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Low temperature lattice specific heat of dilute alloys based on palladium

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Abstract. The low-temperature lattice specific heat of palladium-based dilute alloys **Pd**Ag, **Pd**Rh, **Pd**Ru, **Pd**Mo and **Pd**Nb has been studied theoretically on the basis of Green function theory. A nearest-neighbour impurity model with central and non-central force-constant changes has been employed to discuss the crystal impurity problem. The effect of volume changes has also been considered. The lattice specific heat in these alloys largely depends on the central force-constant change which seems to be quite high in a few cases. The possible origin of such high force-constant changes in these alloys has been discussed.

1. Introduction

Although it cannot match the resolution of some powerful experimental techniques the lattice specific heat has been the most thoroughly studied technique for investigating the frequency spectrum of solids. The method of lattice specific heat is applicable to all classes of materials and involves all kinds of symmetry modes. Theoretically it is found that isolated heavy impurities can give rise to resonance modes with sharp peaks in the frequency spectrum of imperfect crystals. Consequently one would expect that the specific heat of such a crystal should increase anomalously in the low-temperature range. This suggestion was first made by Kagan and Iosileveskii [1] and independently by Lehmann and DeWames [2]. The prediction was verified experimentally by Panova and Samoilov [3] who measured lattice specific heats of Mg–Pb alloys. Their measured results are in close agreement with mass defect theory indicating the isotopic behaviour of heavy lead impurities. Subsequently a number of experimental measurements of specific heat have been made on different crystals containing substitutional impurities [4–17]. Hartmann *et al* [8] have studied **Al**Ag alloys and compared their measurements with Green function calculations on the basis of mass defect approximation and have concluded that only 80% of the increase in lattice specific heat may be understood on the basis of mass defect, thereby indicating local force-constant softening. In subsequent theoretical analysis of lattice specific heat, the effect of mass change at the impurity site and force-constant changes induced by impurity have been taken into account [18–24].

Apart from the mass change and change in force constants between the impurity and its immediate neighbours the presence of impurities gives rise to lattice expansion

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or contraction. Thus the total change in lattice specific heat consists of two parts: the lattice part, due to mass and force-constant changes and the volume part, due to volume changes. The change in specific heat due to volume change is, in general, smaller than the lattice part but it is significant. Recently Ram and Bijalwan [25–27] have discussed the lattice specific heat of dilute alloys based on copper where the inadequacy of the treatment of volume-induced changes in earlier works [28,29] has been emphasised. Agrawal [30] has obtained an analytical expression for the lattice specific heat of doped crystals and has observed that significant changes in specific heat may occur even in the absence of low-frequency resonance modes. The dilute alloys discussed in the present paper fall in this category. Huq and Moody [31] have measured the specific heat of dilute alloys based on palladium but they have not discussed their results theoretically. In the present paper, therefore, we have analysed the measured lattice specific heat on the basis of the usual Green function theory [32] employing realistic models for the impurity and the host lattice and taking proper account of the volume expansion effect. A nearest-neighbour impurity model including variation in the central and non-central force constants and perfect crystal phonons of palladium calculated on the basis of the sixth-neighbour axially symmetric force-constant model derived by Miller and Brockhouse [33] on the basis of neutron scattering measurements has been employed. By matching the defect model to the measured lattice specific heat we have derived the defect parameters, especially the change in the nearest-neighbour central force constant. Palladium being a transition metal, the forces are long-ranged and vary in quite a complicated way; even so a force-constant analysis of the measured phonon dispersion has revealed that the first-neighbour forces are dominant [33] and as such a parameter characterising the impurity–host interactions should prove quite useful in discussing other dynamical properties of these dilute alloys. The force-constant changes obtained are discussed in the light of electronic properties of these alloys.

In § 2 we briefly describe the calculation of changes in the lattice specific heat for the lattice part and the volume part. The calculated results for different dilute alloys are discussed in § 3 and compared with the experimental measurements.

2. Lattice specific heat of an alloy

As already pointed out, the presence of impurities affects the lattice specific heat in two ways: (i) the lattice part, due to mass and force-constant changes around the impurity and (ii) the volume part, due to volume change. The volume change corresponding to homogeneous expansion of the lattice is called image expansion and gives rise to softening of forces throughout the lattice. Thus the lattice specific heat of an alloy is expressed as

$$C_{\mathrm{L}}^{\mathrm{alloy}} = C_{\mathrm{L}}^{\mathrm{pure}} + \Delta C_{\mathrm{L}}^{\mathrm{image}} + \Delta C_{\mathrm{L}} \tag{1}$$

where $C_{\mathrm{L}}^{\mathrm{alloy}}$ and $C_{\mathrm{L}}^{\mathrm{pure}}$ are the lattice specific heat of the alloy and the pure metal, respectively, and $\Delta C_{\mathrm{L}}^{\mathrm{image}}$ is the change in lattice specific heat due to image expansion while ΔC_{L} is the change due to localised perturbation characterised by mass change and the force-constant changes.

The Debye temperatures of the ideal lattice and alloys are known from experimental measurements. If volume-induced change in the Debye temperature is known then the lattice specific heat of the pure crystal, alloy and expanded lattice ($C_{\mathrm{L}}^{\mathrm{pure}}$ $\Delta C_{\mathrm{L}}^{\mathrm{image}}$)

Table 1. The change in Debye temperature due to volume expansion $\Delta\theta_D^{image}$ and the Debye temperature of expanded lattices and alloys. The θ_D of pure palladium is 275.46 K.

Alloys	Concentration (at.%)	$\Delta\theta_D^{image}$(K)	Expanded lattice θ_D(K)	Alloy θ_D(K)
PdAg	0.96	−0.18	275.27	273.51
	1.90	−0.37	275.09	271.61
PdRh	1.02	0.07	275.53	275.46
PdRu	1.02	0.12	275.58	276.45
	2.03	0.25	275.70	280.58
PdMo	0.93	0.06	275.52	279.52
	2.01	0.13	275.59	289.63
PdNb	2.03	−0.18	275.28	287.26

can be calculated using the T^3 dependence of the lattice specific heat at very low temperatures.

The change in Debye temperature due to volume expansion can be calculated with the help of the Grüneisen constant γ as

$$\nu = -\frac{\ln \theta_D}{\ln V}\left(\text{or} -\frac{\Delta\theta_D}{\theta_D}\right) = \gamma\,\frac{\Delta V^{image}}{V} \tag{2}$$

where ΔV^{image} is the volume change due to uniform expansion or contraction of the lattice. The change in volume due to image expansion can be calculated in terms of the total volume change and Poisson ratio. The total volume change due to different impurities in various metals is given by King [34]. The Grüneisen constant for Pd is 2.3 [35]. Using these values and the Poisson ratio (=0.39) the change in Debye temperature is calculated using equation (2) and is given in table 1 along with measured values of the Debye temperatures of the pure lattice and different alloys. The difference between the Debye temperatures of the alloy and the expanded lattice is accounted for by local perturbation.

The change in specific heat due to local perturbation is

$$\Delta C_L(T) = N_d k \int_0^\infty d\omega \Delta Z(\omega)\left(\frac{\hbar\omega}{2kT}\right)^2 \text{cosech}^2\left(\frac{\hbar\omega}{2kT}\right) \tag{3}$$

where $\Delta Z(\omega)$ is the change in density of states due to a single impurity and N_d is the total number of impurities in the lattice.

The change in density of states in terms of phaseshift is [25–27]

$$\Delta Z(\omega) = \frac{1}{\pi}\frac{d\theta(\omega)}{d\omega}. \tag{4}$$

The use of expression (4) in (3) results in

$$\Delta C_L(T) = \frac{-2N_d k}{\pi}\int_0^\infty d\omega\,\frac{\theta(\omega)}{\omega}\left\{\text{cosech}^2\left(\frac{\hbar\omega}{2kT}\right)\right.$$
$$\left.\times\left[1-\left(\frac{\hbar\omega}{2kT}\right)\coth\left(\frac{\hbar\omega}{2kT}\right)\right]\right\}\left(\frac{\hbar\omega}{2kT}\right)^2. \tag{5}$$

The results can further be simplified using group theory, $\theta(\omega)$ is expressed as the sum of phaseshifts, θ_ν, pertaining to different irreducible representations of the point group of the impurity site

$$\theta(\omega) = \sum_\nu \theta_\nu(\omega).$$

The change in the density of states and hence the change in lattice specific heat may be written as

$$\Delta C_L(T) = \sum_\nu \Delta C_L^\nu(T) \tag{6}$$

where $\Delta C_L^\nu(T)$ is the contribution due to the νth irreducible subspace.

3. Calculated results and discussion

We have calculated the lattice part of the change in the specific heat in the dilute alloys: **Pd**Ag, **Pd**Rh, **Pd**Ru, **Pd**Mo and **Pd**Nb at very low temperature (0–5 K). For the above five palladium-based alloys measurements have been made by Huq and Moody [31]. The calculation follows the usual steps: the generation of the perfect lattice phonons, calculation of the Green functions the perturbation and Green function matrices in different irreducible representations, the calculation of the phaseshift $\theta(\omega)$ and finally the specific heat. For the calculation of the perfect lattice phonons we use a sixth nearest-neighbour axially symmetric model derived by Miller and Brockhouse [33] on the basis of Born–von Karmon fit to the measured dispersion curves in neutron scattering experiments. In the computation of the Green function a modified method of Gilat–Raubenheimer [36] has been followed. For an isolated impurity in an FCC lattice in the nearest-neighbour impurity model the perturbation and Green function matrices are of dimension 39×39. To simplify the calculation the point group symmetry O_h of the impurity site has been exploited to block diagonalise the perturbation and Green function matrices, which enter the calculation of the phaseshift. The 39-dimensional total representation may be written as follows:

$$\Gamma = A_{1g} + A_{2g} + 2E_g + 2F_{1g} + 2F_{2g} + A_{2u} + E_u + 4F_{1u} + 2F_{2u}.$$

The detailed expressions for resonance denominator, which appear in the expression for $\theta(\omega)$ in various irreducible representations, are obtained by using relevant symmetry coordinates [37]. Employing equation (3) the impurity contribution to the specific heat has been determined taking different values of the nearest-neighbour central and non-central force-constant change parameters Δf and $\Delta f'$. The calculation is also performed in the mass defect approximation. It is observed that in all the cases the mass defect contribution is very small, an expected result in view of the similar masses of host palladium and impurities (Ag, Rh, Ru, Mo and Nb). The force-constant changes obtained which result in best fit to the experimental data are presented in table 2. It is readily seen that in most cases the central force-constant change plays the dominant role while the effect of non-central force-constant changes is minor, unlike the case of copper-based alloys where the inclusion of non-central force-constant change is not only necessary but is instrumental in obtaining a good fit in many cases (Bijalwan and Ram [27]).

Now we will discuss individually the calculated change in the lattice specific heat in different dilute alloys.

(i) **Pd**Ag. The calculated change in lattice specific heat for two different concentrations (0.96 and 1.9 at.%) of Ag is plotted in figure 1 along with the experimental points. The contribution of mass defect is very low as expected, since the difference between the masses of Pd and Ag is small. It is seen that the central force constant decreases and the non-central force constant increases although the contribution due to non-central force-constant change is not important. The best fit to the data is obtained with $\Delta f = 0.252 f_{11}^0$ and $\Delta f' = 0.00021 f_{11}^0$. f_{11}^0 is the ideal lattice nearest-neighbour central force constant and is equal to 41.760 N m^{-1} [33].

(ii) **Pd**Rh. The calculated results along with the experimental points for an Rh concentration of 1.02 at.% are shown in figure 2. In this case the contribution due to mass defect is very low and a decrease in the central force constant is observed.

The force constants obtained are $\Delta f = -0.19 f_{11}^0$ and $\Delta f' = -0.00005 f_{11}^0$, here again the contribution of the non-central force constant is insignificant.

(iii) **Pd**Ru. In figure 3 we have plotted the calculated results and experimental measurement for the two concentrations 1.02 and 2.03 at.% of Ru. Different sets of force constants Δf and $\Delta f'$ were tried in an attempt to fit the experimental data at both concentrations but no single set (Δf, $\Delta f'$) is able to explain the measured lattice specific heat in this system. In view of this we have tried different sets of force-constant-change parameters for different concentrations. The calculated results presented in figure 3 refer to two different sets of Δf and $\Delta f'$. The force-constant changes obtained are $\Delta f = 0.135 f_{11}^0$, $\Delta f' = 0.0002 f_{11}^0$ (at 1.02 at.%) and $\Delta f = 0.46 f_{11}^0$, $\Delta f' = 0$ (at 2.03 at.%). Again the non-central force constants are seen to be unimportant.

(iv) **Pd**Mo. The calculated change in lattice specific heat at two different concentrations 0.93 and 2.01 at.% of Mo along with the experimental points is plotted in figure 4. Here again we get different force-constant changes at different concentrations. The central force-constant change at 0.93 at.% is $\Delta f = 1.015 f_{11}^0$ and at 2.01 at.% is $\Delta f = 1.97 f_{11}^0$, the non-central force-constant change is zero at both concentrations. It is seen that the force-constant changes obtained are quite high, especially at the higher concentration.

(v) **Pd**Nb. In figure 5 we present the calculated change in lattice specific heat in **Pd**Nb 2.05 at.% along with the experimental points. The derived central force-constant change is $\Delta f = 1.45 f_{11}^0$ while the non-central force-constant change is zero. Here again the change in central force constant is quite high.

Table 2. Values of force constants obtained (in N m^{-1}).

Alloys	Concentration (at.%)	Δf	$\Delta f'$
PdAg	0.96	−10.5235	0.0088
	1.90		
PdRh	1.02	−7.9344	−0.0021
PdRu	1.02	5.6276	0.0084
	2.03	19.2096	0.0209
PdMo	0.93	42.3864	0.00
	2.01	82.2672	0.00
PdNb	2.03	60.5520	0.00

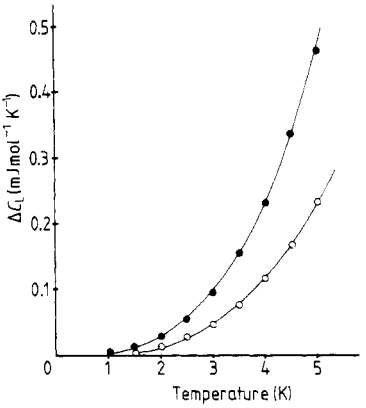

Figure 1. Enhancement in lattice specific heat in **Pd**Ag 0.96 at.% (○) and **Pd**Ag 1.9 at.% (●). Points are experimental results for two alloys and the full curves represent calculations for $\Delta f = -10.5235$ N m^{-1} and $\Delta f' = 0.0088$ N m^{-1}.

The force-constant changes obtained are used to investigate the possible occurrence of impurity modes, i.e. resonance and localised modes. In all the systems studied here no resonance modes are observed. This is to be expected because low-frequency resonance modes are known to cause an anomalous increase in the lattice specific heat at low temperatures and are largely the result of large mass disorders — a situation not found with the present dilute alloys. We have found a localised mode at $\omega_l = 7.21$ THz in **Pd**Ru 2.03 at.%. The existence of a localised mode is consistent with the observed reduction in specific heat, as for each localised mode one gets a contribution $N_d\,\delta(\omega - \omega_l)$ to the total spectrum which has to be compensated by a corresponding amount missing in the band mode region ($0 \leqslant \omega \leqslant \omega_{max}$) to satisfy the sum rule $\int d\omega \Delta Z(\omega) = 0$ for substitutional impurities (Bijalwan and Ram [26]). This missing part of the spectrum at low frequencies, being relevant at low temperatures, causes the reduction in lattice specific heat. Unfortunately there is no experimental measurement to compare with the predicted localised mode frequency. Such localised modes may be observed in, for example, neutron scattering measurements. Unlike the known localised modes in other dilute alloys: **Cu**Al [38], **Nb**Ta [39] and **Rb**K [40],

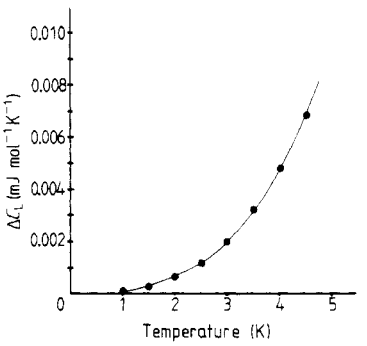

Figure 2. Enhancement in lattice specific heat in **Pd**Rh 1.02 at.% (●). Points are experimental results and the full curve represents calculations for $\Delta f = -7.9344$ N m^{-1} and $\Delta f' = -0.0021$ N m^{-1}.

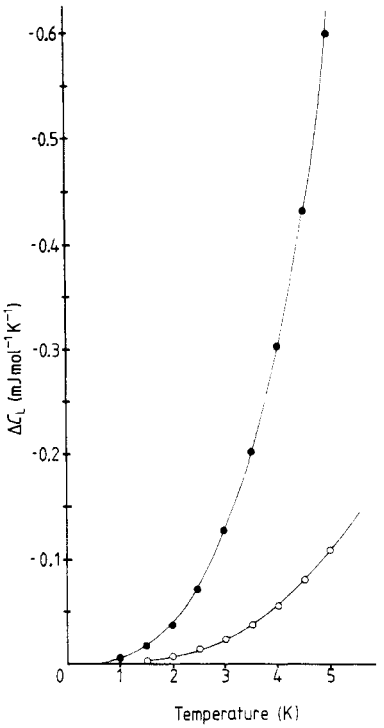

Figure 3. Reduction in lattice specific heat in **Pd**Ru 1.02 at.% (○) and 2.03 at.% (●). Points are experimental results and the full curves represent calculations for $\Delta f = 5.6376$ N m^{-1} and $\Delta f' = 0.0084$ N m^{-1} (at 1.02 at.%) and $\Delta f = 19.2096$ N m^{-1} and $\Delta f' = 0$ (at 2.03 at.%).

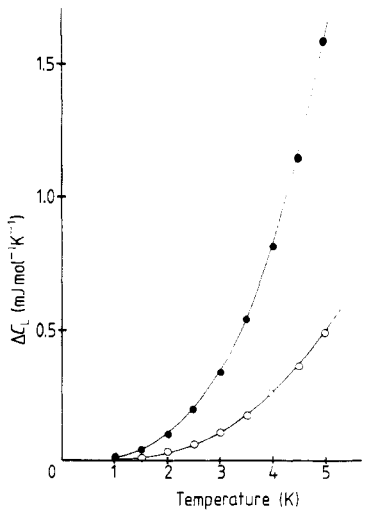

Figure 4. Reduction in lattice specific heat in **Pd**Mo 0.93 at.% (○) and 2.01 at.% (●). Points are experimental results and the full curves represent calculations for $\Delta f = 42.3864$ N m^{-1} and $\Delta f' = 0$ (0.93 at.%) and $\Delta f = 82.2672$ N m^{-1} and $\Delta f' = 0$ (2.01 at.%).

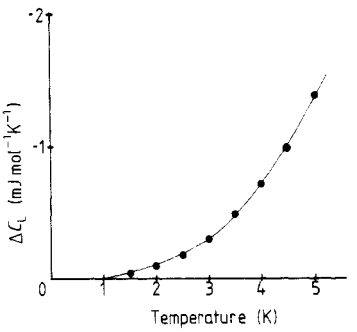

Figure 5. Reduction in lattice specific heat in **Pd**Nb 2.03 at.% (●). Points are experimental results and the full curve represents calculations for $\Delta f = 60.5520$ N m^{-1} and $\Delta f' = 0$.

where the mode is largely a result of large mass disorder, the localised mode in **Pd**Ru seems to be a result of a large variation of force constants.

Although no resonance mode is found, analysis of the specific heat of different dilute alloys shows that the dominant contribution comes from the F_{1u} irreducible representation in which the impurity moves. The change in specific heat largely depends on the change in nearest-neighbour central force constant and the effect of changes in the non-central force constant is not important. As shown in table 2, there is a very small increase in the non-central force constant in **Pd**Ag and **Pd**Ru and a negligible decrease in **Pd**Rh while it is zero in the case of **Pd**Mo and **Pd**Nb. This result is in contradiction to the case of copper-based alloys where non-central forces are found to be quite effective in explaining lattice specific heat [27]. We note that an increase (decrease) in central force constants results in decrease (increase) in lattice specific heat.

In the following we try to understand the force-constant changes obtained from the analysis of the specific heat in different dilute alloys. Although the forces in a metal are generally long-ranged and cannot be discussed properly without an adequate description of electron–phonon interaction a force analysis of phonon dispersion has shown that the first-neighbour forces in palladium are dominant; investigation of the variation of the parameter characterising the nearest-neighbour central force constant in different alloys is therefore interesting and worthwhile. The host palladium has a $4d^{10}$ configuration while all the alloying metals belong to the same 4d transition series and, except for silver, all have a partially filled 4d shell. An unfilled electronic shell has a significant effect on the interatomic force system. Different transition metals have marked differences in their phonon dispersion, indicating strong dependence of the interatomic force constants on the electronic structure of these metals. In view of expected differences in electronic structure of these metals, i.e. Pd and the different impurities, it does not seem to be unusual that large changes in atomic force constants are obtained as a result of addition of impurities with a partially filled 4d shell. As a matter of fact, the velocity of long-wavelength sound waves is proportional to $(N(E_F))^{-1/2}$, $N(E_F)$ being the electronic density of states at the Fermi surface, which is indicative of frequency level and thereby of interatomic forces. On a simple band theory the electronic specific heat coefficient γ is directly proportional to the density of electronic states at the Fermi surface, though corrections for electron–phonon, electron–electron and magnetic interactions are introduced. From measured γ [31] we see that, except in **Pd**Rh where

an increase in $N(E_F)$ may be inferred, there ought to be a decrease in $N(E_F)$ in all the dilute alloys; we note a sharp decrease in **Pd**Mo and **Pd**Nb. If we assume a rigid band model for these transition metals, the above estimate regarding the density of states at the Fermi surface is in agreement with band-structure calculations of Pd [41], Mo [42] and Nb [43]. The decrease (increase) in electronic density of states at the Fermi level indicates an increase (decrease) in phonon frequencies of the alloys compared with host palladium. This explains, in a qualitative way, the large increase in the nearest-neighbour central force constant in dilute alloys **Pd**Ru, **Pd**Mo and **Pd**Nb and a decrease in the case of **Pd**Rh. In the case of **Pd**Ag, where a rigid band model is not applicable, no such simple qualitative explanation based on band structure could be possible.

Finally, some comments regarding the concentration dependence of force-constant changes (Δf, $\Delta f'$) would seem to be in order. Normally with a low impurity concentration these parameters should be independent of concentration, or at most a weak dependence could be expected. Contrary to this a strong dependence on impurity concentration, such as obtained in the case of **Pd**Ru and **Pd**Mo, could be due to inadequacy of the localised defect model. However, as long as defect–defect interactions are ignored, the result is unlikely to be changed much even with an extended defect model. In this context we note the following:

(i) Atomic force constants near the defect depend on the electronic structure in a complicated way and in the alloy the electronic density of states would be quite different to that of the pure metals as a result of mixing of different states, electron charge transfer and the change in the Fermi energy.

(ii) A slight change in E_F may result in large changes in $N(E_F)$ and therefore any regular variation in $N(E_F)$ with concentration is not expected.

(iii) Palladium has a large electronic specific heat, and with large expected changes in the electronic density of states it may well be possible that the electronic specific heat is not linear with T, and so to that extent θ_D derived from $C=\gamma T+\beta T^3$ for different alloys may be in error.

In view of these factors the force-constant changes are expected to be concentration dependent and the results obtained seem to be all the more reasonable. A nonlinear variation of θ_D with changes in the alloy composition also indicates concentration dependence. However, it must be remarked that the present discussion is only qualitative in nature and that a microscopic electronic theory would be the real answer for estimating the change in force constants near the defects.

Acknowledgments

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