Deviation from the Bloch law in ferromagnetic materials with an intermediate valence

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A term linear in temperature has been detected in ferromagnetic materials $CuCr_2S_4$, $Cd_{1-x}M_xCr_2Se_4$ (M = In, Ag) in the variation of magnetization in the spin-wave region. Such a deviation from the Bloch law is accounted for by the intermediate valence of chromium ions.

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The temperature dependence of magnetization in ferromagnetic materials usually obeys the Bloch law, $\delta M(T) \propto T^{3/2}$, in the low-temperature region. This dependence, a consequence of the spin-wave theory, is valid at $T \ll T_C$, where T_C is the Curie temperature.

The situation is quite different in a ferromagnetic material with an intermediate valence (IV), whose spin-wave theory was formulated in Ref. 1. The material in question is one in which the band and atomic states coexist and in which the resonance level $\Omega = E(d^n) - E(d^{n-1})$ is close to the Fermi level ϵ_F. Here $E(d^n)$ is the ground-state energy of the n-electronic term with an atomic configuration d^n and spin $S(n)$. In this case there is a degeneracy of two rigid-body configurations d^n and cd^{n-1}, where c is a band electron. Because of this degeneracy, the ground state of the system is a mixture of the indicated two configurations with the probabilities $W(n)$ and $W(n-1)$, respectively. The magnetization of an IV ferromagnetic material can be represented in the form

$$M(T) = W(n-1)M_{S(n-1)}(T) + W(n)M_{S(n)}(T). \tag{1}$$

The "partial magnetizations" $M_S(T)$ obey the Bloch law, and the temperature-dependent coefficients $W(n)$ are determined by the parameters Ω and ϵ_F and by the matrix elements of the Coulomb and exchange interactions. Expanding all the values in a series in powers of T, we obtain the following expression for the magnetic moment per ion (in Bohr magnetons):

$$M(T) = M(0) - 3(S(n-1) - S(n))n_c(0)\ln\frac{p - n_c(0)}{1 - p + n_c(0)}\,\frac{T}{\epsilon_F + 3\tilde{\Omega}}$$

$$- \left[1 - 3(S(n-1) - S(n))n_c(0)\frac{I(0)(S(n-1) - S(n)) + I/2}{\epsilon_F + 3\tilde{\Omega}}\right] Z_{3/2}(H/T)$$

$$\times (a^2 T/4\pi a(0)^{3/2} + 0(T^2). \tag{2}$$

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Here $0<\hat{n}_c(0)<1$ is the density of band holes at $T=0$ (the case in which Ω is near the ceiling of an almost filled band is analyzed), p is the total hole density, $\tilde{\Omega}$ is the level Ω which was renormalized due to the interactions, $I(0)$ and J are the interatomic and intratomic exchange interactions, $\alpha(0)$ is the spin-wave rigidity at $T=0$, a is the lattice parameter, and $Z_p(x)=\Sigma_{n=1}^{\infty} n^{-p}e^{-nx}$. Thus the distinguishing feature of IV ferromagnetic materials is the linear term with respect to T in the temperature dependence of the magnetization. The physical cause of this is the redistribution of electrons between the band and the atomic states.

In this letter we are reporting the results of an experimental study of low-temperature magnetization of IV ferromagnets. We have selected chalcogenide chromium spinels as an object of investigation. The existence of an IV state ($Cr^{3+} \rightleftarrows Cr^{4+}$) in $CuCr_2X_4$ (X = S, Se) has been confirmed by using the NMR method.[2] We have also investigated the semiconductors $Cd_{1-x}M_xCr_2Se_4$, where M = In and Ag, in which the IV is attributable to the variation of electron density due to doping.[3,4]

The magnetization measurements were performed using a vibrational magnetometer with a superconducting solenoid in the temperature range of 4.2 K to 200 K and magnetic-field range of 0 to 70 kOe. The measurement accuracy of the magnetization variation was 0.07 G. The temperature was controlled with an accuracy of 0.2 degree.

Since a strong paraprocess was observed in the compounds with intermediate balance the measurement of $M(T)$ was carried out in 70-kOe field. The experimental results presented in Fig. 1 are well approximated by the dependence

$$(\sigma_0 - \sigma(T))/\sigma_0 T = a + \beta T^{1/2} Z_{3/2}(2\mu_B H/kT), \qquad (3)$$

where σ_0 is the specific magnetization at $T=0$. The field in the argument of the Z function includes the field of the crystalline anisotropy and the demagnetizing field;

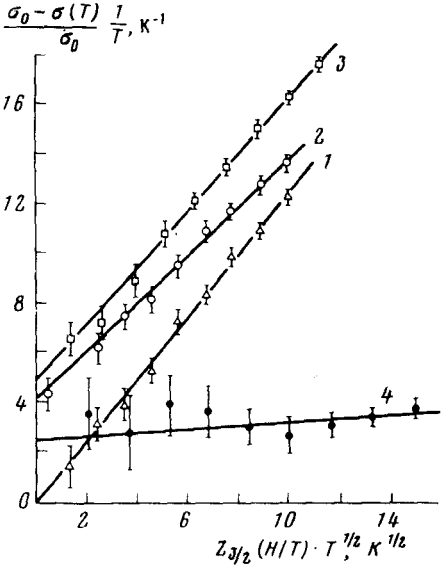

FIG. 1. Temperature dependence of magnetization. The numbers on the curves correspond to the number of the sample in Table I.

TABLE I.

		σ_0, G · cm³/g	$\alpha \times 10^4$, K^{-1}	$2.612 \times \beta \times 10^4$, K$^{-3/2}$
1	$CdCr_2Se_4$	63.67	0	3.28
2	$Cd_{0,995}Ag_{0.005}Cr_2Se_4$	59.62	4.19	2.53
3	$Cd_{0,97}In_{0.03}Cr_2Se_4$	60.64	4.83	3.01
4	$CuCr_2S_4$	64.27	2.54	0.19

these fields, however, are small compared with the 70-kOe external field. The parameters α, β, and σ_0 (see Table I) have been determined on a computer using the method of least squares and ten experimental points in the range of 4.2 K to 50 K. The slope of the lines in Fig. 1 determines β and the intercept on the Y axis determines α. In the stoichiometric compound $CdCr_2Se_4$ $\alpha = 0$ (with an accuracy to experimental errors). This is attributable to the absence of IV. The contribution from the linear term at 4.2 K is approximately 80% of the spin-wave contribution in $Cd_{1-x}M_xCr_2Se_4$, and it is 7 times greater in $CuCr_2S_4$ than the contribution from the $T^{3/2}$ term.

It is worth noting that the data for the doped samples coincide with the theoretical formula (3), which was obtained by ignoring the impurity effects. This apparently indicates that the conclusions reached about the rigid band (the impurity electrons or holes, rather than the impurity level, fill the band) are legitimate. Their mobility, however, need not necessarily have a band nature because of Anderson's localization, for example.

We note that a deviation from the Bloch law in $CuCr_2S_4$, which was mentioned previously in Ref. 5, has been attributed to a possible presence of a gap in the spin-wave spectrum. However, a linear $\sigma(T)$ dependence has not been detected in Ref. 5.

An estimate of the contribution to $M(T)$, which is linear with respect to temperature, using Eq. (2) and the characteristic parameters for chromium spinels gives a value $\alpha = 10^{-3} - 10^{-4}$ K^{-1}, consistent with the values of α determined from the experiment.

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