

## Impurity model for mixed-valent Mn<sup>3+</sup>/Mn<sup>4+</sup> ions

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Intermediate valent tri- and tetravalent manganese ions play an important role in LaMnO<sub>3</sub>-based systems. We consider a Mn impurity with five orbitals in cubic symmetry which hybridize with conduction electrons. The exchange interaction in the *d* shell maximizes the impurity spin. We study the valence of the Mn impurity as a function of the splitting of the *e<sub>g</sub>* to *t<sub>2g</sub>* orbitals in zero magnetic field and for the totally spin-polarized state. The lifting of the degeneracy of the *e<sub>g</sub>* levels due to a small quadrupolar field, related to the Mn-O bond length or a Jahn-Teller effect, is also investigated. Possible implications on the magnetoresistance are discussed. [S0163-1829(97)02346-1]

### I. INTRODUCTION

Recently, Jin *et al.*<sup>1</sup> discovered a 1000-fold change in the resistivity in La<sub>0.67</sub>Ca<sub>0.33</sub>MnO<sub>3</sub> films when a magnetic field is applied close to the Curie temperature. In view of potential applications the study of this effect, now known as colossal magnetoresistance, has quickly spread to other compounds of the LaMnO<sub>3</sub> family.<sup>2</sup> Most attempts to theoretically explain the phenomenon invoke the double-exchange mechanism.<sup>3</sup> The large magnetoresistance occurs close to the metal-insulator and paramagnetic-ferromagnetic transitions of the compounds and a recent study on O<sub>18</sub> substitution<sup>4</sup> strongly suggests that the coupling to the lattice, either in the form of polarons or the Jahn-Teller effect, plays an important role.<sup>5,6</sup> The coupling to the lattice distortions manifests itself in changes of the Mn-O bond lengths, i.e., in local quadrupolar distortions in an otherwise cubic environment.

The manganese ions exist in a mixed trivalent-tetravalent state in which each of the three *t<sub>2g</sub>* orbitals is singly occupied with their spin coupled to a total spin  $S=3/2$ . The *e<sub>g</sub>* orbitals, on the other hand, are empty for Mn<sup>4+</sup> and occupied by one 3*d* electron in Mn<sup>3+</sup>, which is ferromagnetically correlated with the *t<sub>2g</sub>* electrons. The intermediate valence character of the Mn ions arises from the *e<sub>g</sub>* electron, which may be localized at the Mn ion or become an itinerant electron either via hopping or hybridization.<sup>7</sup> Lifting the degeneracy of the two *e<sub>g</sub>* levels corresponds to a local change in the Mn-O bond lengths.

Colossal magnetoresistance is a collective phenomenon of a lattice of Mn and O atoms, as clearly manifested by the nearby metal-insulator and paramagnetic-ferromagnetic transitions. We study here the partial aspect of an isolated Mn impurity embedded in a crystal represented by a band of conduction electrons. As in the physics of heavy fermions, the solution of the single-impurity problem is believed to be an important step toward the understanding of the full lattice problem. The model under consideration is the multichannel generalization of the Anderson impurity model introduced and solved by means of Bethe's ansatz by Tsvetlik and Wiegmann,<sup>8</sup> now with the additional crystalline field terms.

The ground state of the impurity is then no longer the orbital singlet, but has a more complex structure since the *t<sub>2g</sub>* and *e<sub>g</sub>* orbitals are not equally populated.

The Hamiltonian  $H=H_0+H_{cf}$  is given by<sup>8,9</sup>

$$\begin{aligned}
 H_0 = & \sum_{km\sigma} v_F(k-k_F) c_{km\sigma}^\dagger c_{km\sigma} + \epsilon \sum_{m\sigma} d_{m\sigma}^\dagger d_{m\sigma} \\
 & + V \sum_{km\sigma} (c_{km\sigma}^\dagger d_{m\sigma} + d_{m\sigma}^\dagger c_{km\sigma}) \\
 & - \frac{1}{2} U \sum_{mm'\sigma\sigma'} d_{m\sigma}^\dagger d_{m'\sigma'}^\dagger d_{m'\sigma} d_{m\sigma}
 \end{aligned} \quad (1)$$

and

$$\begin{aligned}
 H_{cf} = & \frac{1}{5} \Delta_c \sum_{\sigma} \left( 3 \sum_{m \in e_g} n_{m\sigma} - 2 \sum_{m \in t_{2g}} n_{m\sigma} \right) \\
 & + \frac{1}{2} \Delta_q \sum_{\sigma} (n_{e_{g1\sigma}} - n_{e_{g2\sigma}}) .
 \end{aligned} \quad (2)$$

Here  $c_{km\sigma}^\dagger$  creates a conduction electron with momentum  $k$  in the orbital channel  $m$  and spin  $\sigma$ , and  $d_{m\sigma}^\dagger$  creates a localized electron with orbital symmetry  $m$  and spin  $\sigma$ . The kinetic energy is linearized about the Fermi level ( $v_F$  is the Fermi velocity, to be equated to one below),  $V$  is the hybridization matrix element,  $\epsilon$  is the one-particle energy of the *d* electrons, and  $U$  is the exchange coupling strength, which for  $U>0$  favors aligned spins. A strong  $U$  then maximizes the spin of the *d* shell of the Mn ion as required by the first Hund rule. In the absence of crystalline fields the maximum spin is then  $n/2$ , where  $n$  is the number of orbital channels. The two terms in Eq. (2) represent the cubic and quadrupolar crystalline fields, splitting the *d* orbitals into *t<sub>2g</sub>* and *e<sub>g</sub>*, and lifting the degeneracy of the two *e<sub>g</sub>* levels, respectively. (The splitting of the *t<sub>2g</sub>* levels by the quadrupolar field can be neglected because they are filled shells for the Mn ions.)

Tsvetlik and Wiegmann<sup>8</sup> diagonalized model (1) in the limit  $U \gg \epsilon - U(n-1)/2 \gg nV^2/2$  where the configuration

with  $n$  localized electrons hybridizes with states of the configuration with  $(n-1)$  localized electrons. In the integer valent limit the Bethe ansatz solution corresponds to the exactly spin-compensated multichannel Kondo problem with a singlet ground state. This situation is experimentally realized in dilute alloys of Fe and Cr in simple metallic hosts, such as Cu and Ag.<sup>9</sup> Excellent agreement between theory and experiment for the susceptibility, the specific heat, the magnetization, and the low-temperature resistivity was obtained for the dilute FeCu system in terms of only one fitting parameter (the Kondo temperature).<sup>10</sup> A similar comparison for the alloys FeAg and CrCu was also successful.<sup>11</sup>

In this paper we use Tsvetlik and Wiegmann's<sup>8</sup> exact solution to study effects of the crystalline field splittings on the orbital manifold. The manganese ions are in a cubic environment, so that the  $t_{2g}$  and  $e_g$  levels have different energy. Each of the  $t_{2g}$  orbitals is simply occupied, giving rise to a total spin  $S=3/2$ , while the occupation of the  $e_g$  levels depends on the cubic crystalline field strength  $\Delta_c$ . The quadrupolar splitting of the  $e_g$  orbitals, which arises from the coupling to the lattice, is believed to be small and is studied in linear response. The integral equations of the exact solution become very complicated when the orbital singlet condition is lifted. Therefore we limit ourselves to investigate two limiting cases, namely, the zero-magnetic-field situation and the fully-spin-polarized Mn impurity. The latter case is important because colossal magnetoresistance takes place close to the Curie temperature of the paramagnetic-ferromagnetic transition, and due to strong short-range correlations, the spin of the Mn impurity is expected to be at least partially oriented. Note that in the present model all localized electrons are ferromagnetically correlated maximizing the spin.

The rest of the paper is organized as follows. The scattering matrix and the Bethe ansatz integral equations for the ground state<sup>8</sup> are restated in Sec. II. In Sec. III the integral equations are solved as a function of cubic crystalline field in zero magnetic field and for the spin-polarized state with  $n=5$  and  $n=4$ . The  $n=4$  situation simulates the situation of an infinite Coulomb repulsion among the  $e_g$  orbitals (simple occupation). For the cases with  $n=5$  we also obtain the linear response to a quadrupolar field (Jahn-Teller or polaronic effect). The magnetoresistance is also briefly discussed. Concluding remarks follow in Sec. IV.

## II. BETHE ANSATZ EQUATIONS

Since the Hamiltonians (1) and (2) commute, the eigenstates of  $H_0$  are also the eigenstates of the total Hamiltonian and only the energy eigenvalues change. The scattering matrix for the two-electron problem factorizes into the scattering matrices within the spin and orbital sectors,  $\hat{S}(k) = \hat{S}_\sigma(k) \otimes \hat{S}_m(k)$ , where<sup>8</sup>

$$\begin{aligned}\hat{S}_\sigma(k) &= (k\hat{I}_\sigma - iV^2\hat{P}_\sigma)/(k - iV^2), \\ \hat{S}_m(k) &= (k\hat{I}_m + iV^2\hat{P}_m)/(k + iV^2).\end{aligned}\quad (3)$$

Here  $k$  is the momentum transfer and  $\hat{I}_\sigma$ ,  $\hat{I}_m$ ,  $\hat{P}_\sigma$ , and  $\hat{P}_m$  are the identity and permutation operators for the spin and orbital indices, respectively. Each of the scattering matrices (3) separately satisfies the triangular Yang-Baxter relation.

Hence, their product also does, which is the necessary condition for the integrability of the model.

The Bethe ansatz solution is now straightforwardly constructed in terms of  $(n+1)$  sets of rapidities, namely, one set for the charges  $\{k_j\}$ , one set of spin rapidities  $\{\lambda_\alpha\}$ , and  $(n-1)$  sets of orbital rapidities  $\{\mu_\alpha^{(l)}\}$ ,  $l=1, \dots, n-1$ . Each eigenstate of the system is specified by its rapidities, which satisfy the discrete Bethe ansatz equations. The rapidities have in general complex values and for the ground state in the thermodynamic limit they can be classified according to<sup>8</sup> (i) real charge rapidities  $k$  corresponding to unpaired propagating electrons, (ii) complex-conjugated charge rapidities related to the spin rapidities via  $k^\pm = \lambda \pm i\frac{1}{2}V^2$  (all  $\lambda$  are real) representing pairs of electrons with opposite spin, (iii) real orbital rapidities  $\mu^{(l)}$  for spin-unpaired electrons in specific orbital channels, and (iv) complex conjugated orbital rapidities  $\mu^{(l)\pm} = \Lambda^{(l)} \pm i\frac{1}{2}V^2$  (all  $\Lambda^{(l)}$  are real) corresponding to spin-paired electrons in the different orbital channels. This general structure simplifies with the orbital singlet condition, where all the orbital channels are equally populated. In the presence of crystalline fields, however, the orbital levels are occupied differently, breaking in this way the orbital singlet.<sup>12</sup>

The actual occupation of the states depends on the magnetic field, the chemical potential, and the crystalline fields, and is best studied in terms of the distribution functions for the rapidities and their holes, i.e.,  $\rho(k)$  and  $\rho_h(k)$  for the real charge rapidities,  $\sigma(\lambda)$  and  $\sigma_h(\lambda)$  for the spin rapidities,  $\zeta_l(\mu)$  and  $\zeta_{lh}(\mu)$  for the real orbital rapidities, and  $\kappa_l(\Lambda)$  and  $\kappa_{lh}(\Lambda)$  for spin paired orbital rapidities. The ground-state Bethe ansatz equations then take the form<sup>13</sup>

$$\begin{aligned}\rho_h + \rho + a_1 \star \sigma - s \star A_{11} \star \zeta_1 - s \star A_{12} \star \kappa_1 \\ = (1/2\pi) + (1/L)a_1(k-1/J),\end{aligned}\quad (4)$$

$$\begin{aligned}\sigma_h + \sigma + a_2 \star \sigma + a_1 \star \rho - s \star A_{21} \star \zeta_1 - s \star A_{22} \star \kappa_1 \\ = (1/\pi) + (1/L)a_2(\lambda-1/J),\end{aligned}\quad (5)$$

$$\begin{aligned}\zeta_{jh} + A_{11} \star C_{jk} \star \zeta_k + A_{12} \star C_{jk} \star \kappa_k \\ = \delta_{j1} s \star (A_{11} \star \rho + A_{12} \star \sigma),\end{aligned}\quad (6)$$

$$\begin{aligned}\kappa_{jh} + A_{22} \star C_{jk} \star \kappa_k + A_{21} \star C_{jk} \star \zeta_k \\ = \delta_{j1} s \star (A_{21} \star \rho + A_{22} \star \sigma),\end{aligned}\quad (7)$$

where  $\star$  denotes convolution,  $V$  has been equated to one, and  $J = V^2/\pi(\epsilon - \epsilon_F)$  is the Kondo exchange with  $\epsilon_F$  being the Fermi energy. The integration kernels are the Fourier transforms of

$$a_n(\omega) = \exp(-n|\omega|/2), \quad s(\omega) = 1/[2\cosh(\omega/2)],$$

$$\begin{aligned}A_{nm}(\omega) = \coth(|\omega|/2) \{ \exp(-|\omega||n-m|/2) \\ - \exp[-|\omega|(n+m)/2] \},\end{aligned}$$

$$C_{jk}(\omega) = \delta_{jk} - s(\omega)(\delta_{jk-1} + \delta_{jk+1}). \quad (8)$$

The right-hand sides of Eqs. (4) and (5) represent the driving terms of the integral equations. The distribution functions can be separated into a host (electron gas) contribution

(independent of  $L$ ) and an impurity part, which arises from the  $1/L$  driving terms. In Sec. III we only study the impurity contributions. The energy, the total number of electrons, the magnetization, and the population of the orbitals are given by

$$\begin{aligned} E/L &= \int dk k \rho(k) + 2 \int d\lambda \lambda \sigma(\lambda), \\ N/L &= \int dk \rho(k) + 2 \int d\lambda \sigma(\lambda), \\ S_z/L &= \frac{1}{2} \int dk \rho(k), \\ m^{(l)} &= \sum_{j=l+1}^n n_j = \int d\mu \zeta_l(\mu) + 2 \int d\Lambda \kappa_l(\Lambda), \end{aligned} \quad (9)$$

where  $n_j$  is the population of the  $j$ th orbital level arranged such that  $n_1 \geq n_2 \geq \dots \geq n_n$ .

### III. RESULTS

In this section we solve the Bethe ansatz integral equations for the impurity in three limiting cases to study the effects of the crystalline field splitting.

#### A. Zero magnetic field

In zero magnetic field the magnetization vanishes and all the electrons are spin paired. Hence, necessarily  $\rho(k) \equiv 0$  and  $\zeta_j(\mu) \equiv 0$  for all  $j$ . We consider  $n=5$  (five  $d$  orbitals) split into a lower-lying  $t_{2g}$  triplet and an excited  $e_g$  doublet. Hence  $n_1 = n_2 = n_3$  and  $n_4 = n_5$  (no quadrupolar splitting), so that the rapidities  $\Lambda^{(l)}$  for  $l=1, 2$ , and  $4$  fill the entire real without leaving holes, i.e.,  $\kappa_{1h}(\Lambda) = \kappa_{2h}(\Lambda) = \kappa_{4h}(\Lambda) \equiv 0$ . Fourier transforming Eq. (7) we express  $\kappa_1(\Lambda)$ ,  $\kappa_2(\Lambda)$ , and  $\kappa_4(\Lambda)$  as a function of the remaining densities and eliminate them from the system of equations. The remaining two equations involve  $\sigma(\lambda)$ ,  $\sigma_h(\lambda)$ ,  $\kappa_3(\Lambda)$ , and  $\kappa_{3h}(\Lambda)$ .

Both  $\sigma(\lambda)$  and  $\kappa_3(\Lambda)$  give rise to valence fluctuations of the impurity. The fluctuations induced by  $\sigma$  are global charge fluctuations, which in the Kondo limit are less interesting than the fluctuations between the  $t_{2g}$  and  $e_g$  levels. We consider here  $t_{2g}$  orbitals that are integer valent, i.e., no global charge fluctuations. The energy scales are also very different: On the one hand, the fluctuations in the charge sector are of the order of the hybridization width  $V^2$ , while on the other hand the fluctuations in the orbital sector are of the order of the Kondo temperature and the crystalline field splitting. The former can be suppressed by choosing  $\sigma_h(\lambda) \equiv 0$  or, equivalently, by placing the impurity  $t_{2g}$  levels well below the Fermi level. The problem is in this way reduced to a single equation, namely,

$$\kappa_{3h}(\Lambda) + \kappa_3(\Lambda) = a_5(\Lambda - 1/J). \quad (10)$$

Here  $\kappa_3$  is nonzero in the interval  $[-\infty, Q]$  and zero elsewhere, while  $\kappa_{3h}$  is nonzero in the interval  $[Q, \infty]$  and zero elsewhere. Hence the population of the  $e_g$  levels is given by

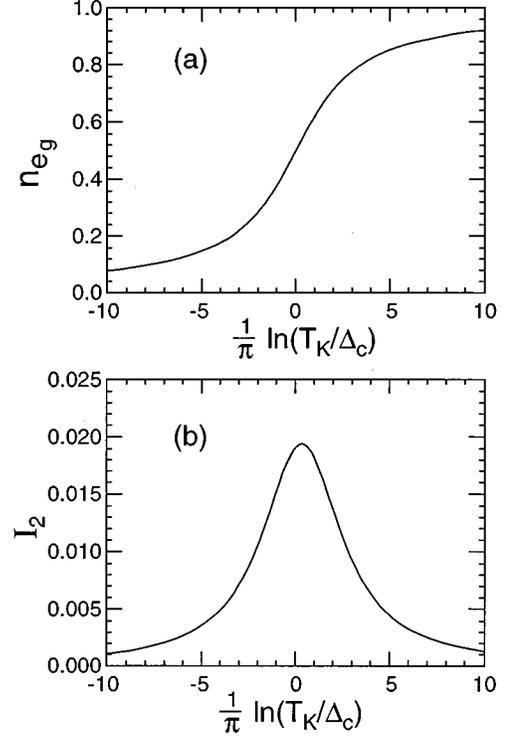


FIG. 1. (a) Occupation of one  $e_g$  orbital and (b) the response function  $I_2$  as a function of  $T_K/\Delta_c$  for  $n=5$  in the absence of a magnetic field. The splitting of the  $e_g$  levels due to a quadrupolar field is proportional to the function  $I_2$ .

$$n_{e_g1} + n_{e_g2} = 1 + \frac{2}{\pi} \arctan\left(\frac{Q-1/J}{2.5}\right), \quad (11)$$

and each of the  $t_{2g}$  levels contains exactly one electron. This follows from the last of the equations (9). Following the usual notation we parametrize  $Q-1/J = (1/\pi) \ln(T_K/\Delta_c)$ , where  $T_K$  is the Kondo temperature. With increasing cubic crystalline field  $\Delta_c$  the population of each of the  $e_g$  levels monotonically decreases from 1 for zero splitting to 0 for very large splitting, as displayed in Fig. 1(a). The characteristic energy is the Kondo temperature. For small and large splitting the dependence on  $\Delta_c$  is logarithmic, i.e.,  $5/|\ln(T_K/\Delta_c)|$ , which is characteristic of the asymptotic freedom of the respective spins,  $S=5/2$  and  $S=3/2$ , respectively.

Assuming that the quadrupolar splitting is much smaller than the cubic splitting, we can treat the splitting of the  $e_g$  levels in perturbation theory. The splitting is determined by the  $\kappa_{4h}(\Lambda)$  density. There are now two coupled integral equations yielding  $\kappa_3(\Lambda)$ ,  $\kappa_{3h}(\Lambda)$ ,  $\kappa_4(\Lambda)$ , and  $\kappa_{4h}(\Lambda)$ . The integral equation determining the splitting of the  $e_g$  levels is

$$\begin{aligned} \kappa_{4h}(\Lambda) + \kappa_4(\Lambda) + \int_{-\infty}^B d\Lambda' a_2(\Lambda - \Lambda') \kappa_4(\Lambda') \\ = \int_{-\infty}^Q d\Lambda' a_1(\Lambda - \Lambda') \kappa_3(\Lambda'), \end{aligned} \quad (12)$$

where  $\kappa_4$  is nonzero in the interval  $[-\infty, B]$  and zero elsewhere, while  $\kappa_{4h}$  is the complementary function, and we parametrize  $B-1/J = (1/\pi) \ln(T_K/\Delta_c)$ . The function  $\kappa_3(\Lambda)$  on the right-hand side of Eq. (12) plays the role of the driv-

ing term for the splitting of the  $e_g$  levels. The second equation is again Eq. (10), but with an additional driving term involving an integral over  $\kappa_{4h}$ . Since  $\kappa_{4h}$  is small, we can neglect this term in the integral equation for  $\kappa_3$ , and use the solution of Eq. (10) in Eq. (12). This approximation only changes  $\kappa_4$  in higher order than linear in  $\Delta_q$  [the corrections are of order  $(\Delta_q/\Delta_c)^3$ ]. Equation (12) can now be solved with the Wiener-Hopf method, and the leading contribution for  $B \rightarrow \infty$  is

$$\int_B^\infty d\Lambda \kappa_{4h}(\Lambda) = \exp[-\pi(B-Q)] I_2(Q-1/J),$$

$$I_2(Q-1/J) = \left(\frac{2}{\pi e}\right)^{1/2} \int_{-\infty}^0 dx e^{\pi x} a_5(x+Q-1/J),$$

$$n_{e_g 1} = n_{e_g} - \exp[-\pi(B-Q)] I_2(Q-1/J),$$

$$n_{e_g 2} = n_{e_g} + \exp[-\pi(B-Q)] I_2(Q-1/J),$$

$$n_{e_g} = \frac{1}{2} + \frac{1}{\pi} \arctan\left(\frac{Q-1/J}{2.5}\right). \quad (13)$$

Since  $B-Q = (1/\pi) \ln(\Delta_q/\Delta_c)$ , the splitting of the  $e_g$  levels is indeed proportional to  $\Delta_q$ . The function  $I_2(Q-1/J)$  is displayed in Fig. 1(b) and shows features characteristic of a charge susceptibility, namely, a maximum for  $\Delta_c \approx T_K$ . Note that the main assumption in this calculation is  $\Delta_q \ll \Delta_c$ .

### B. Spin-polarized ground state

Equations (4)–(7) again simplify in the spin-polarized limit, where all electrons are unpaired and hence the densities  $\sigma(\lambda)$  and  $\kappa_l(\Lambda)$  for  $l=1, \dots, 4$  are all identically zero. If we consider only the cubic crystalline field splitting between the  $t_{2g}$  and  $e_g$ , then the  $\mu^{(l)}$  for  $l=1, 2$ , and  $4$  fill the entire real axis without leaving holes so that  $\zeta_{lh}(\mu) \equiv 0$  for  $l=1, 2$ , and  $4$ . Fourier transforming Eqs. (4) and (6) the system of equations can be reduced to two coupled integral equations for  $\rho(k)$ ,  $\rho_h(k)$ ,  $\zeta_3(\mu)$ , and  $\zeta_{3h}(\mu)$ . Both densities  $\rho$  and  $\zeta_3$  give rise to charge fluctuations, the former between the impurity and the conduction band, while the latter induces transitions between the two crystalline field multiplets. As for the zero-magnetic-field case we suppress the global charge fluctuations by equating  $\rho_h(k)$  identically to zero. The remaining integral equation only involves  $\zeta_3$  and  $\zeta_{3h}$

$$\zeta_3(\mu) + \zeta_{3h}(\mu) + \int_Q^\infty d\mu' a_2(\mu - \mu') \zeta_{3h}(\mu')$$

$$= a_4(\mu - 1/J) + a_6(\mu - 1/J), \quad (14)$$

where the function  $\zeta_3(\mu)$  is nontrivial only in the interval  $[-\infty, Q]$  and the hole distribution is the complementary function. The integration limit parametrizes the cubic field strength  $Q-1/J = (1/\pi) \ln(T_K/\Delta_c)$ . This equation can be solved either numerically or with the Wiener-Hopf method. The population of the  $t_{2g}$  levels is one electron per orbital (since  $\rho_h \equiv 0$ ) and the occupation of each  $e_g$  orbital is one for  $\Delta_c \rightarrow 0$  and tends to zero for  $\Delta_c \gg T_K$ . Here  $\frac{1}{2}(n_{e_g 1} + n_{e_g 2})$  as a function of  $\ln(\Delta_c/T_K)$  is shown in Fig. 2(a).

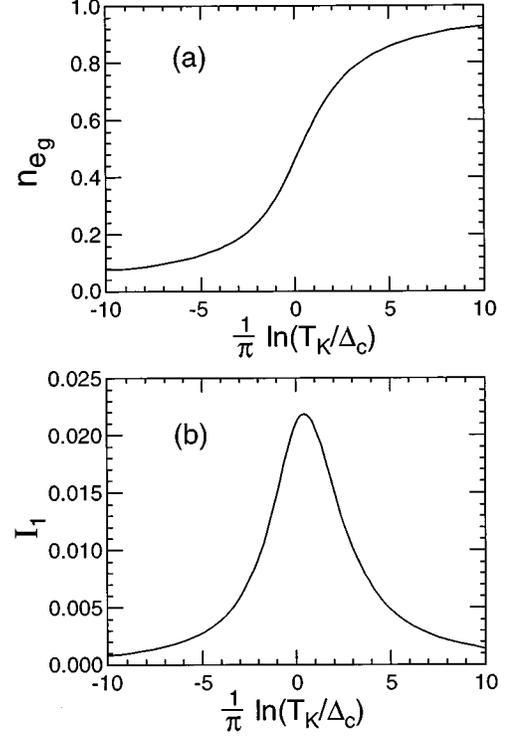


FIG. 2. (a) Occupation of one  $e_g$  orbital and (b) the response function  $I_1$  as a function of  $T_K/\Delta_c$  for  $n=5$  for the spin-polarized impurity. The splitting of the  $e_g$  levels due to a quadrupolar field is proportional to the function  $I_1$ .

In order to study the splitting of the  $e_g$  doublet as a consequence of the quadrupolar crystalline field we also have to consider  $\zeta_4(\mu)$ . If  $\Delta_q \ll \Delta_c$ , the feedback of the holes in the  $\mu^{(4)}$  band on the distribution of  $\mu^{(3)}$  rapidities is small and can be neglected for the purpose of studying the splitting in linear response. The integral equation satisfied by  $\zeta_4$  and  $\zeta_{4h}$  is then

$$\zeta_{4h}(\mu) + \zeta_4(\mu) = s \star \zeta_3(\mu), \quad (15)$$

where  $\zeta_4(\mu)$  is nontrivial in the interval  $[-\infty, B]$  and  $\zeta_{4h}(\mu)$  is the complementary function. The crystalline field is parametrized as  $B-1/J = (1/\pi) \ln(T_K/\Delta_q)$ , so that a small splitting corresponds to a large  $B$ . To leading order in  $\Delta_q/\Delta_c = \exp[-\pi(B-Q)]$  we obtain

$$\int_B^\infty d\mu \zeta_{4h}(\mu) = \exp[-\pi(B-Q)] I_1(Q-1/J),$$

$$I_1(Q-1/J) = \frac{1}{\pi} \int_{-\infty}^0 dx e^{\pi x} \zeta_3(x+Q),$$

$$n_{e_g 1} = n_{e_g} - \exp[-\pi(B-Q)] I_1(Q-1/J),$$

$$n_{e_g 2} = n_{e_g} + \exp[-\pi(B-Q)] I_1(Q-1/J), \quad (16)$$

where  $n_{e_g}$  is the occupation per orbital in the absence of quadrupolar splitting. The function  $I_1(Q-1/J)$  is displayed in Fig. 2(b), showing a maximum when  $\Delta_c \approx T_K$ . Note that in this calculation it is assumed that  $\Delta_q \ll \Delta_c$ .

Comparing Figs. 1 and 2 we see that the occupations of the  $e_g$  orbitals and the response to the quadrupolar splitting in zero field are very similar to those of the spin-polarized state. Assuming that these quantities have a similar behavior at intermediate magnetic fields, we may conclude that the single-Mn-impurity model does not suggest a change in the Mn-O bond length as a function of magnetic field; i.e., the Jahn-Teller or polaron distortion is not very magnetic field dependent.

### C. Magnetoresistance

The impurity model, of course, only gives limited insight into the transport properties. Within the framework of impurity scattering the zero-temperature resistivity is given by Friedel's sum rule; i.e., an electron in the partial wave of orbital symmetry  $m$  and spin component  $\sigma$  acquires a phase shift  $\delta_{m\sigma} = \pi n_{m\sigma}$ .<sup>14,15</sup> In zero field the ground state is a singlet, so that the occupation of the  $t_{2g}$  levels is 1/2 per spin component and for the  $e_g$  orbitals it is a fraction smaller than 1/2. This situation is dramatically different in a large magnetic field (compared to  $T_K$ ). For the spin-polarized state the phase shifts of the partial waves with  $t_{2g}$  symmetry are either 0 or  $\pi$ , giving rise to no resistivity. The same holds for the  $e_g$  phase shifts for spin components opposite to the magnetic field. Hence, only conduction electrons with the symmetry of the  $e_g$  orbitals and spin component parallel to the magnetic field scatter (assuming that the  $e_g$  levels are not empty) non-trivially. The contributions of the different spin components and orbitals add in parallel. Hence, the impurity model predicts a dramatic drop of the zero-temperature resistivity as a function of magnetic field. Note that the polarization of the impurity occurs on the energy scale  $T_K$ , while the polarization of the conduction band takes place on a scale of the order of the bandwidth. Hence, a spin-polarized impurity does not mean that all itinerant electrons have to have the same spin component; i.e., there are also down-spin conduction electrons.

### D. Coulomb repulsion among the $e_g$ orbitals

In the impurity model (1) both of the  $e_g$  orbitals can be occupied by one electron, since there is no Coulomb repulsion among the electrons, other than the exchange maximizing the total spin of the impurity. With increasing  $\Delta_c$  the number of localized  $d$  electrons increases from 3 (the  $t_{2g}$  orbitals) to 5 (all  $d$  orbitals are singly occupied). An infinite Coulomb repulsion among the  $e_g$  electrons would prevent the population of the  $e_g$  levels by more than one electron. This additional Coulomb repulsion, however, destroys the integrability of the model.

This repulsion can be introduced in an approximate way by considering  $n=4$  instead of  $n=5$ . There are then effectively only four orbitals, three  $t_{2g}$  levels, and one  $e_g$  state. This approach, however, neglects the twofold degeneracy of the  $e_g$  orbitals. In this subsection we briefly discuss the effect of the cubic crystalline field on the  $n=4$  manifold for the two limiting situations of zero magnetic field and the spin-polarized impurity. The procedure is similar to the one followed previously.

In the absence of a magnetic field all electrons are spin paired so that  $\rho \equiv 0$  and  $\zeta_l \equiv 0$  for all  $l$ . If we consider a cubic

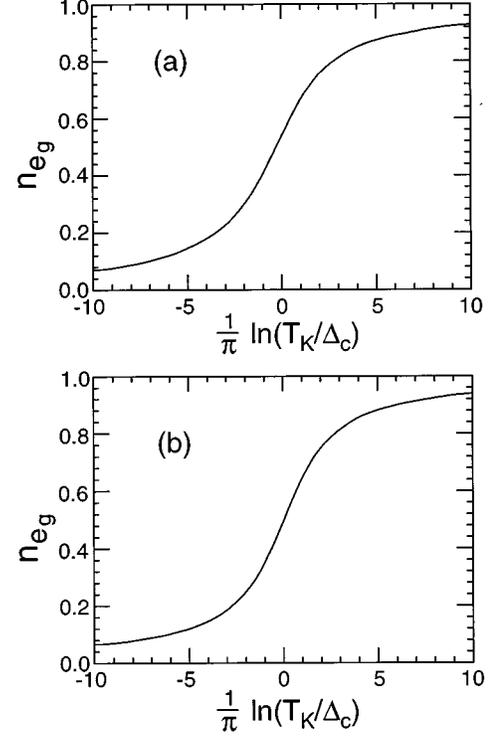


FIG. 3. Occupation of the  $e_g$  orbital as a function of  $T_K/\Delta_c$  for  $n=4$  for (a) zero magnetic field and (b) the spin-polarized impurity.

crystalline field, we have that  $\kappa_{1h} \equiv \kappa_{2h} \equiv 0$ , and if the charge fluctuations with the conduction band are suppressed, we have in addition  $\sigma_h \equiv 0$ . Fourier transforming Eqs. (4)–(6) can be reduced to one integral equation for  $\kappa_3$ ,

$$\begin{aligned} \kappa_{3h}(\Lambda) + \kappa_3(\Lambda) + \int_{-\infty}^Q d\Lambda' a_2(\Lambda - \Lambda') \kappa_3(\Lambda') \\ = a_5(\Lambda - 1/J), \end{aligned} \quad (17)$$

where the notation is the same as before. This integral equation can either be solved numerically or via the Wiener-Hopf method. The result for the population of the  $e_g$  level,  $n_{e_g} = 2 \int_{-\infty}^Q d\Lambda \kappa_3(\Lambda)$ , is shown in Fig. 3(a) as a function of  $\ln(T_K/\Delta_c)$  and is qualitatively similar to the per orbital occupation in the absence of the additional Coulomb repulsion.

For the spin-polarized situation we have only unpaired electrons so that  $\sigma \equiv 0$  and  $\kappa_l \equiv 0$  for all  $l$ , and if we consider a cubic crystalline field, we have in addition that  $\zeta_{1h} \equiv \zeta_{2h} \equiv 0$ . The charge fluctuations with the conduction band are suppressed if  $\rho_h \equiv 0$  and Eqs. (4)–(6) are straightforwardly reduced to a single integral equation for  $\zeta_3$ :

$$\zeta_{3h}(\mu) + \zeta_3(\mu) = a_4(\mu - 1/J). \quad (18)$$

Using the same notation,  $Q - 1/J = (1/\pi) \ln(T_K/\Delta_c)$ , we have

$$n_{e_g} = \int_{-\infty}^Q d\mu \zeta_3(\mu) = \frac{1}{2} + \frac{1}{\pi} \arctan\left(\frac{Q - 1/J}{2}\right), \quad (19)$$

which is displayed in Fig. 3(b). The dependence of  $n_{e_g}$  on  $\Delta_c$  for the spin-polarized impurity is again very similar to the zero-field case.

The arguments presented above for the magnetoresistance and their limitations remain valid if the occupation of the  $e_g$  levels is restricted to one.

#### IV. CONCLUDING REMARKS

We considered an isolated Mn impurity in an intermediate-valence state. The hybridization of the  $d$  electrons with the conduction band leads to a ground-state wave function that is a linear superposition of the  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  configurations. The spins of the localized  $d$  electrons are all aligned maximizing the total spin in accordance with the first Hund rule. This is accomplished by the large exchange interaction  $U$  in the Hamiltonian (1). A cubic crystalline field lifts the degeneracy of the  $d$  orbitals and splits them into a lower-lying  $t_{2g}$  triplet and the excited  $e_g$  doublet. The occupation of the  $t_{2g}$  states is one electron per orbital, while the population of the  $e_g$  states depends on the crystalline field splitting.

Except for the crystalline field splitting the impurity is the variant of Anderson's model introduced by Tsvetick and Wiegmann<sup>8</sup> which for the orbital singlet and in the limit of integer valence reduces to the spin-compensated multichannel Kondo problem.<sup>16,17</sup> The multichannel model is integrable and its Bethe ansatz solution<sup>8</sup> can be taken over for the present situation since  $H_0$  and  $H_{cf}$  commute. The crystalline fields break the orbital singlet condition and considerably complicate the structure of the ground state. Crystalline fields for the integer-valent multichannel Kondo model have been considered in Ref. 12 and give rise to new critical behavior in the overcompensated case.

Due to the additional complications arising from the crystalline field, we confined ourselves to investigate two limiting situations, namely, the zero-magnetic-field case and the totally-spin-polarized impurity. The characteristic energy scale is the Kondo temperature which for the multichannel impurity is independent of the number of channels and their occupation. As a function of the cubic crystalline field we studied the occupation of the  $e_g$  levels and the linear response to a splitting of the  $e_g$  levels due to a small quadrupolar crystalline field. Both quantities are essentially the same in the two limiting cases of zero magnetic field and total spin polarization. The response to the quadrupolar splitting is related to the coupling of the ion to the lattice (polaron or Jahn-Teller) and hence to the effective Mn-O bond length. Within the limitations of an impurity model, this result suggests that the Mn-O bond length does not play a

fundamental role in the magnetic properties of the  $\text{LaMnO}_3$  compounds and possibly neither in colossal magnetoresistance. In contrast, the double-exchange mechanism involves correlated hopping between the sites. This aspect is, of course, not contained in the isolated-impurity model. Hence, the two-impurity model (contains the simplest form of double exchange) will ultimately determine the importance of local quadrupolar distortions.

We also discussed the negative magnetoresistance arising from the impurity. On the one hand, in the absence of a magnetic field, all scattering phase shifts are different from 0 or  $\pi$ , so that there is significant scattering. On the other hand, for the spin-polarized impurity all down-spin phase shifts are zero and the  $t_{2g}$  phase shift for up-spin electrons is  $\pi$ . Hence, only up-spin electrons in the  $e_g$  channels are actually scattered and the total resistivity due to the impurity is zero. In other words, we expect a very large negative magnetoresistance.

Although perhaps too simplistic, it is useful at this point to speculate on the consequences of the impurity model on the magnetoresistance of the lattice. The orbital channels are only good quantum numbers locally but not conserved globally, in contrast to the spin. But since down-spin electrons are not scattered in the spin-polarized case independently of the orbital channel, they give rise to no resistivity. Hence, neglecting potential scattering due to doping centers, the magnetoresistance of the compound in large magnetic fields is expected to be very small.

One drawback of the multichannel Anderson model is that it allows the single occupation of both  $e_g$  orbitals. A large Coulomb repulsion should prevent this in a realistic  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ion. This situation cannot be dealt with satisfactorily within the present model. We considered  $n=4$  instead of the usual five orbitals. This simplistic approach neglects the orbital degeneracy of the  $e_g$  orbitals, but may give an indication of what occurs for the full problem. Also in this case the  $e_g$  occupation in zero magnetic field is similar to the spin-polarized state, confirming in this way our results and conjectures. If the orbital degeneracy of the  $e_g$  levels is kept (without double occupancy), we expect an orbital singlet to form via the quadrupolar Kondo effect.

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