

FIG. 6. Typical plot of inverse susceptibility and spontaneous magnetization when  $\xi < 2.5$  (magneto-crystalline energies are neglected).

physical anomalies which are expected of the lower transition point  $T_1$ .

(1) The behavior of the susceptibility  $\chi$  is remarkable when the upper transition point is antiferromagnetic. By decreasing  $T$  we first observe the usual discontinuity in slope at  $T_N$ . Then  $\chi$  increases and becomes infinite at  $T_1$ . The qualitative behavior of  $1/\chi$  is shown on Fig. 6. Experimental results very similar in their general appearance to the graph of Fig. 6 have been obtained in antiferromagnetic CrSb doped with a small amount of MnSb.<sup>12</sup> The pure compound CrSb is known to be of the antiferromagnetic layer type.<sup>13</sup> It may be that electron transfer is allowed between chromium and manganese atoms, in which case our model could be applied.

(2) Below  $T_1$  both ferromagnetic and antiferromagnetic neutron lines occur simultaneously. Above  $T_1$  only one type is observed. A phenomenon of this type has been indeed quoted by Wollan and Koehler for some mixed manganite samples.<sup>2</sup>

(3) The specific heat shows a (small) discontinuity at  $T=T_1$ .

(4) The electrical conductivity is favored by inter-layer transfer. We accordingly expect a slight discontinuity in slope at  $T=T_1$ . The sign of this discontinuity will depend on the type of order above  $T_1$ . However, our oversimplified model is not applicable to this problem, and we are not able to make more detailed predictions as regards this point.

#### IV. LOCAL SPIN DISTORTIONS

##### 1. Bound States

The simple model of Secs. II and III did not take into account any possible bound states of the carriers. Such bound states may in fact occur, especially when the amount of impurities is very small. For instance, each  $\text{Ca}^{2+}$  substituted for  $\text{La}^{3+}$  in  $\text{LaMnO}_3$  acts as an

effective charge  $-e$  and is able to accept one carrier (a hole) in a localized orbit. We intend to show that the over-all effects of an assembly of such centers on the ionic spin system are similar to those of the free carriers considered in the preceding Section. We consider in particular the extreme case where the wave functions relative to different impurity centers do not overlap (very small  $x$ ). In analogy with the known properties of color centers in alkali halides, we expect the wave functions to be of rather small extension; in the above example, the hole will be shared by the eight manganese atoms surrounding the impurity, as shown on Fig. 7.

We first consider a single impurity center in an unperturbed antiferromagnetic matrix, and restrict ourselves to the following simple example: the pure material is an "alternating" ferromagnet of one simple cubic [see Fig. 2(c)] or bcc structure, with exchange integral  $J$  coupling each spin to its  $z$  neighbors. The Zener electron (or hole) is strongly bound and can only occupy *two* neighboring sites (1) and (2). The transfer integral is  $t_{12} = b \cos(\theta_{12}/2)$  as before, and the propagation equations which replace (2) are

$$\begin{aligned} (E-U)\alpha_1 &= b \cos(\theta_{12}/2)\alpha_2 \\ (E-U)\alpha_2 &= b \cos(\theta_{12}/2)\alpha_1 \end{aligned} \quad (43)$$

where  $U$  is the binding energy. (Note that the value of  $b$  may be modified by the attractive potential.) The ground state corresponds to

$$E_D = U - b \cos(\theta_{12}/2). \quad (44)$$

This is the analog, for a localized state, of Eq. (7) which applied to an extended state. In both cases, a small departure of  $\theta_{12}$  from  $\pi$  decreases the double exchange energy in first order and increases the exchange energies only in second order, so that a canted arrangement will be stable. Here, however, the final configuration corresponds to a local distortion of the spin system, and is accordingly more difficult to compute. We shall first derive the amount of canting by a simple "rigid field approximation" (RFA) where all ionic spins other than  $\mathbf{S}_1$  and  $\mathbf{S}_2$  are assumed to retain their original orienta-

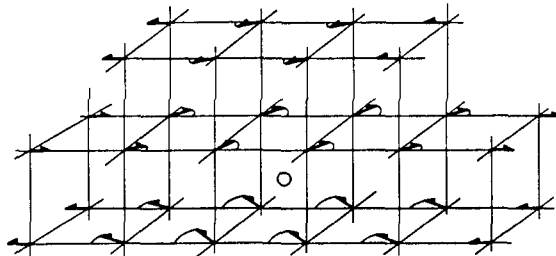


FIG. 7. Local spin distortion in  $\text{LaMnO}_3$ . The bound hole is localized on eight manganese atoms (black circles) around the impurity center  $\text{Ca}^{2+}$  (open circle). All ionic spins remain in one plane [here taken to be (001)]. Deflections are maximum close to the impurity center, but they decrease only slowly with distance.

<sup>12</sup> T. Hirone, S. Maeda, and I. Tsubokawa, J. Phys. Soc. (Japan) 11, 1083 (1956); E. W. Gorter and F. K. Lotgering, J. Phys. Chem. Solids 3, 238 (1957).

<sup>13</sup> A. I. Snow, Revs. Modern Phys. 25, 127 (1953).

tion.  $\mathbf{S}_1$  and  $\mathbf{S}_2$  have opposite deflections  $\epsilon$  and  $-\epsilon$  and  $\theta_{12} = \pi - 2\epsilon$ . The increase in exchange energy is

$$E_{ex} = 2|J|S^2[2(z-1)(1-\cos\epsilon) + 1 - \cos 2\epsilon]. \quad (45)$$

The minimum of the sum of (44) and (45) corresponds to

$$-b \cos\epsilon + 2|J|S^2[2(z-1) + 4 \cos\epsilon] \sin\epsilon = 0. \quad (46)$$

This always gives a solution  $\epsilon$ , with the limiting forms

$$\begin{aligned} \epsilon &= \frac{b}{4|J|S^2(z+1)}; & (b/z|J|S^2 \ll 1) \\ \epsilon &= \frac{\pi}{2} - \frac{4|J|S^2(z-1)}{b}; & (b/z|J|S^2 \gg 1). \end{aligned} \quad (47)$$

A bound Zener electron *always* gives rise to a local distortion of the spin system. This is to be contrasted with the effects which are obtained with pure exchange, when some adequate substitution simply changes the sign of one exchange integral, between (1) and (2). In the latter case there is also a strongly inhomogeneous constraint applied to the spin system. However, this results in a local spin distortion only if the new (ferromagnetic) exchange integral exceeds a well-defined threshold value ( $J_{new} > \frac{1}{2}(z-1)|J|$  in RFA, and  $J_{new} > \frac{1}{2}(z-2)|J|$  by an exact calculation).

We have proved that in the vicinity of each impurity center there is an unbalanced magnetic moment due to the special effects of double exchange. There is however one feature which is deliberately neglected in the RFA: a local deflection of spins (1) and (2) is always accompanied by smaller distortions on the neighboring sites, the amplitude of which decreases only slowly with distance. These "wings" may be studied with good accuracy by making use of Green's function techniques, an example of which is given in Appendix 3. If we now consider not only one impurity but a dilute assembly of these, the "wings" result in a coupling of the unbalanced moments carried by the different impurity centers. At low temperatures it is energetically favorable for these moments to line up, thus reducing the spin distortions in the matrix. As a result we expect to observe a nonzero spontaneous moment, increasing linearly with  $x$ , and the over-all magnetic behavior is very similar to what we found in Sec. II by discussing free carriers. We also expect the "interlocking" between different centers to preserve this ordered state up to some critical temperature  $T_1$ , above which the unbalanced moments exhibit a paramagnetic behavior. Here again, the conclusions of the "free carrier model" and of the "color center model" are not very different.

We now mention briefly some phenomena for which both models do *not* lead to the same predictions for very dilute impurity systems. These are: (1) optical absorptions; (2) electrical conductivities; (3) nuclear resonance at anion sites; (4) neutron diffraction. The

nuclear resonance lines are widely broadened, because the long-range part of the spin distortion due to each individual impurity center is responsible for inhomogeneous hyperfine fields. Consequently this type of experiment seems difficult to carry out. Neutron diffraction studies, on the other hand, could give some very interesting information on local spin distortions. This is discussed in Appendix 3, the main conclusions of which may be summarized as follows. (a) The distortions lead to diffuse peaks around the superlattice line. Superlattice lines for which the scattering vector is parallel to the spin direction in the pure material are extinguished and consequently most favorable. (b) There is always a parasitic spin wave scattering even at low temperatures (because of the strong zero point motion effects in antiferromagnets). (c) However, spin wave emission is an inelastic process while scattering by static distortions is strictly elastic. As a result, by a suitable geometrical arrangement one can make the spin wave scattering very diffuse so that it will be automatically subtracted with the background. The final requirement is that the neutron spectrometer should be able to analyze an angular distribution corresponding to a diffuse peak whose integrated intensity is roughly  $x$  times smaller than the intensity of a typical magnetic line of the unperturbed structure. A typical value of  $x$  (small enough to reduce overlap between separate distortions) is 0.1, so that this figure is not prohibitive.

## 2. Self-Trapped Carriers

Sections II and III applied the "free carrier" model to layer and chain antiferromagnets, where the carriers are always allowed to move within each chain or layer. The "alternating" antiferromagnetic structures (where all neighbors of a  $+$  spin are  $-$  spins) are somewhat different; in the unperturbed structure the carriers are not allowed to move; it is then more favorable for each individual carrier to build up a *local* distortion of the spin lattice in which it becomes "self-trapped." The resulting centers are able to move only slowly, and their physical properties are modified. In practice, we are not very much concerned in effects such as a change in effective mass, because the slow carriers will always fall into bound states. We are mainly interested in the shape of the local distortions and in interactions between them.

We first show that self-trapping will indeed occur. The argument will be written down for a simple cubic or body-centered cubic "alternating" antiferromagnet, each ionic spin having  $z$  equivalent neighbors, with exchange couplings  $2JS^2 \cos\theta_{ij}$ , transfer integrals  $b \cos(\theta_{ij}/2)$ , and carrier concentration  $x$  defined as before. Let us first compute the gain in energy for a uniform canting of both sublattices in the free carrier model, as in Sec. II. We obtain

$$E_{free} = -\frac{1}{2}Nzb^2x^2/|J|S^2. \quad (48)$$

It is convenient to introduce the paramagnetic Néel point  $T_N = [(2|J|S^2z)/3k_B]$  of the pure material, and the dimensionless ratio  $\eta = b/k_B T_N$ , so that Eq. (48) becomes:

$$E_{\text{free}}/k_B T_N = -(N/12)z^2\eta^2x^2. \quad (49)$$

We now consider another possible configuration, with noninteracting localized states, and compute the corresponding energy by making use of a variational principle. We assume that the carrier to be considered is trapped on some magnetic site (which we call 0 for instance) with an amplitude  $\alpha_0$ , but we also allow it to have a nonzero amplitude  $\alpha_1$  on the  $z$  neighboring spins. As far as the ionic spins are concerned, we assume that they all retain the same orientation which they had in the pure material, except for  $S_0$ , which is allowed to make an arbitrary angle  $\theta$  with the common direction of the  $z$  neighboring spins. The exchange energy, counted from the initial configuration ( $\theta = \pi$ ) is

$$E_{\text{ex}} = 2|J|S^2z(1 + \cos\theta). \quad (50)$$

The wave equation for the trapped carrier takes the restricted form

$$\begin{aligned} E\alpha_0 &= zb \cos(\theta/2)\alpha_1 \\ E\alpha_1 &= b \cos(\theta/2)\alpha_0 \end{aligned} \quad (51)$$

and the ground-state carrier energy is

$$E_D = -b\sqrt{z} \cos(\theta/2). \quad (52)$$

By taking the minimum of  $E_{\text{ex}} + E_D$  we obtain an overestimate of the energy per trapped carrier  $E_1$

$$E_1/k_B T_N = -(z/24)\eta^2 \quad \text{if } \eta < 12/\sqrt{z} \quad (53a)$$

$$= 6 - \sqrt{z}\eta \quad \eta > 12/\sqrt{z}. \quad (53b)$$

Actually this estimate is not accurate for large couplings ( $\eta \gg 1$ ) where the "radius" of the trapped carrier exceeds one interatomic distance. Equation (53) is sufficient for our purposes, however, and shows that  $E_1$  is negative. The total energy of the trapped carriers  $NxE_1$  is proportional to  $x$ , while the energy (49) corresponding to uniform canting goes like  $x^2$ . At low  $x$  the self-trapped configuration is always more stable. The following remarks should be made.

(1) Equation (49) represents the average effect of an attractive interaction between carriers via the ionic spins; each carrier tends to cant the antiferromagnetic lattice and decreases the energy of all other carriers at the bottom of the band. This explains the  $x^2$  dependence of (48).

(2) In layer antiferromagnets, the energy of the free carrier model contains a negative term, due to intralayer motion, and proportional to the number of carriers  $x$ ; self-trapped states are much less favored in such structures. (Of course, in practice, we shall find bound states as explained earlier.) Another viewpoint, leading to the same result, is the following: in a layer or chain antiferromagnet spin distortions contribute

only to a part of the band energy, and the coupling between carriers and ionic spins is moderately strong when compared with the unperturbed energy of the carriers. On the other hand, the coupling is very strong in an alternating antiferromagnet, since *all* the carrier energy is due to distortions of the spin arrangement.

The over-all effect of self-trapped carriers on magnetostatic properties is complex, and probably unobservable because of the existence of bound states. We shall restrict ourselves here to a few qualitative remarks, related to the behavior of the mixed manganites with *high*  $Mn^{4+}$  content. Pure  $CaMnO_3$  is an alternating antiferromagnet (simple cubic). The mixtures of neighboring compositions are not conducting and do not show any ferromagnetic behavior. This has been interpreted by Goodenough<sup>14</sup> by means of a qualitative model which is somewhat related to self-trapping. He assumes that the extra electron reverses the spin  $S_0$  of the central site ( $\theta$  going from  $\pi$  to 0) but leaves all other spins unaltered. This then results in a simple reduction of the sublattice magnetization, and does not bring in any noncompensated moment, since there is an equal number of trapped carriers on both sublattices. We are not quite satisfied with this explanation, for the following reason: from Eqs. (50) and (52) we may show that the actual configuration of  $S_0$  is canted ( $0 < \theta < \pi$ ) when  $\eta < 12z^{-1/2}$ . For larger  $\eta$ 's, our simple variational wave function yields a ground state which agrees with the Goodenough picture, but it is not a good approximation any more. In fact it is easy to see that for such values of  $\eta$  the whole configuration built up by  $S_0$  and its six nearest neighbors becomes canted with respect to the more distant spins. In all cases there is a noncompensated magnetic moment directed perpendicularly to the spin direction of the unperturbed structure. Furthermore, this moment is always accompanied by a long-range distortion of the spin lattice. Exactly like in the case of bound states, we expect these long-range distortions to couple ferromagnetically the moments due to different carriers, in contradiction with experiment. We do not believe that the discrepancy can be explained within our simple model.

## V. CONCLUSIONS

The special form of the double exchange coupling is such that all antiferromagnetic (and also all ferrimagnetic) spin arrangements are distorted as soon as some Zener carriers are present. This is due to the fact that electron transfer lowers the energy by a term of first order in the distortion, while the initial exchange energy is increased only in second order. If the Zener carriers are free to move in the structure, the distortion will usually correspond to a uniform canting of the sublattices. If they are bound or nearly bound, the distortion is nonhomogeneous, but the average effects are similar to the above. In practice the second alternative

<sup>14</sup> J. B. Goodenough, *Phys. Rev.* **100**, 564 (1955).