Quantum temperature oscillations of the magnetization in the ferromagnetic semiconductor n-$HgCr_2Se_4$

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A new quantum effect, predicted theoretically by V. V. Val'kov and S. G. Ovchinnikov [Sov. Phys. Solid State **23**, 2032 (1981)], has been observed: temperature oscillations of the magnetization in a variable-valence system. The amplitude of the oscillations decreases with increasing temperature and decreasing field, just as in the de Haas–van Alphen effect. The effective mass is estimated as $m^* = 0.01 m_0$. © *1995 American Institute of Physics.*

Studies of quantum oscillations in a magnetic field have shown that increasing the temperature leads only to damping of the oscillations. It is well known that for a degenerate Fermi system the temperature corrections to the chemical potentials are small: $\delta\mu \sim (T_2/E_f)$. The situation is different in systems with variable valence, where a narrow peak is present in the density of localized states near the Fermi level, and a redistribution of the electrons between the conducting (c) and localized [$d(f)$] states can occur as the temperature increases. As a result, a stronger temperature dependence of the chemical potential appears: $\delta\mu \sim T$. If such a system is placed into a quantizing magnetic field H, then quantum oscillations can be observed by changing T in a fixed field H. This effect was predicted theoretically in Ref. 1. In the present paper we report the results of the experimental confirmation of this effect.

The degenerate ferromagnetic semiconductor n-$HgCr_2Se_4$ was chosen as the object of investigation. This choice was made for two reasons: First, doped chromium chalcogenide spinels exhibit variable-valence effects which are associated with the coexistence of Cr^{3+} and Cr^{2+} ions for the n-type material and Cr^{3+} and Cr^{4+} for the p-type material; second, in n-$HgCr_2Se_4$ single crystals the carrier mobility increases appreciably as the temperature T decreases. This makes it easier to observe quantum oscillations. We employed n-$HgCr_2Se_4$ single crystals, grown at the N. S. Kurnakov Institute of General and Inorganic Chemistry. The mobility in these crystals was $\eta \approx 1000$ cm^2/(V·s) at $T = 77$ K. The magnetization was measured with a vibrating-coil magnetometer with a superconducting solenoid. The magnetic field was applied along the $\langle 110 \rangle$ axis of the crystal.

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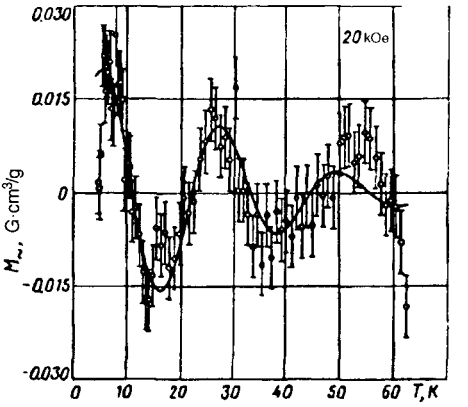

FIG. 1. Temperature dependence of the magnetization of $HgCr_2Se_4$ after subtracting from it the spin-wave contribution. External field: $H=20$ kOe.

Many electrical and magnetic properties of magnetic semiconductors can be successfully described on the basis of the s-d exchange model.[2] It is more convenient to study the variable-valence effects in a more general many-electron model, for which the spin-wave theory was constructed in Ref. 3. As shown in Ref. 3, the redistribution of electrons between itinerant and localized carriers introduces a linear dependence on the temperature for both the chemical potential and the magnetization:

$$M(T)=M_0-\alpha T-\beta T^{3/2}Z_{3/2}(2\mu_b/k_bT). \tag{1}$$

A contribution to the magnetization which is linear in T and which destroys Bloch's law has been observed experimentally in $CuCr_2S_4$, in doped $CdCr_2Se_4$ (Ref. 4), and in $HgCr_2Ce_4$ (Ref. 5).

For a ferromagnet with variable valence the magnetization in a quantizing magnetic field can be written in the form

$$M(B,T)=M_0-\alpha T-\beta T^{3/2}Z_{3/2}(2\mu_bB/k_bT)+M_\sim(B,T), \tag{2}$$

where $M_\sim(B,T)$ is an oscillatory function of T and $1/B$. The temperature dependences $M_\sim(T)$ at $H=20$ and 60 kOe are shown in Figs. 1 and 2, respectively. The quantity $M_\sim$ was determined from the experimentally measured magnetization by subtracting the spin-wave contributions written in Ref. 1. The vertical lines indicate the error in the measurement of the magnetization. We see that the amplitude of the oscillations is an order of magnitude larger than the experimental error. The solid line in Figs. 1 and 2 is determined by the formula

$$M_\sim(T)=\frac{a_1T\sin(2\pi T/a_3+a_4)}{\sinh(a_2T)}. \tag{3}$$

The decrease in the amplitude of the oscillations with increasing T occurs here just as for the de Haas–van Alphen field oscillations and is described by the formula $x/\sinh(x)$, where $x=2\pi^2k_bT/\hbar\omega_c$. A least-squares fit of expression (3) to the experimental data

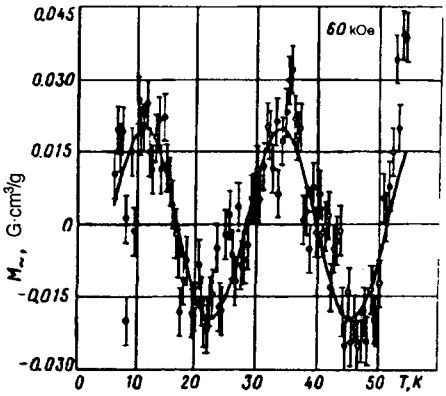

FIG. 2. Same as in Fig. 1, $H=60$ kOe.

gives for $H=20$ kOe the coefficients $a_3=22.47$ K and $a_2=7.465\times10^{-2}$ K^{-1}. This value of a_2 gives the effective mass $m^*=0.01m_0$. The decrease in the amplitude of the oscillations in Fig. 2 for $H=60$ kOe can be calculated with this value of the effective mass. At $T=40$ K, the factor $x/\sinh(x)$ is equal to 0.855, so that in the temperature range $T<40-50$ K the amplitude of the oscillations is virtually independent of the temperature because of the strong field.

Investigation of the standard de Haas–van Alphen oscillations in the experimental samples gave a $1/B$ period of 1.577×10^{-6} Oe^{-1}, which corresponds to light carriers with $m^*\simeq0.01m_0$. The area of the extremal cross section of the Fermi surface is $S=6.08\times10^{13}$ cm^{-2}, which gives for the carrier concentration $n\sim2.87\times10^{18}$ cm^{-3}, in agreement with the Hall-effect data. Since the deviations from a simple spin-wave dependence (1) become substantial as the temperature continues to increase, large deviations from the oscillatory dependence (3) appear in the temperature dependences $M_\perp(T)$.

For a crude, purely qualitative explanation of the reasons for the contributions, linear in T, to the chemical potential, we shall consider the following model (Fig. 3). At $T=0$, the localized level E_L is empty. The total density of states is

$$g(E)=g_C(E)+g_L(E), \quad g_L(E)=N_L\delta(E-E_L),$$

where N_L is the number of localized states, and $g_C(E)$ is a continuous function of E. We find the chemical potential from the condition

$$N_e=\int_0^\infty g(E)f_F(E)dE. \tag{4}$$

At $T=0$ we have

$$N_e=\int_0^{E_f} g_c(E)dE,$$

and at $T\neq0$ we find the following expression from Eq. (4) if the condition $k_bT\ll E_F$ is satisfied:

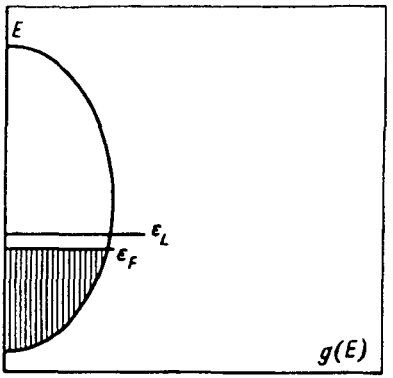

FIG. 3.

$$N_e = N_e + (\mu - E_F) g_c(E_F) + \frac{\pi^2}{6} T^2 g_c(E_F) + \frac{N_L}{\exp[(E_L - \mu)/k_b T] + 1}. \quad (5)$$

We thus obtain the following expression for $E_L - E_F \ll k_b T \ll E_F$:

$$\mu = E_L - 2k_b T. \quad (6)$$

The formulas presented above should be treated only as an illustration of the appearance of the strong temperature corrections to the chemical potential in systems with variable valence. For computational results in realistic models, taking into account the many-electron effects, we direct the reader to Refs. 1 and 3. Nonetheless, the nonmonotonic behavior introduced into the total density of states by the presence of the contributions of localized states near the Fermi level is characteristic of systems with variable valence.

It should be noted that the temperature oscillations in a quantizing magnetic field were studied previously in the semimagnetic semiconductors[6] $Hg_{1-x}Mn_xTe$, although in that case the large temperature corrections to the chemical potential arose for a different reason. In Ref. 6, two peaks, rather than oscillations, were observed experimentally in the temperature dependence of the magnetoresistance. As analyzed in the review in Ref. 7, these peaks are not associated with temperature oscillations, but rather they are due to the temperature changes in the contributions of the itinerant and impurity holes to the conductivity.

In summary, we note that the quantum temperature oscillations in systems with a variable valence, which were predicted in Ref. 1, were observed in the degenerate ferromagnetic semiconductor n-type $HgCr_2Se_4$. A comparison with the de Haas–van Alphen field oscillations shows that the temperature oscillations are produced by light carriers with concentration $n_e \sim 10^{18}$ cm^{-3} and high mobility. The effective mass of the carriers is $m^* = 0.01 m_0$.

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