Application of the Pseudo-Spin Model to the Lowest-Temperature Phase Transition of the Mixed Crystal $(NH_4)_{2(1-x)}K_{2x}Pb[Cu(NO_2)_6]$

Wolfgang Windsch and Horst Braeter
Fachbereich Physik, Universität Leipzig, Leipzig, Germany

Julio A. Gonzalo
Departamento de Física Aplicada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain

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Mizuno et al. developed a jumping model to explain the nonlinear decrease of the phase transition temperature in the mixed crystals $(NH_4)_{2(1-x)}K_{2x}Pb[Cu(NO_2)_6]$ with $0 \leqq x \leqq 1$. Their implications and results are compared with model parameters and with the results of calculation within the Ising model with transverse field. It comes out that the assumption of a temperature independent transient time in the jumping model corresponds to the admission of tunneling in the Ising model.

1. Introduction

Several crystals undergoing a structural phase transition show a nonlinear dependence of the transition temperature on the amount of substitution of one or more ions or molecular groups in the unit cell by other ions or molecular groups. If in such a substitutionally disordered mixed crystal the transition temperature $T_c(x)$ becomes zero for a critical mole fraction x_c of the substituent, i.e. $T_c(x_c) = 0$, and the low-temperature phase is not stable for $x > x_c$, the behaviour of this system can only be understood if quantum effects are taken into account [1, 2].

One of the most widely adopted models to describe the lattice dynamics of crystals with impurities is the coupled anharmonic oscillators model [2, 3]. In the limiting case of order-disorder transitions, i.e. when the bond energy for the order-disorder units is small compared to the height of the barrier $A^2/(4B)$ in the double-well single particle potential $U = -(A/2)Q^2 + (B/4)Q^4$ the above mentioned model is equivalent to the Ising model. To take into account the quantum effects one should consider the Ising model with transverse field (IMTF), i.e. the Hamiltonian [2]

$$\hat{H} = \Omega \sum_i \hat{S}_i^x - \frac{1}{2} \sum_{i \neq j} J_{ij} \hat{S}_i^z \hat{S}_j^z, \tag{1.1}$$

where the $\hat{S}_i^x$ and $\hat{S}_i^z$ are pseudo-spin operators. The phase transition temperature T_c is given by the equation

$$k\,T_c = \frac{\Omega}{\ln \dfrac{1+x}{1-x}}, \tag{1.2}$$

where $x = 2\,\Omega/I$ and $I = \sum_{i \neq j} J_{ij}$.

Here the transition temperature T_c is given by the competition between the tunneling field Ω and the effective interactions J_{ij}, which are defined as matrix elements over the wave functions that describe the symmetric and the antisymmetric states in the double well single particle potential.

In this paper, results of calculations using the IMTF are compared with the results obtained using a model which was developed in D. Nakamura's group for the mixed crystal ammonium$_{1-x}$ potassium$_x$ lead (II) hexanitrocuprate $(NH_4)_{2(1-x)}K_{2x}Pb[Cu(NO_2)_6]$.

Both models lead with some minor approximations to the same expression for the dependence of the phase transition temperature $T_c(x)$ on the potassium concentration [4].

2. Nakamura's Model

The pure crystal $(NH_4)_2Pb[Cu(NO_2)_6]$ undergoes at $T_c(0) = 94$ K a transition between a ferrodistortive

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Reprint requests to Prof. Dr. W. Windsch, Fachbereich Physik, Universität Leipzig, Linné-Str. 5, O-7010 Leipzig, Germany.

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(F) ordered low-temperature phase and an antiferrodistortive (AF) ordered phase. Substituting NH_4^+ by ND_4^+ results in a small increase of the transition temperature to 99 K. A gradual substitution of NH_4^+ by K^+ causes a nonlinear decrease of the transition temperature $T_c(x)$, where x is the mole fraction of the potassium ions. For $x = 0.228$ a transition temperature $T_c(0.228) = 56$ K was obtained, and experiments show that for $x = 0.276$ the low-temperature F-phase is not stable.

The model is based on the well known structure [5] of the AF-phase of $(NH_4)_2Pb[Cu(NO_2)_6]$.

The elongated $[Cu(NO_2)_6]^{4-}$ octahedra are ferrodistortively and antiferrodistortively ordered as shown in Figure 1. EPR investigations revealed in the low-temperature phase only ferrodistortive ordering, all $[Cu(NO_2)_6]^{4-}$ are oriented in parallel. Since the substitution of the tetrahedral NH_4^+ by the spherical K^+ destabilizes the F-phase, it is assumed that the reorientation of the ammonium ions plays an important role for the transition. It is assumed that for a stable orientation of NH_4^+ during a residential time τ the F-phase is realized and for a rotational state within a transient time τ^* the higher-temperature AF-phase is realized. The n-n F and AF interactions ($J_F > 0$, $J_{AF} < 0$) of the elongated $[Cu(NO_2)_6]^{4-}$ octahedral are summed up and time averaged. For the concentration dependence of the time averaged coupling

$$\overline{J(x)} = \frac{3}{4}\left[(1-x)\frac{\tau J_F + \tau^* J_{AF}}{\tau + \tau^*} + x J_{AF}\right] \tag{2.1}$$

is obtained. The phase transition occurs when $\overline{J(x)} = 0$.

Taking the transient time τ^* to be temperature independent and for the residential time τ an Arrhenius ansatz ($\tau = \tau_\infty \exp[E_a/k\,T]$), an expression for the concentration dependence of the transition temperature is obtained:

$$T_c(x) = \frac{T_c(0)}{1 - \alpha \ln(1 - \beta x)}. \tag{2.2}$$

With the two fitting parameters

$$\alpha = \frac{k\,T_c(0)}{E_a} = 0.26 \quad \text{and} \quad \beta = \frac{J_F - J_{AF}}{J_F} = 4$$

the experimental findings are well reproduced.

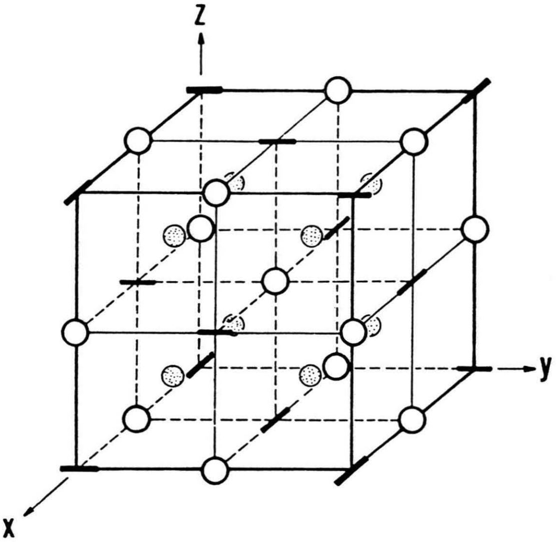

Fig. 1. Antiferrodistortive order of elongated $[Cu(NO_2)_6]^{4-}$ octahedra in $(NH_4)_2Pb[Cu(NO_2)_6]$. Open circles and the circles with dots denote Pb^{2+} and NH_4^+, respectively. The elongated octahedra are represented by thick bars, the orientations of which coincide with the axis of elongation. The structure is illustrated for the high temperature cubic unit cell [4].

3. Application of the Pseudo-Spin Model

The spin-spin interaction J_{ij} in the mixed crystal is proportional to the effective dipole moments μ_i, μ_j of the order-disorder units,

$$J_{ij} = \mu_i I_{ij} \mu_j. \tag{3.1}$$

We assume that the same type of Hamiltonian holds for both constituents of the mixed crystal. The transverse field Ω_i and the effective dipole moments are random variables. They may be either one of the values Ω_1, Ω_2 and μ_1, μ_2 in dependence on the occupation of the considered lattice site by one or the other constituent. We assume that the dipole-dipole coupling parameter I_{ij} is independent of the type of order disorder units at the lattice sites, $I_0 = \sum_{i \neq j} I_{ij}$.

The transition temperature is given by the divergence of the static homogeneous susceptibility. Calculation of the susceptibility using random phase approximation and virtual crystal approximation leads to an equation [6] which can be used to obtain the concentration dependent transition temperature

$T_c(x)$:

$$(1-x)\,\mu_1^2 \frac{I_0}{2\,\Omega_1} \operatorname{tgh} \frac{\Omega_1}{2\,k\,T_c(x)} + x\,\mu_2^2 \frac{I_0}{2\,\Omega_2} \operatorname{tgh} \frac{\Omega_2}{2\,k\,T_c(x)} = 1\,. \tag{3.2}$$

Experimentally it was found that deuteration of $(NH_4)_2Pb[Cu(NO_2)_6]$ results in only a weak change of the transition temperature. Therefore we may assume for the tunneling fields $\Omega_1 \approx \Omega_2 = \Omega$. Then we obtain

$$\operatorname{tgh} \frac{\Omega}{2\,k\,T_c(x)} = \frac{2\,\Omega}{\mu_1^2 I_0 [1 - x(1 - (\mu_2^2/\mu_1^2))]} = \frac{2\,\Omega}{J_0(x)}\,. \tag{3.3}$$

If we take into account that $T_c(x_c) = 0$ for the critical potassium concentration x_c, we obtain

$$k T_c(x) = \frac{\Omega}{\ln \dfrac{2 - a(x + x_c)}{a(x_c - x)}}\,, \tag{3.4}$$

where $a = 1 - (\mu_2^2/\mu_1^2)$ is fixed by the ratio of the strengths of the dipole moments of both constituents. Since substitution of NH_4^+ by K^+ lowers the transition temperature $T_c(x)$ one has $\mu_2^2 < \mu_1^2$. For the effective pseudo-spin coupling constant $J_0(x)$ a linear dependence on the potassium concentration is obtained in this approximation:

$$J_0(x) = J_0(0)(1 - a\,x)\,. \tag{3.5}$$

To compare this result with (2.1) we consider

$$\frac{\Omega}{k\,T_c(0)} - \frac{\Omega}{k\,T_c(x)} = \ln \frac{2 - a\,x_c}{a\,x_c} - \ln \frac{2 - a(x + x_c)}{a(x_c - x)} = \ln\left(1 - \frac{x}{x_c}\right) - \ln\left(1 - \frac{a\,x}{2 - a\,x_c}\right). \tag{3.6}$$

Taking $a < 1$ and $x < x_c = 0.25$ into account, a numerical evaluation shows that the second term may be neglected and we obtain

$$T_c(x) = \frac{T_c(0)}{1 - \dfrac{k\,T_c(0)}{\Omega} \ln\left(1 - \dfrac{x}{x_c}\right)}\,. \tag{3.7}$$

This equation has exactly the same form as (2.2) derived by Nakamura's group. Now the equivalent fitting parameters are $k\,T_c(0)/\Omega$ and x_c.

It has to be stressed that within the IMTF an expression for $T_c(x)$ which is equivalent to (2.2) is obtained only for concentration independent tunneling Ω.

With $T_c(0) = 94$ K the fitting parameters become $\Omega/k = 361$ K and $x_c = 0.25$.

With these values the ratio of the dipole moments becomes

$$\mu_2/\mu_1 = (1 - a)^{1/2} = 0.91\,. \tag{3.8}$$

It is seen that in the case of K^+ the long-range interaction forces are smaller than in the case of NH_4^+.

The long-range coupling parameters for both pure components may be obtained as

$$J_0(0) = (2\,\Omega/k)/(1 - a\,x_c) = 754 \text{ K}$$

and

$$J_0(1) = J_0(0)(1 - a) = 626 \text{ K}.$$

In the first case the ratio between the tunneling field and the long-range coupling $(2\,\Omega/k)/J_0(0) = 0.96$ is smaller than unity and the system can order, whereas in the second case with $(2\,\Omega/k)/J_0(1) = 1.15$ the ordering forces are smaller than the tunneling field.

At the critical concentration holds $J_0(x_c) = 2\,\Omega$. For $x > x_c$ the low-temperature phase is suppressed by the tunneling.

4. Comparison of the Two Models

At first sight it is surprising that both completely different models lead to the same expression for the concentration dependence of the transition temperature. Nakamura's model seems to be purely classical whereas the IMTF takes into account quantum tunneling, and no approximation was done to fit the models. Therefore it seems interesting to look for some relations between the underlying physical pictures.

In Nakamura's model the transition temperature $T_c(x)$ is given by the competition of the time and concentration averaged ferrodistortive ($J_F > 0$) and antiferrodistortive ($J_{AF} < 0$) interactions between the elongated $[Cu(NO_2)_6]^{4-}$ octahedra whereas in the pseudo-spin model $T_c(x)$ is given by the competition of the concentration averaged long-range ordering interactions between dipoles $J_0(x)$ and the tunneling Ω.

Both models describe the behaviour of the system at the quantum limit, i.e. $\mathrm{d}T_c/\mathrm{d}x \to \infty$ for $x \to x_c$.

From (3.3) follows that in the pseudo-spin model the critical concentration x_c is given by

$$J_0(x_c) = J_0(0)\left[1 - \left(1 - \frac{\mu_1^2}{\mu_2^2}\right)x_c\right] = 2\,\Omega\,. \tag{4.1}$$

For the low temperature phase to be stable, the potassium concentration may increase up to x_c where this condition is fulfilled. The tunneling field we assumed to be concentration independent and, by definition, it is also independent of temperature.

In Nakamura's model the critical concentration is given by

$$\frac{J_F - J_{AF}}{J_F}\,x_c = 1\,; \tag{4.2}$$

it is fixed only by the strength of both interactions which have opposite signs. If we temporarily adopt that the Arrhenius ansatz would be valid at the quantum limit ($T_c(x_c) \to 0$). This would mean that for $T \to 0$ the residential time goes like $\tau \to \infty$. This means $\tau \gg \tau^*$ and the transient time τ^* would be negligible. This implies a static compensation of the interactions,

$$J_F(1 - x_c) = -J_{AF}\,x_c\,. \tag{4.3}$$

For such a case one expects a linear concentration dependence of the transition temperature $T_c(x)$ [7],

Therefore it is supposed that in Nakamura's model the nonlinearity in $T_c(x)$ is introduced by the assumption of a temperature independent transient time τ^*. Then the system is dynamic even at very low temperatures.

From (4.1) and (3.5) one obtains

$$1/x_c = (J_0(0) - J_0(1))/(J_0(0) - 2\,\Omega)\,. \tag{4.4}$$

A comparison with (4.2) shows the relation between the model parameters:

$$\begin{aligned} J_F &= J_0(0) - 2\,\Omega\,, \\ J_{AF} &= J_0(1) - 2\,\Omega\,. \end{aligned} \tag{4.5}$$

The AF coupling has the correct sign since $J_0(x > x_c) < 2\,\Omega$.

So the introduced ferro- and antiferrodistortive interactions between the elongated $[Cu(NO_2)_6]^{4-}$ octahedra are within the pseudo-spin model equivalent to the concentration averaged dipolar interactions on both ends of the concentration scale reduced by the tunneling field. $J_0(0)$ and $J_0(1)$ correspond to pure NH_4^+ and to pure K^+, respectively.

The jump model with an assumption of a residential and transient time is successful in some cases in describing the anomalous temperature dependence of NQR frequencies. But as was shown by Brown [8] it suffers from inconsistencies if regarded as an accurate physical model. Often it is used to introduce an additional parameter for fitting the experiments. But in the manner adopted by Nakamura's group it determines the dynamics of the system at very low temperatures.

This is easily seen by a comparison of the influence of the tunneling field Ω and the reciprocal transient time $1/\tau^*$ on the stability limit x_c of the low temperature phase. From (2.1) for $x = 0$ one obtains

$$\frac{\tau^*}{\tau(T_c(x=0))} = \frac{-J_F}{J_{AF}} = \frac{\tau^*}{\tau_{CO}}\,. \tag{4.6}$$

The ratio of the couplings J_F and J_{AF} fixes the transient time τ^*. Then the stability limit is given by

$$x_c = \frac{1}{(\tau_{CO}/\tau^*) + 1}\,. \tag{4.7}$$

Comparison of (4.4) and (4.7) shows that an increase of Ω to $J_0(0)$ as well as an increase of $1/\tau^*$ to infinity reduces the stability limit of the low temperature phase, the critical concentration x_c, to zero.

To conclude, one may ask if it is reasonable within the framework of the model of coupled oscillators to assume an equal tunneling probability and an equal dipole-coupling parameter. In the quasiharmonic approximation the tunneling field is given by

$$\Omega_i = \frac{1}{2}\,\frac{A_i^2}{4\,B_i}\,\frac{3}{4}\,\frac{e^{-\sqrt{2}/\lambda_i}(1 + \lambda_i/\sqrt{2})}{(1 - e^{-2\sqrt{2}/\lambda_i})}\,, \tag{4.8}$$

where the quantum parameters λ_i satisfy the relation

$$\lambda_i = \hbar\sqrt{A_i/m_i}/(A_i^2/B_i)\,. \tag{4.9}$$

To have tunneling it is only necessary that λ_i is sufficiently large.

For the dipole-coupling parameter one gets in the same approximation

$$I_{0i} = \frac{1}{4}\,\frac{A_i}{B_i}\,\varphi_{0i}\,\frac{1}{1 - e^{-2\sqrt{2}/\lambda_i}}\,. \tag{4.10}$$

Here $\varphi_{0i} = \sum_{l \neq k} \varphi_{lk}^{(i)}$ characterizes the strength of the coupling constants.

Equation (4.8) shows that even for strongly different substituents the depth of the single-particle potential may differ in such manner that $\Omega_1 \approx \Omega_2$. On the other hand, from (4.10) follows $I_{01} \approx I_{02}$ if the product of the squared width of the single particle potential A_i/B_i and the lattice parameter φ_{0i} is nearly constant.

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