effective field H_{eff} depends on temperature and external magnetic field in a reasonable way. The role of critical fluctuations in the vicinity of Curie point appears to be important. We believe this point of view on the magnetic semiconductor $FeCr_2S_4$ and its relatives deserve to be taken into consideration.

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