Environmental influence on the nuclear spin-lattice relaxation rate in Cu_xPt_{1-x}

J. Banhart
Institut für Physikalische Chemie, Universität München, Sophienstrasse 11, D-8000 München 2, Federal Republic of Germany

P. Weinberger
Institut für Technische Elektrochemie, Technische Universität Wien, Getreidemarkt 9, A-1060 Wien, Austria

H. Ebert[a] and J. Voitländer
Institut für Physikalische Chemie, Universität München, Sophienstrasse 11, D-8000 München 2, Federal Republic of Germany

The influence of the surrounding atomic configuration on the nuclear spin-lattice relaxation rate of Pt in disordered Cu_xPt_{1-x} alloys has been studied theoretically by calculating the electronic structure of CuPt clusters embedded in a coherent potential approximation medium. The resulting average nuclear spin-lattice relaxation rate is found to be in a very satisfying agreement with experiment.

I. INTRODUCTION

In substitutional alloys the nuclear spin-lattic relaxation rate maps neighborhood-dependent partial local densities of states (DOS) at the Fermi energy. For this reason it offers the possibility to investigate the effects of short-range order and segregation in a rather direct way. Within the framework of multiple scattering theory the relaxation rate can be calculated as a function of configuration and—in the case of binary alloys—its dependence on the number of atoms of one component occupying a particular shell of neighbors or the short-range order parameters, respectively, can be studied. A comparison with the corresponding results for the statistically disordered case allows a quantitative illustration of the validity of the coherent potential approximation (CPA). Furthermore, a comparison with experimental values can be used to interpret data corresponding to one and the same "macroscopical" concentration, however, obtained from samples of different preparational origin and therefore different states of order. In the present paper the theoretical Pt nuclear spin-lattic relaxation rate in Cu_xPt_{1-x} is discussed for a number of concentrations considering all possible configurations of a first-neighbor shell cluster and are compared with available experimental data. For $Cu_{50}Pt_{50}$ also short-range order effects resulting from a shell of second neighbors are taken into account. In addition, experimental order-dependent specific heats are discussed.

II. THEORETICAL FRAMEWORK

The presented calculations were performed using the fully relativistic embedded cluster method (ECM)[1] and are based on results obtained within the framework of the fully relativistic Korringa-Kohn-Rostoker (KKR) CPA method.[2] In terms of the so-called scattering-path operator τ^{ij} the DOS corresponding to a particular site i occupied by species α and cluster configuration J can be obtained from the expression

$$n_i^\alpha(E) = -(1/\pi)\,\mathrm{Im\ Tr}\,\mathsf{R}^\alpha[\tau^J]_{ii}, \tag{1}$$

where the supermatrix τ^J is defined by its elements

$$[\tau^J]_{ij} = \{(t_{\alpha(i)}^{-1} - t_c^{-1})\delta_{ij} + [\tau^{-1}]_{ij}\}^{-1}. \tag{2}$$

The size of the supermatrix is $N \times 2 \times (l_{\max}+1)^2$, where N is the number of atoms of the cluster and $l_{\max}$ is the maximal angular momentum quantum number used. In Eq. (2) t_α is the single site t matrix of species α and in Eq. (1) R^α is a matrix of radial integrals[3]

$$\mathsf{R}^\alpha_{QQ'} = \int Z^\alpha_Q(\mathbf{r}) Z^\alpha_{Q'}(\mathbf{r}) d^3r, \quad Q = (\kappa,\mu). \tag{3}$$

The configuration-dependent DOS can now be used to calculate configuration-dependent nuclear spin-lattic relaxation rates

$$(T_1T)^{-1}_{J,\alpha} = 4\pi k_B \hbar \left(\gamma_n \frac{e}{2}\right)^2 \left(\sum_\kappa \frac{2j+1}{6j(j+1)} \times [n_\kappa^{J,\alpha}(E_F)\bar{R}^{\,\alpha}_{\kappa,\kappa}(E_F)]^2 + \sum_{\kappa>0} \frac{1}{3j+1} n_\kappa^{J,\alpha}(E_F) n_{-\kappa-1}^{J,\alpha}(E_F) \times [\bar{R}^{\,\alpha}_{\kappa,-\kappa-1}(E_F)]^2\right), \tag{4}$$

where the $\bar{R}^{\,\alpha}_{\kappa,\kappa'}(E_F)$ are renormalized radial integrals according to Eq. (3.20) of Ref. 4. For further numerical details see Ref. 5.

III. RESULTS AND DISCUSSION

As the number of atoms of a particular species in a first-neighbor shell cluster varies from 0 to 12 for a fcc lattice a total of 144 configurations has to be considered. Going beyond a first shell of neighbors, the number of configurations increases dramatically. For $Cu_{50}Pt_{50}$, it can be argued[6] that

[a] Present address: Siemens AG,ZFETPH11, Paul-Gossen-Str. 100, D-8520 Erlangen, FRG.

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in accordance with the CuPt structure short-range ordering seems to occur not in the first shell, but in the second shell or beyond. This particular case can easily be handled in the present approach, because by putting "effective" (CPA) atoms at the positions of the first shell only 10 different second-shell configurations have to be considered. Including the second shell, however, implies that the size of the matrix in Eq. (2) increases from 234 for one shell to 342.

In Fig. 1 one can see that in $Cu_{50}Pt_{50}$ the effects on the Pt nuclear spin-lattice relaxation rate due to changes in the local atomic arrangement are quite pronounced. These effects are found to be large for the first-shell cluster [Fig. 1(a)] as well as for the second-shell cluster [Fig. 1(b)]. As compared to $Cu_{50}Pt_{50}$ the effects in $Cu_{71}Pt_{29}$ on the Pt relaxation rate due to changes of the configuration are much less drastic. This, of course, has to be expected since in $Cu_{71}Pt_{29}$ the Fermi level falls into the onset of the s band above the d band. It should be noted from Fig. 1 that values to the right of the CPA result are due to "likewise" ordering (segregation), whereas the values to the left incorporate the cases with "antilikewise" ordering (short-range ordering, SRO). In terms of the Warren–Cowley SRO parameters α_r, which are defined for an A atom at the center as

$$\alpha_r = 1 - n_r^B/(c_B n_r), \tag{5}$$

where n_r is the number of all the atoms in the rth shell, n_r^B that of the B atoms, and values to the right of the CPA value correspond to positive α_r and vice versa.

Figure 2 summarizes the results obtained for various "macroscopical" concentrations and compares them to the experimental ones given by Itoh, Asayama, and Kobayashi.[6] From this figure it seems that on the scale of T_1T for Cu-rich Cu_xPt_{1-x} alloys such at $Cu_{71}Pt_{29}$ local arrangement effects are of minor importance. By comparing the theoretical values with the experimental data,[7] it is evident from Fig. 2 that for Cu-rich or Pt-rich Cu_xPt_{1-x} alloys the agreement is excellent. Unfortunately in Ref. 6 no account is given of how the samples were prepared. It is therefore difficult to comment on the fact that for $Cu_{50}Pt_{50}$ the experimental value is considerably below the CPA value in the regime of segregation.

By approximating the DOS for the long-range ordered state in $Cu_{50}Pt_{50}$ by a two-shell cluster corresponding to the occupations in the CuPt structure, one effectively includes also a third shell, since this third shell contains in the ordered structure six atoms of each kind.[5] This situation is well represented by the embedding CPA medium. Together with the DOS for the statistically disordered case (CPA) this approximated DOS for the ordered case can be compared to the experimental values for the linear coefficient of the specific heat γ. The coefficient γ is predicted by the calculations to change from 1.34 to 1.08 mJ/K^2 mol due to ordering. This result is in nice agreement with the experimental findings for disordered[7,8] (1.59 mJ/K mol) and ordered[7] (1.03 mJ/K mol) CuPt alloys.

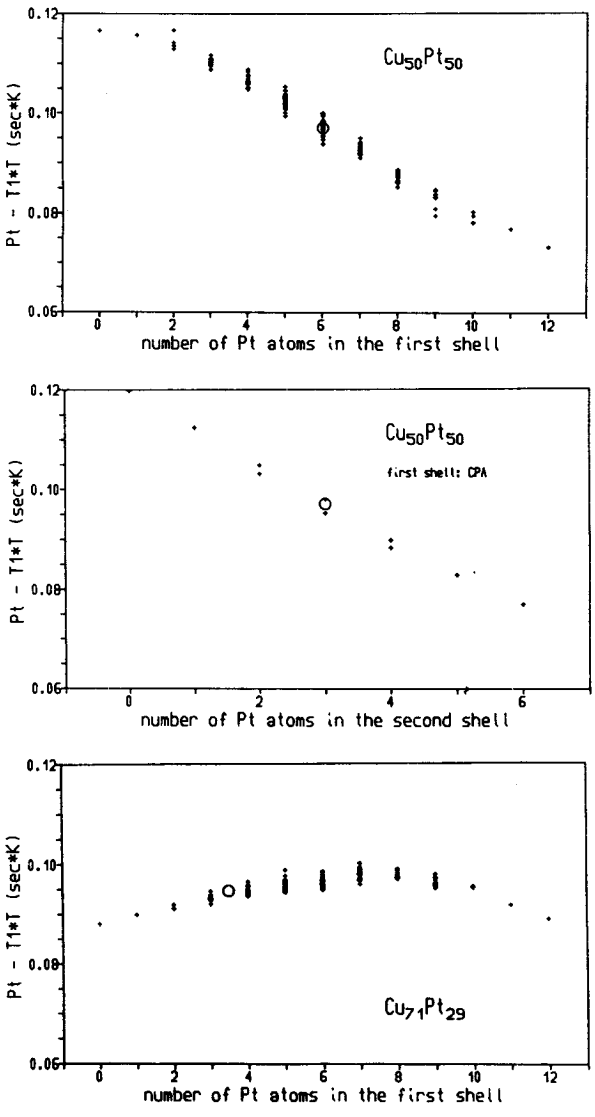

FIG. 1. Pt nuclear spin-lattice relaxation rate in Cu_xPt_{1-x} for various atomic configurations. The crosses represent the possible configurations, while the circles give the CPA results. (a) Pt in $Cu_{50}Pt_{50}$ with the occupation of the first-neighbor shell varied. (b) Pt in $Cu_{50}Pt_{50}$ with the occupation of the second-neighbor shell varied and CPA atoms in the first shell. (c) as for (a) but for $Cu_{71}Pt_{29}$.

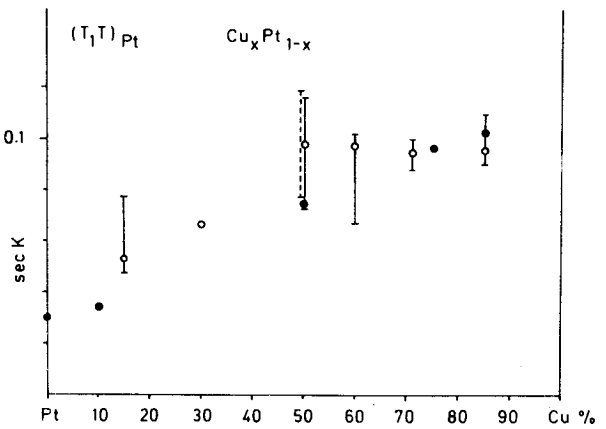

FIG. 2. Pt nuclear spin-lattice relaxation rate in Cu_xPt_{1-x}; solid circles: experiments (Ref. 7); open circles: KKR-CPA results; solid bars: range of variation due to changes of configuration in the first-neighbor shell; dashed bar: range of variation due to changes of configuration in the second-neighbor shell.

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