sorptions and absorption A lie lower than the red-shifting absorption. Finally, we feel that our data on single-crystal films of $CdCr_2S_4$ taken in conjunction with these on bulk samples of the other magnetic chromium chalcogenide spinels is consistent with an exciton model for the magnetic red shift.

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THEORY FOR THE GIANT SUSCEPTIBILITIES OF DILUTE MAGNETIC ALLOYS

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The giant susceptibilities and their suppression by small magnetic fields observed for dilute La–rare-earth alloys are explained quantitatively by assuming clustering of localized spins.

Many experiments on dilute alloys containing transition-metal or rare-earth impurities[1-4] have demonstrated ordering of the localized spins. Although the spin ordering is known to arise essentially from the Ruderman-Kittel indirect exchange coupling, it has been shown by Hilsch and Korn[1] that the magnetic properties of dilute magnetic alloys depend sensitively on the distribution of the localized spins. This is further demonstrated by the giant susceptibilities recently observed for LaGd, LaGdIn, and similar alloys.[3] It was shown that the giant susceptibilities depend sensitively on the concentration of paramagnetic impurities and that they can be suppressed by small magnetic fields.[3] From the experimental results obtained for a variety of dilute alloys in which clustering of magnetic impurities has been studied carefully,[1] Hilsch and Korn reached the conclusion that these anomalous magnetic properties[3] result from clustering of local spins.

In the following we present a simple theory for the complex spin order present in dilute magnetic alloys which permits a quantitative analysis of their magnetic properties. It is shown that impurity-spin order, consisting of short-range quasiferrimagnetic spin coupling and long-range quasiantiferromagnetic spin order, can explain quantitatively the giant susceptibilities and their drastic decrease observed as shown in Figs. 1 and 2 for relatively small magnetic fields[3] and also for decreasing paramagnetic impurity concentrations. Previous theories for the magnetic properties of very dilute magnetic alloys by Klein and Brout and by Marshall[5] yielded the observed peak in the susceptibility $\chi(T)$ around the magnetic ordering temperature T_M, but in sharp contrast to experiment that the maximal value of $\chi(T)$ is independent of the concentration of paramagnetic impurities and smaller than the Curie susceptibility $\chi_B(T)$ obtained by taking the free-ion value for the magnetic moment of the impurity. More recently, the interesting effective molecular field theory by Liu[6] yielded the observed functional dependence of the susceptibility maximum on the concentration of paramagnetic impurities, but yielded quantitative results for $\chi(T)$ at $T \sim T_M$ which turned out to be an order of magnitude smaller than the observed ones.[3] No theory so far has been concerned with the anomalous magnetic field dependence of the giant susceptibilities at $T \sim T_M$ as observed by Finnemore and co-workers.[3]

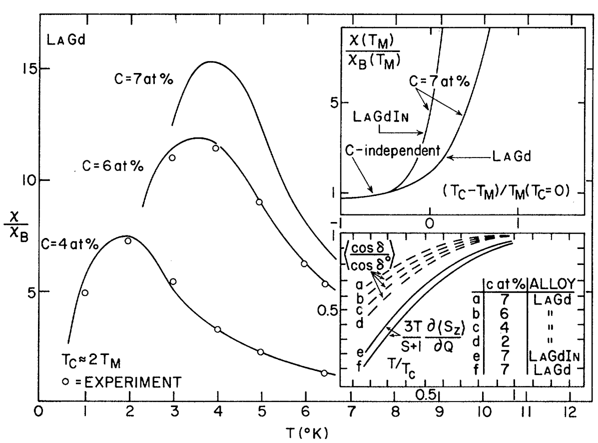

FIG. 1. The susceptibility of LaGd and LaGdIn calculated from the approximate expression

$$\frac{\chi}{\chi_B} = \langle\cos^2\theta_{ij}\rangle \frac{\partial\langle S_z\rangle}{\partial(SQ/T)} \times\left(1-\frac{T_C}{T}\left\langle\frac{\cos\theta_{ij}}{\cos\theta_{ij}^0}\right\rangle \frac{3S}{S+1}\frac{\partial\langle S_z\rangle}{\partial(SQ/T)}\right)^{-1}.$$

For $\langle\cos\theta/\cos\theta^0\rangle$ and $\partial\langle S_z\rangle/\partial Q$ we assume a dependence on T and C as shown in figure. $\langle\cos^2\theta\rangle$ is taken to be equal to 0.45 ($C=2$ at.%), 0.55 ($C=4$ at.%), 0.65 ($C=6$ at.%), and 0.75 ($C=7$ at.%).

The observed dependence of the susceptibility on temperature, impurity concentration, and magnetic field shown in Figs. 1 and 2 suggests clearly that neither long-range impurity ferromagnetism as considered by Abrikosov and Gor'kov[7] nor very short-range spin order is present, but rather spin order of complex structure.[1] While $\chi(T)$ exhibits a finite peak around the magnetic ordering temperature T_M similar to what is observed for antiferromagnetic order, the observed susceptibilities $\chi(T)$ for $T \sim T_M$ are typically much larger than what is expected for perfect long-range antiferromagnetic order. This observation and also the observed superconducting properties[3,4] suggest local ferrimagnetic order. Furthermore, the observed drastic reduction of $\chi(T)$ for $T \sim T_M$ by small magnetic fields ($H \ll \mu_B^{-1}k_B T_M$) indicates inhomogeneities in the paramagnetic impurity distribution and suggests quasiantiferromagnetic long-range spin order.[1] In view of the spatial oscillations of the Ruderman-Kittel interaction, one expects a quasiantiferromagnetic long-range spin order such that the paramagnetic Curie temperature T_C is zero if the localized spins are statistically distributed. However, one expects that T_C is positive if inhomogeneities in the spin distribution occur which lead to short-range quasiferrimagnetic spin order.

The experimental results shown in Figs. 1 and 2 can be explained qualitatively as follows. When the temperature decreases towards T_C, then as long as long-range spin order is absent, the spin system behaves as if it would undergo a ferromagnetic phase transition at the paramagnetic

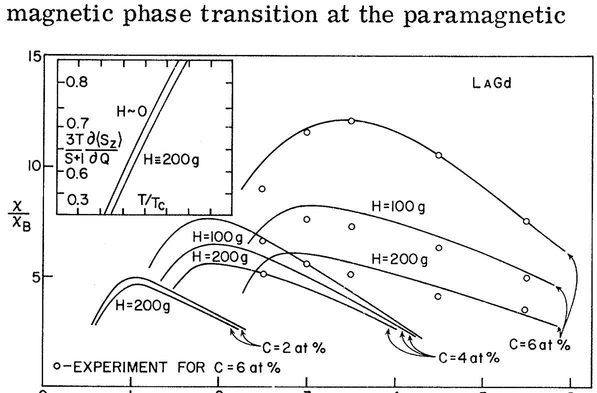

FIG. 2. Magnetic field dependence of $\chi(T)$ as resulting from the dependence of $\partial\langle S_z\rangle/\partial Q$ on H, which is assumed to be as shown in the figure. The curve $[3T/(S+1)]\,\partial\langle S_z\rangle/\partial Q$ for $H=100$ G is assumed to lie halfway between those for $H=0$ and $H=200$ G.

Curie temperature T_C. If $T_C > 0$ then, because of the inhomogeneities in the paramagnetic impurity distribution, short-range quasiferrimagnetic spin order appears already above T_C and causes a deviation of $\chi(T)$ from the Curie-Weiss law. Provided now that the onset of local molecular fields occurs sufficiently close to T_C (and $T_C > T_M$), then, of course, one expects χ and χ/χ_B to be very large at $T \sim T_C$. χ will cease to increase when quasiantiferromagnetic long-range order occurs at $T \sim T_M$. At temperatures below T_M, χ is expected to decrease because of the increasing local molecular fields acting on the localized spins and because of the continuing further increase in the long-range quasiantiferromagnetic spin order. If $T_C < T_M$, then $\chi \lesssim \chi_B$ will deviate from the Curie law at $T \sim T_M$, where long-range quasiantiferromagnetic order appears. Obviously, one expects that the degree of perfect long-range antiferromagnetic order increases for $T_C \to 0$ and that $\chi \sim \chi_B$ if $T_C \to 0$.[1] Clearly, $\chi(T_C)$ and consequently $\chi(T_M)$ are expected to increase if the quasiferromagnetic short-range order increases, since then simply more spins tend to order ferromagnetically at T_C. Hence, for alloys for which T_C increases with increasing concentration c of paramagnetic impurities, one expects that $\chi(T_C)$ and $\chi(T_M)$ increase with c. Finally, the drastic decrease of χ at $T \sim T_M$ arising from small magnetic fields ($H \ll \mu_B^{-1} k_B T_M$) results, since already small magnetic fields can easily align those spins which as a result of inhomogeneities in the spin distribution feel weak molecular fields. This leads to an increase of the molecular fields acting on the spins within the spin clusters which are primarily responsible for the deviation of χ from the Curie-Weiss law. As a result, one expects $\chi(T_M)$ and also T_M to decrease when H increases, even if $\mu_B H \ll k_B T_M$.

For a quantitative study of the susceptibility, we use for the total magnetization per unit volume of the system of localized spins and conduction electrons the expression

$$\vec{M}(\vec{H}, T, c) = \chi_0 \vec{H} + g\mu_B \sum_i \left\langle \vec{S}_Z{}^i\left(\frac{SQ_i}{T}\right)\right\rangle, \quad g = g_0\left(1 + \frac{g_{el}}{g_0}\frac{\chi_0}{4\mu_B{}^2}\langle J\rangle\right). \tag{1}$$

Here χ_0 is the Pauli susceptibility of the conduction electrons; g_0 and g_{el} are the Landé factors for the localized spins and conduction electrons, respectively; μ_B is the Bohr magneton, and $\langle J\rangle$ denotes the average s-f or s-d exchange integral. $\langle \vec{S}_Z{}^i\rangle$ is the expectation value of the ith localized spin in the direction of its molecular field $\vec{Q}_i$ which is given by

$$\vec{Q}_i = g\mu_B \vec{H} + \sum_{j\neq i} F_{ij}(\vec{r}_{ij})\langle \vec{S}_Z{}^j\rangle, \tag{2}$$

where F_{ij} describes the spatial dependence of the Ruderman-Kittel interaction involving the localized spins i and j separated by the distance r_{ij}. Note that neglecting crystal anisotropy fields, F_{ij} is given by

$$F_{ij}(r_{ij}) = [9\pi Z^2 J^2/(2p_F r_{ij})^4 \epsilon_F][2p_F r_{ij}\cos(2p_F r_{ij}) - \sin(2p_F r_{ij})],$$

where p_F denotes the Fermi wave number of the conduction electrons having the Fermi energy ϵ_F and Z is the number of conduction electrons per atom. The susceptibility in the direction of the magnetic field is given by

$$\chi(H, T, c) = \chi_0 + g\mu_B \textstyle\sum_i (\partial/\partial H)(\langle S_Z{}^i\rangle \cos\theta_{i,H}), \tag{3}$$

where

$$\theta_{i,H} = \sphericalangle(\vec{H}, \vec{Q}_i).$$

Assuming $\langle S_Z{}^i\rangle = \langle S_Z{}^i(SQ_i/T)\rangle$, then one finds for χ the expression

$$\chi(H, T, c) = \chi_0 + g\mu_B \sum_i \left(\langle S_Z{}^i\rangle \frac{\partial \cos\theta_{i,H}}{\partial H} + \cos\theta_{i,H}\frac{\partial\langle S_Z{}^i\rangle}{\partial Q_i}\frac{\partial Q_i}{\partial H}\right), \tag{4}$$

where

$$\frac{\partial Q_i}{\partial H} = g\mu_B\left(\cos\theta_{i,H} + H\frac{\partial\cos\theta_{i,H}}{\partial H}\right) + \sum_{j\neq i} F_{ij}(r_{ij})\left(\langle S_Z{}^j\rangle\frac{\partial\cos\theta_{ij}}{\partial H} + \frac{\partial Q_j}{\partial H}\frac{\partial\langle S_Z{}^j\rangle}{\partial Q_j}\cos\theta_{ij}\right), \tag{5}$$

and $\theta_{ij} = \sphericalangle(\vec{Q}_i, \vec{Q}_j)$. Assuming $\partial Q_j/\partial H \approx \partial Q_i/\partial H$, then $\chi(H, T, c)$ is approximately given by

$$\chi = \chi_0 + g\mu_B \sum_i \left\{ \langle S_Z{}^i \rangle \frac{\partial \cos\theta_{i,H}}{\partial H} + \frac{\partial \langle S_Z{}^i \rangle}{\partial (Q_i/T)} \left[\frac{g\mu_B(\cos\theta_{i,H} + H\partial \cos\theta_{i,H}/\partial H) + \sum_{j \neq i} F_{ij} \langle S_Z{}^j \rangle \partial \cos\theta_{ij}/\partial H}{T - S \sum_{j \neq i} F_{ij} \cos\theta_{ij} \partial \langle S_Z{}^j \rangle / \partial (SQ_j/T)} \right] \right\}. \tag{6}$$

Introducing the paramagnetic Curie temperature T_C which is given by

$$T_C = \frac{S(S+1)}{3} \sum_{j \neq i_0} F_{i_0 j}(\vec{r}_{i_0 j}) \cos\theta_{i_0 j}{}^0, \tag{7}$$

then Eq. (6) can be rewritten as

$$\chi = \chi_0 + g\mu_B \sum_i \left\{ \langle S_Z{}^i \rangle \frac{\partial \cos\theta_{i,H}}{\partial H} + \cos\theta_{i,H} \frac{\partial \langle S_Z{}^i \rangle}{\partial (Q_i/T)} \left[\frac{g\mu_B(\cos\theta_{i,H} + H\partial \cos\theta_{i,H}/\partial H) + \sum_{j \neq i} F_{ij} \langle S_Z{}^j \rangle \partial \cos\theta_{i,H}/\partial H}{T - T_C + \Delta_i(H, T, c)} \right] \right\}. \tag{8}$$

where

$$\Delta_i(H, T, c) = \frac{S(S+1)}{3} \sum_{j \neq i} F_{ij} \cos\theta_{ij}{}^0 \left(1 - \frac{3}{S+1} \frac{\cos\theta_{ij}}{\cos\theta_{ij}{}^0} \frac{\partial \langle S_Z{}^j \rangle}{\partial (SQ_j/T)} \right). \tag{9}$$

Here, $\theta_{ij}{}^0$ denotes θ_{ij} for Q_i and Q_j much smaller than $k_B T$. One finds from Eq. (2) for $\partial \cos\theta_{i,H}/\partial H$ the approximate expression

$$Q_i \frac{\partial \cos\theta_{i,H}}{\partial H} = -g\mu_B + \cos\theta_{i,H} \frac{\partial Q_i}{\partial H} + \sum_{j \neq i} F_{ij} \left(\frac{\partial \langle S_Z{}^j \rangle}{\partial H} \cos\theta_{j,H} + \langle S_Z{}^j \rangle \frac{\partial \cos\theta_{j,H}}{\partial H} \right). \tag{10}$$

Note that Eq. (10) can be approximately solved by assuming that

$$\partial \cos\theta_{j,H}/\partial H \approx \partial \cos\theta_{i,H}/\partial H$$

and by expressing $\cos\theta_{ij}$, which appears in Q_i, in terms of $\cos\theta_{i,H}$ and $\cos\theta_{j,H}$.

Equations (6) and (8) explain the giant susceptibilities, their dependence on the concentration of paramagnetic impurities, and the sensitive dependence of $\chi(T_M)$ on small magnetic fields. This is demonstrated by the numerical results for χ shown in Figs. 1 and 2 which were obtained by using Eq. (6) or (8). Obviously, Eqs. (6) and (8) imply that $\chi(T)$ remains finite if some spins feel molecular fields already at $T > T_C$ as a result of spin clustering. Then, for $T > T_C$ and $T \to T_C$, $\chi(T)$ increases less rapidly than according to the Curie-Weiss law, since $\Delta_i(T)$ starts to increase. χ continues to increase below T_C until quasispiral long-range order appears. Then χ decreases rapidly since $\langle \cos\theta_{ij} \rangle$ decreases and $(\partial \langle S_Z{}^i \rangle / \partial Q_i) \to 0$, and since then the numerator in the dominant second term in the brackets in Eq. (6) or (8) approaches T. Note that $\langle \cos\theta_{ij} \rangle$ means the statistical average over distribution of local field directions. It is now apparent that one finds $\Delta_i \to 0$ and thus giant susceptibilities with $\chi \gg \chi_B$ if $T_C > 0$ with $T_C > T_M$, and if the inhomogeneous onset of local fields occurs at temperatures very close to T_C. If the paramagnetic impurities are uniformly distributed, then one expects a random orientation of the spins and, consequently, $\langle \cos\theta_{ij} \rangle \cong 0$. Then Eq. (7) yields $T_C \cong 0$, and it follows that Eqs. (6) and (8) predict in agreement with experiment[1] that for quasiantiferromagnetic long-range order with $\langle \cos\theta_{ij}(T_M) \rangle < 0$, the susceptibility $\chi(T)$ should be always smaller than χ_B. If, with increasing localized spin concentration, more spin clusters occur and the spin clusters become bigger and the range of the quasiferrimagnetic short-range spin order increases, then it follows approximately from Eq. (7) that

$$T_C \cong \frac{S(S+1)}{3} c \sum_{j \neq i_0} F_{i_0 j} \langle \cos\theta_{i_0 j}{}^0 \rangle.$$

Also, it follows approximately from Eq. (6) in agreement with experiment that

$$T_M \approx \left| \frac{\langle \cos\theta_{ij}(T_M) \rangle}{\langle \cos\theta_{ij}{}^0 \rangle} \right| T_C \lesssim T_C,$$

since one finds for helical-like long-range order that $\langle \cos\theta_{ij}(T_M) \rangle \lesssim \langle \cos\theta_{ij}{}^0 \rangle$. If now $T_C - T_M$ increases, then clearly $\langle\cos\theta_{ij}\rangle$, $\langle\cos\theta_{ij}^0\rangle$, and $\langle\cos\theta_{ij}(T_C)\rangle/\langle\cos\theta_{ij}^0\rangle$ increase with increasing c simply as a result of a larger separation of the onset of short-range ferrimagnetic order from the onset of quasiantiferromagnetic order. It follows then from Eq. (9) that Δ_i decreases for increasing c. Also, if T_C-T_M increases, then $\sum_i\langle S_Z^i\rangle$, $\sum_i\cos\theta_{i,H}$, $(\partial\cos\theta_{i,H}/\partial H)_{H\to 0}$, $(\partial\times\cos\theta_{ij}/\partial H)_{H\to 0}$, and thus χ are expected to increase when c increases. This conclusion becomes more obvious if we assume for simplicity for the moment that the spin clusters act approximately like giant spins. Finally, if the magnetic field increases, then for the spins which feel a stronger molecular field the quantity $\partial\langle S_Z^j\rangle/\partial(SQ_j/T)$ decreases as a result of the alignment by H of the free or nearly free spins; but as long as $\mu_BH \ll k_BT_M$, $\cos\theta_{ij}$ is not expected to change much for those spins i and j within each cluster which contribute most to Δ_i. It is apparent from Eq. (8) that even a relatively small increase of Δ_i due to H can cause a large decrease of χ if $T\sim T_C$ and if $\Delta_i(T\sim T_C, H\to 0)$ is small. Furthermore, χ decreases if H increases since $\partial\cos\theta_{i,H}/\partial H$, $\partial\cos\theta_{ij}/\partial H$, and the factor $\partial\langle S_Z^i\rangle/\partial(SQ_i/T)$ in front of the second term within the brackets of Eq. (8) are expected to decrease rapidly, if H increases, as a result of inhomogeneities in the magnetic impurity distribution and spin clusters.

Figures 1 and 2 show numerical results for the dependence of $\chi(T)$ on the concentration of Gd in LaGd and LaGdIn, and for the magnetic field dependence of $\chi(T)$ in LaGd,[3] which were obtained by using Eq. (8), and for the dependence of Δ_i, $\cos^2\theta_{i,H}$, $\partial\cos\theta_{i,H}/\partial H$, and $\partial\langle S_Z^i\rangle/\partial Q_i$ on c and H approximations simulating a behavior as expected on physical grounds, according to the above-given qualitative discussion of our theory. The anomalous dependence of χ on H implies, as shown in Fig. 3, that the peak in the specific heat $C(T)$ of LaGd (and similar alloys) decreases rapidly around T_M if $T_M < T_C$ and if H increases.

In summary, by using molecular field theory and assuming clustering of localized spins, we have explained quantitatively the giant susceptibilities and their anomalous magnetic field dependence.[3] This verifies quantitatively the conclusion reached by Hilsch and Korn[1] that magnetic impurity clustering affects significantly the magnetic behavior of dilute magnetic alloys.

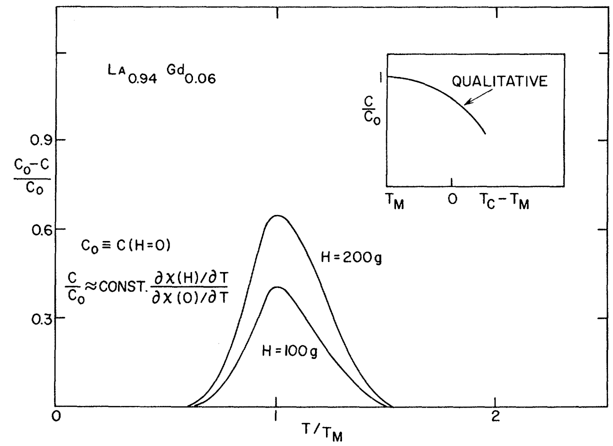

FIG. 3. Approximate calculation of the magnetic field dependence of the specific heat $C(T)$ of the localized spins.

In particular, our calculations show that for alloys with a homogeneous distribution of local spins, and hence $T_C\to 0$, one obtains (a) $\chi(T) \lesssim \chi_C(T)$, (b) $\chi(T_M)/\chi_B(T_M)$ to be independent of c, (c) $\chi_{\rm LaGd}(T)\approx\chi_{\rm LaGdIn}(T)$, and (d) $\chi(T\sim T_M, H) \approx \chi(T\sim T_M, H\to 0)$ if $\mu_BH \ll k_BT_M$. These results agree with the results obtained previously by Hilsch and Korn[1] for alloys in which local spin clustering is absent.

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