Competition of Zener and polaron phases in doped CMR manganites

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Abstract

Inspired by the strong experimental evidence for the coexistence of localized and itinerant charge carriers close to the metal-insulator transition (MIT) in the ferromagnetic (FM) phase of colossal magnetoresistive (CMR) manganites, for a theoretical description of the CMR transition we propose a two-phase scenario with percolative characteristics between equal hole-density polaron and Zener band-electron phases.

Motivation

- Transition from a metallic FM low-T phase to an insulating paramagnetic high-T phase observed in hole-doped manganese perovskites $\rightleftharpoons$ unusual dramatic change in their electronic and magnetic properties, including a spectacularly large negative magnetoresistance.

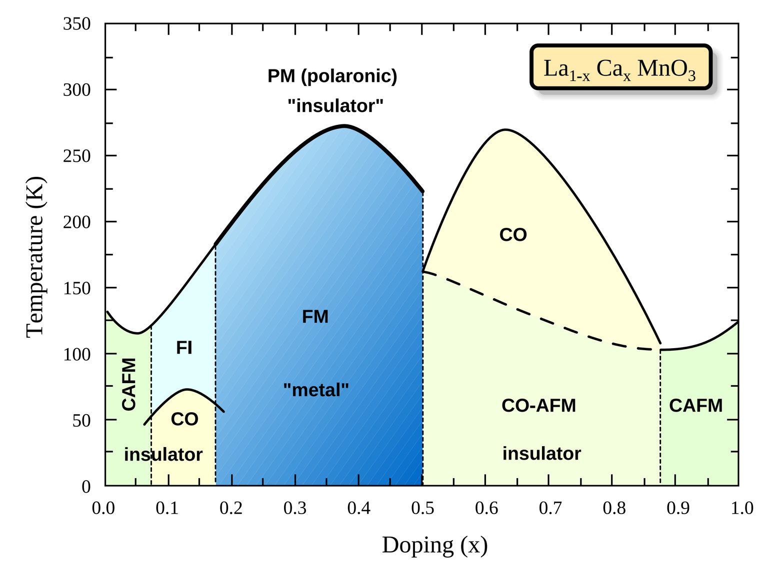


Fig. 1. Schematic phase diagram for $La_{1-x}Ca_xMnO_3$ [after P. Schiffer *et al.*, PRL **75**, 3336 (1995)].

- Link between magnetic correlations & transport properties: Zener's double-exchange (DE) mechanism!
  [C. Zener, Phys. Rev. **82**, 403 (1951); P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955)]
  (DE $\rightsquigarrow$ Maximization of the hopping of strongly Hund's rule coupled Mn e_g-electrons in a polarized background of $S = 3/2$ (t_{2g}) core spins [quantum version - K. Kubo and N. Ohata, J. Phys. Soc. Jpn. **33**, 21 (1972)])

Problem: Even complete spin disorder does not lead to a significant reduction of the electronic bandwidth, and therefore cannot account for the observed scattering rate!
[P. Majumdar and P. B. Littlewood, Nature **395**, 479 (1998)]

Suggestion: Orbital and lattice effects are crucial in explaining the CMR phenomenon!
[A. J. Millis, Nature **392**, 147 (1998)]

Experimental findings

- Small polaron transport above T_c!
  [D. C. Worledge *al.*, PRB **57**, 15267 (1998)]
- X-ray-absorption fine structure & pair distribution data indicate that charge localized and delocalized phases coexist close to the CMR transition!
  [C. H. Booth *et al.*, PRL **80**, 853 (1998); S. J. L. Billinge *et al.*, PRB **62**, 1203 (2000)]
- Zero-field muon spin relaxation and neutron spin echo measurements yield two time scales in the FM phase of $La_{1-x}Sr_xMnO_3$!
  [R. H. Heffner *et al.*, PRL **85**, 3285 (2000)]

$\rightsquigarrow$ Charge carriers partly retain their polaronic character well *below* T_c!

- Small octahedral distortions persist at low T, forming a nonuniform metallic state!
  [A. Lanzara *et al.*, PRL **81**, 878 (1998)]
- Limits of small ($x < 0.1$) and high ($x \sim 1$) hole densities: nanometer scale clusters with different electronic densities
  $\rightsquigarrow$ phase separation scenarios.
  [A. Moreo, S. Yunoki, and E. Dagotto, Science **283**, 2034 (1999)]
- CMR regime ($0.15 < x < 0.5$): even larger clusters are reported - but μm-sized domains, if charged, are energetically unstable (electro-neutrality condition) $\rightsquigarrow$ alternative concept: MIT and associated CMR behaviour might be viewed as a percolation phenomenon.
  [L. P. Gor'kov and V. Z. Kresin, JETP Lett. **67**, 985 (1998); A. Moreo *et al.*, PRL **84**, 5568 (2000)]

$\rightsquigarrow$ Intrinsic inhomogeneities & mixed-phase tendencies play a key role in manganites!

Idea: Two-phase model for the CMR transition

Percolative coexistence of two "intertwined" equal-density phases: metallic double-exchange dominated and polaronic insulating. The MIT transition is driven by a feedback effect which, at T_c, abruptly lowers the fraction of delocalized holes, leading to an collapse of the bandwidth of the Zener state.

A. Delocalized Zener state

Band structure: itinerant e_g charge carriers carry an orbital degree of freedom:

$$t^{x/y}_{\alpha\beta} = \frac{t}{4}\begin{bmatrix} 1 & \mp\sqrt{3} \\ \mp\sqrt{3} & 3 \end{bmatrix} \qquad t^{z}_{\alpha\beta} = t\begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}$$

(basis: $\{\theta = |3z^2 - r^2\rangle,\ \epsilon = |x^2 - y^2\rangle\}$)

$$\rightsquigarrow \varepsilon^{(0)}_{\mathbf{k}\zeta} = -t\Big[\cos k_x + \cos k_y + \cos k_z \pm\Big\{\cos^2 k_x + \cos^2 k_y + \cos^2 k_z - \cos k_x \cos k_y - \cos k_y \cos k_z - \cos k_z \cos k_x\Big\}^{1/2}\Big]$$

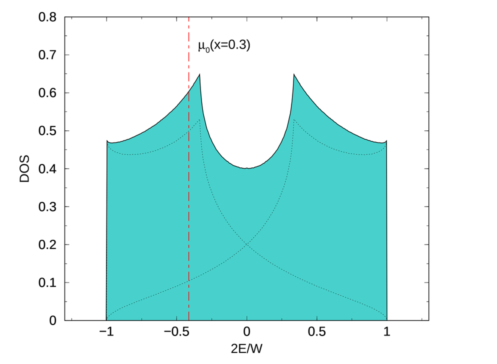


Fig. 2. Density of states corresponding to the band dispersion [$W = 6t$ denotes the bandwidth]. Dotted lines give the DOS of the two ζ-subbands. At optimal doping $x \simeq 0.3$, the chemical potential $\mu_0 \equiv \mu(T=0)$ is located near the lower maximum of the DOS.

Correlations: Kondo lattice Hamiltonian $\Rightarrow$ limit $U \gg J_H \gg t^{x/y/z}_{\alpha\beta}$ $\Rightarrow$ effective transport Hamiltonian for (spinless) e_g holes (cond-mat/0101234)

Assumption: Renormalization of the Zener state bandwidth is driven by two mechanisms:

$$\bar\varepsilon_{\mathbf{k}\zeta} = p^{(f)}\gamma_{\bar S}[\bar S\lambda]\,\varepsilon^{(0)}_{\mathbf{k}\zeta}$$

(i) Effective field $\lambda = \beta g\mu_B H^z_{\rm eff}$ tends to order the ion spins in z-direction $\rightsquigarrow$ temperature- and field-dependent band narrowing due to the Kubo-Ohata factor ($\bar S = S + 1/2 = 2$):

$$\gamma_{\bar S}[z] = \tfrac{1}{2} + \tfrac{\bar S}{2\bar S+1}\coth\!\big(\tfrac{2\bar S+1}{2\bar S}z\big)\left[\coth(z) - \tfrac{1}{2\bar S}\coth\!\big(\tfrac{z}{2\bar S}\big)\right]$$

$\rightsquigarrow$ effective hole transfer amplitude $\tilde t = \gamma_{\bar S}[\bar S\lambda]t$.

(ii) Percolative aspects of the MIT imply the existence of insulating enclaves embedded in the conducting FM (Zener) phase. We assume that the hole hopping amplitude has the value $\tilde t$ inside the conducting region and zero elsewhere. $\rightsquigarrow$ Feedback effect: The bandwidth is renormalized by the size of the FM region $N^{(f)} < N$, or

$$p^{(f)} = N^{(f)}/N,$$

which has to be determined self-consistently.

B. Localized polaronic state

"Polaron" – doped charge carrier (hole) quasi-localized with an associated lattice distortion.

CMR regime - both breathing-mode collapsed (Mn^{4+}) and Jahn-Teller distorted (Mn^{3+}) sites are created when holes become localized, i.e.:

The energy gain due to the Jahn-Teller splitting on localized electron sites without the influence of vacancies is weakened according to

$$(N^{(p)} - N_h^{(p)})E_1 = (x^{-1} - 1)E_1 N_h^{(p)},$$

and a breathing distortion may occur which lowers the energy of the unoccupied e_g level by the familiar polaron shift $E_p = -g^2\omega_0 \to E_2$.

E_1 (E_2) describe effective Jahn-Teller (polaronic) energies in the insulating regions.

The polaronic phase - realized only in a fraction $p^{(p)} = N^{(p)}/N$ of the sample - can be represented approximately by spinless holes having the following site-independent energy

$$\varepsilon_p = \left(x^{-1} - 1\right)E_1 + E_2$$

C. Self-consistency equations

Basic assumption: no large-scale separation of Mn^{3+} and Mn^{4+} ions in the CMR doping regime!

$$\rightsquigarrow\quad x = \frac{N_h}{N} = \frac{N_h^{(f)}}{N^{(f)}} = \frac{N_h^{(p)}}{N^{(p)}}.$$

Introducing the grand-canonical potentials

$$\Omega^{(f)} = -\frac{1}{2\beta}\sum_{\mathbf{k},\zeta=\pm}\ln\left[1 + \mathrm{e}^{\beta(\mu-\bar\varepsilon_{\mathbf{k}\zeta})}\right]$$

$$\Omega^{(p)} = -\frac{N}{\beta}\ln\left[1 + \mathrm{e}^{\beta(\mu-\varepsilon_p)}\right]$$

for holes in the ferromagnetic and polaronic phases, respectively, the free energy

$$\mathcal{F} = N_h\mu + \Omega^{(f)} + \Omega^{(p)} - T\mathcal{S}^{(s)}$$

results, where

$$\mathcal{S}^{(s)} = k_B N\Big\{p^{(f)}\Big[(1-x)\big(\ln\nu_{\bar S}[\bar S\lambda] - \lambda\bar S B_{\bar S}[\bar S\lambda]\big) + x\big(\ln\nu_S[S\lambda] - \lambda S B_S[S\lambda]\big)\Big] + p^{(p)}\Big[(1-x)\ln\nu_{\bar S}[0] + x\ln\nu_S[0]\Big]\Big\}$$

represents the mean-field ion-spin entropy, and

$$\nu_{\bar S}[z] = \sinh(z)\coth\!\big(\tfrac{z}{2\bar S}\big) + \cosh(z)\,,$$
$$B_{\bar S}[z] = \tfrac{2\bar S+1}{2\bar S}\coth\!\big(\tfrac{2\bar S+1}{2\bar S}z\big) - \tfrac{1}{2\bar S}\coth\!\big(\tfrac{z}{2\bar S}\big)\,.$$

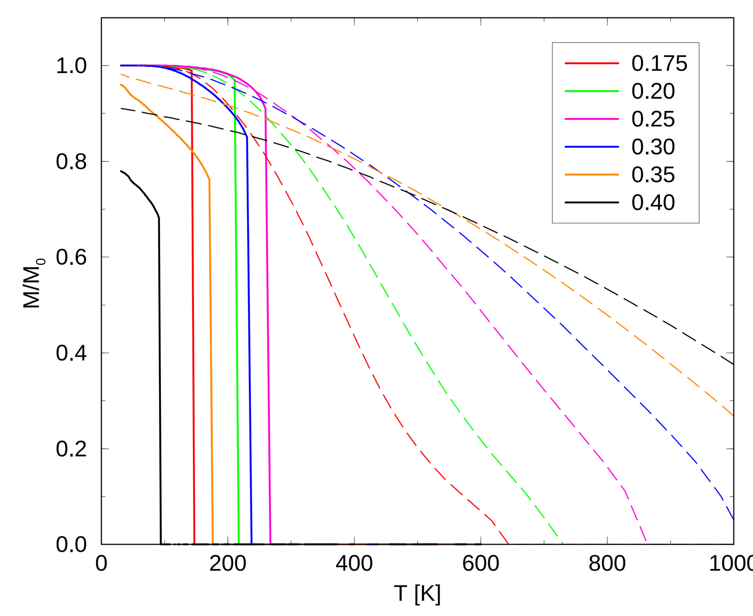
For any T and x, the FM ordering field (λ) and the size of the Zener phase ($N^{(f)}$) have to be determined by minimizing $\mathcal{F}$ on the hyperplane $\mu(\lambda, N^{(f)})$ given by

$$x = \frac{1}{2N}\sum_{\mathbf{k}\zeta}\frac{1}{\mathrm{e}^{\beta(\bar\varepsilon_{\mathbf{k}\zeta}-\mu)}+1} + \frac{1}{\mathrm{e}^{\beta(\varepsilon_p-\mu)}+1}\,.$$

Finally the magnetization can be calculated from

$$M = (1-x)\bar S p^{(f)} B_{\bar S}[\bar S\lambda] + xSp^{(f)}B_S[\bar S]\,. \qquad (1)$$

Numerical results



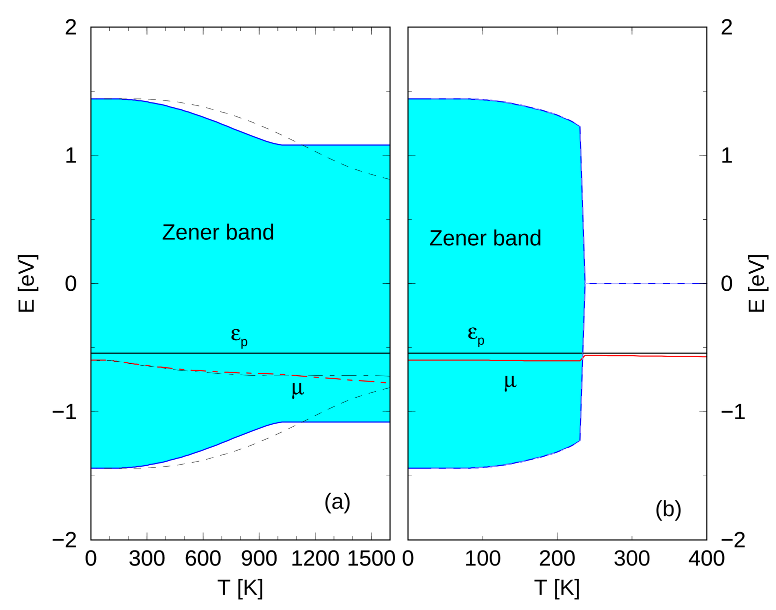


Fig. 3. *Upper panel:* magnetization M, normalized by $M_0 = \bar S - x/2$, as a function of T at various doping levels $x = 0.175, \ldots, 0.4$. Results are shown for the models with (bold lines) and without (thin lines) feedback.
($E_1 = -0.125\ eV$, $E_2 = -0.25\ eV$, $W = 3.6\ eV$)
Lower panel: T-dependences of the Zener band and of the positions of the polaronic level (ε_p) and chemical potential (μ) without (a) and with (b) feedback at $x = 0.3$. Dashed lines: band edges obtained by the use of $\tilde t_\downarrow = \left[\bar S(1 + B_{\bar S}[\bar S\lambda])\right]^2/(2\bar S)(2\bar S+1)t$ instead of $\tilde t$.

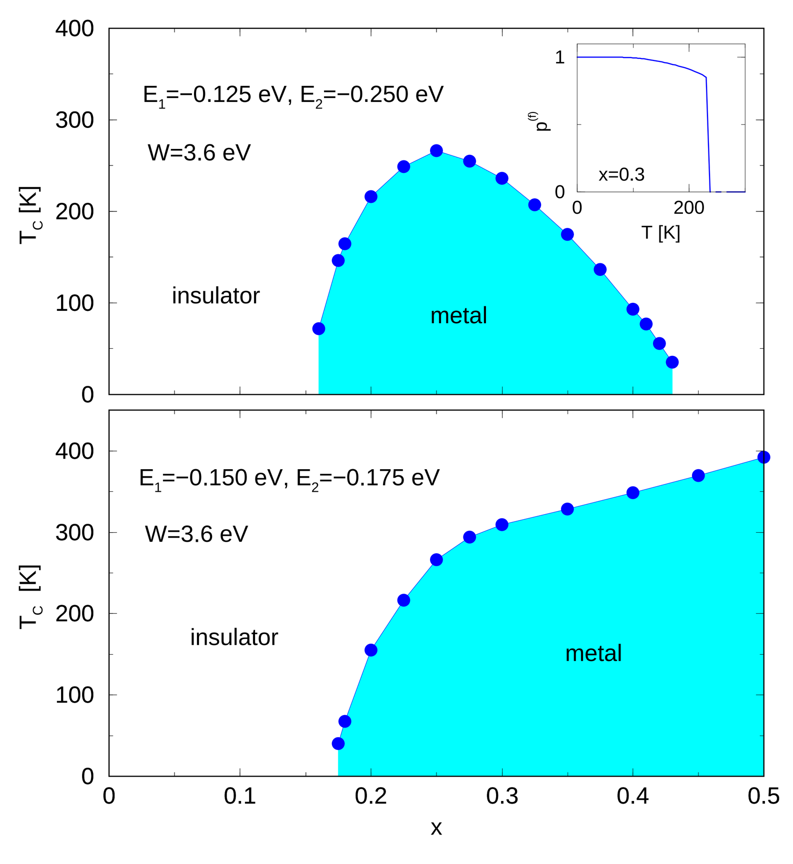


Fig. 4. Phase diagram of the mixed-phase Zener-polaron model with feedback (Inset: fraction of the Zener phase as a function of temperature).

Appendix: Percolative picture

To support the assumption that the bandwidth of the Zener state depends approximately linear on the fraction of the FM region, we consider a site percolation model. Lattice points are occupied with probability p. Adjacent occupied sites will be connected by a hopping matrix element, which is affected by the background of thermalized classical spins. The density of states of the resulting random tight-binding model,

$$\mathcal{H}_p = \sum_{\langle ij\rangle} t^{(p)}_{ij}(\beta\lambda_{\rm eff})(c_i^\dagger c_j + c_j^\dagger c_i),$$

is determined numerically, using kernel polynomial and maximum entropy methods.

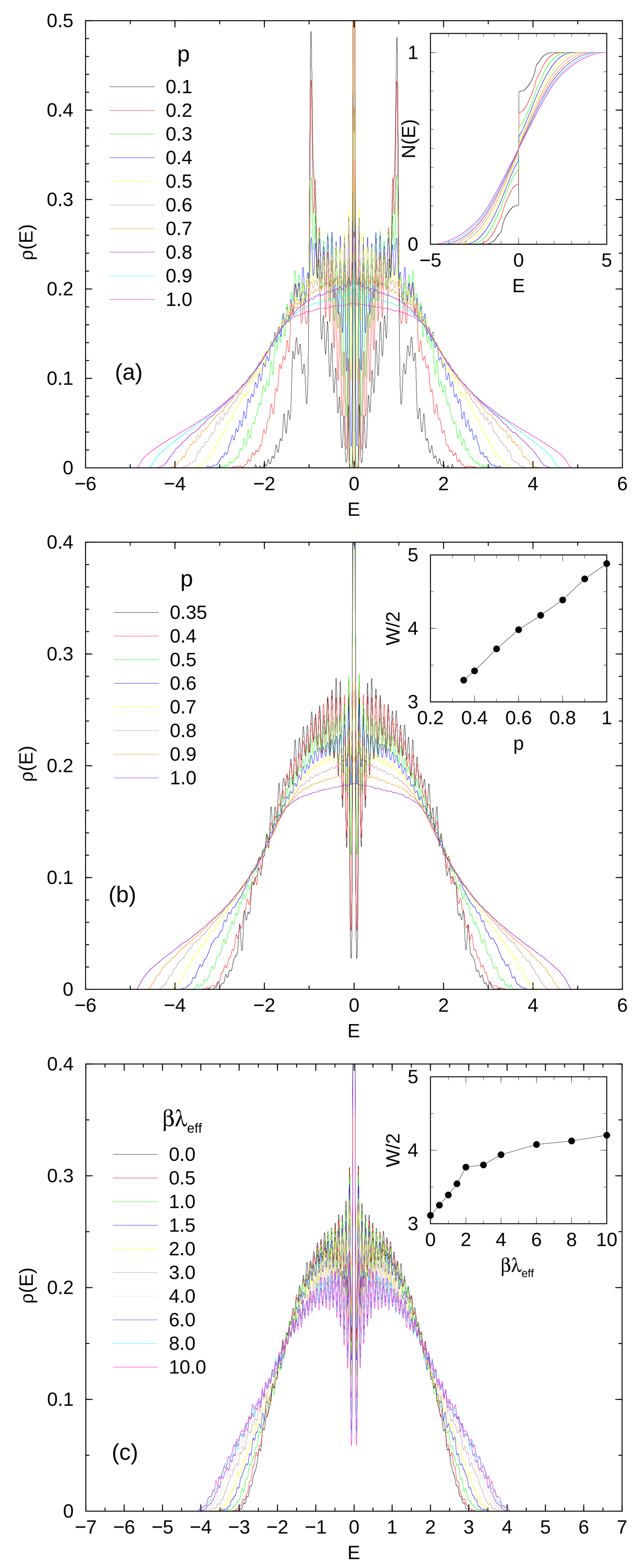


Fig. 5. Density of states (DOS), $\rho(E)$, for the tight-binding site percolation model on a finite 6^3-lattice (PBC) with different occupation probabilities p (a). Contributions from unoccupied sites were projected out. Panel (b) shows the DOS if only states belonging to the "infinite" cluster are taken into account. At $p = 0.5$ the field dependence of $\rho(E)$ is displayed in panel (c). The insets show the integrated DOS $N(E) = \int_{-W/2}^{E} dE\rho(E')$ (a) and the bandwidths as functions of p (b) and the magnetic field $\beta\lambda_{\rm eff}$ (c).

Summary

Proposed mechanism for the (CMR) MIT: percolative two-phase scenario.

- Below the transition temperature T_c, we found polaronic inclusions embedded in a dominant macroscopic metallic phase.
- The bandwidth of the Zener state depends approximately linear on the fraction of the ferromagnetic region.
- The abrupt change, revealed in various electrical and magnetic properties at T_c is attributed to a collapse of the Zener state mainly caused by a percolative feedback mechanism.
- At $T = 0$ the transition is driven by doping and occurs at $x_c \simeq 0.15 - 0.18$.
- At finite temperatures, disorder due to intrinsic inhomogeneities and magnetic scattering act in combination to reduce the mobility of the charge carriers.
- The calculated values of T_c agree fairly well with the experimental ones.

Further details: A. Weiße, J. Loos, and H. Fehske
arXiv:cond-mat/0101234 & arXiv:cond-mat/0101235