# Thermal and Mechanical Properties of Pt-Rh Alloys

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### Abstract

We utilize the many-body potentials developed by Sutton and Chen (1990) within the context of the tight-binding approach to study the bulk properties of metals and metal alloys in molecular dynamics (MD) simulations. In the simulations of Pt-Rh alloys we used the MD algorithms based on an extended Hamiltonian formalism from the works of Andersen(1980), Parrinello and Rahman(1980), Nosé(1984), Hoover(1985) and Çağın(1988). The simulator program that we use generates information about various physical properties during the run time, along with critical trajectory and stepwise information which need to be analysed post production. The thermodynamical and mechanical properties are calculated using the statistical fluctuation expressions over the MD.

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# 1. Introduction

The development of advanced high-performance materials in the industrial world is increasingly coupled with theoretical and computational modelling. In this process, focus is on research areas having direct impact on innovative development of such materials. High-performance metallic alloys find use in various segments of materials and chemical industries as catalysts, and as low-weight and high-strength structural materials. In particular, Pt-Rh alloy is important for catalytic reactions in controlling exhaust gas emissions and $NH_3$ oxidation reactions in fertilizer industries.

The theory and computational efforts require and strive for i) *a priori* determination of the ultimate properties of metals, metallic alloys, ii) simulation and modelling of the processing conditions, and iii) investigating the performance characteristics of these metals and alloys. All these are extremely important for timely, cost-efficient and environmentally compliant development of such advanced materials. With advances in computational speed and emerging new computational algorithms, theoretical and computer simulations are positioned in the midst of this innovative process.

Computer simulations on various model systems usually use simple pair potentials. To account for the directionality of bonding, three-body interactions are also often employed. However, the interactions in metals and metal alloys cannot be represented by simple pairwise interactions. In these systems the electron density plays a dominant role in the interactions and resulting physical properties. Therefore interactions in metals and metal alloys are dominated by many-body interactions. In simple sp-bonded metals this effect may be represented by the interaction potentials derived from model pseudopotentials using second-order perturbation theory (Harrison 1979,1980). Along these lines, we have developed interaction potentials and utilized them to study the properties of simple alkali metal and alkali-metal alloys (Dalgıç et al 1994). However, for d-band metal and metal alloys, the model pseudopotential approach gives way to newer techniques evolved over the past ten years to account for the many-body effects. Among these approaches we can list the empirical many-body potentials based on Norskov's Effective Medium Theory (Norskov 1982), Daw and Baskes' Embedded Atom

Method (Daw and Baskes 1984), Finnis and Sinclair's empirical many-body potentials (Finnis and Sinclair 1984), and more recently the many-body potentials developed by Sutton and Chen(1990) within the context of a tight binding approach (Koleske and Sibener 1993).

In this work we utilized the Sutton-Chen potentials to study the bulk properties of Pt-Rh alloy using molecular dynamics simulations.

## 2. Many-Body Potentials for fcc Metals and Methods

The Sutton-Chen interaction potential is given as the sum of a pairwise repulsion term and a many-body density-dependent cohesion term (Sutton and Chen 1990). The functional form of the interaction potential is as follows:

$$U_i = D(\frac{1}{2} \sum_j u(\mathbf{r_{ij}}) - c\rho_i)$$

where

$$u(r) = (\frac{a}{r})^n$$

$$\rho_i = (\sum_j \phi(r_{ij}))^{\frac{1}{2}}$$

$$\phi(r) = (\frac{a}{r})^m$$

The Sutton-Chen potential parameters $D$, $c$ and $m$ and $n$ are optimized to fit to the 0K properties such as the cohesive energy, zero-pressure condition and the bulk modulus of the fcc metals. We list the values of these parameters for Rh and Pt in Table 1.

As mentioned above, the parametrization of the interaction potentials for these fcc metals are based on the bulk properties at 0K. The functional form is fairly simple in comparison to Embedded Atom Method potentials and is moderately long ranged. The last property makes this set especially attractive for surface and interface studies amongst others, since most of them are very short ranged, (i.e. are fitted up to first or second nearest-neighbour distances).

The above interaction potential can be generalized to describe binary metal alloys in such a way that all the parameters in the Hamiltonian equations are obtained from the parameters of pure metals. The Sutton-Chen interaction potential above is adopted by Rafii-Tabar and Sutton (1991) to a random fcc alloy model in which sites are occupied by two types of atoms completely randomly, such that the alloy has the required average concentration. The equilibrium lattice parameter $a^*$ at 0K of the random alloy is chosen as the universal length scale and the expectation value $E^t$ per atom of the interaction Hamiltonian is given as a function of $a^*$. Rafii-Tabar and Sutton (1991) determined the value of the equilibrium lattice parameter for the random alloy, and calculated elastic constants and the enthalpy of mixing by the *static*-lattice summation method. Once $a^*$ is found the enthalpy of mixing $\Delta H$ per atom at 0K are also obtained from

$$\Delta H = E^t - c_A E^A - c_B E^B$$

where $E^A$ and $E^B$ are the cohesive energies per atom of the elemental $A$ and $B$ metals and the constants are such that $c_A + c_B = 1$.

The Molecular Dynamics(MD) and Monte Carlo(MC) simulation methods (Allen and Tildesley 1987) have long been very important in studying statistical mechanics of many-body systems. In recent years, these methods have increasingly been used in studying more realistic problems to investigate the properties and behaviour of these systems at elevated temperatures and pressures/applied stresses (Çağın 1988a,1988b), in contrast to lattice dynamics and minimization.

The algorithmic advances in the late 1980's have enabled researchers to simulate the dynamics of open systems for studying the phase equilibria (Çağın 1989). This is especially important for our goals; for instance the phase segregation in metal alloys is one of the key problems in the development of advanced high-performance metallic alloys.

In order to investigate the effect of temperature and concentration on the physical properties of random alloys, we use molecular dynamics method to calculate the enthalpy of mixing, the density and the elastic constants at

six different atomic concentrations $(0, 20, 40, 60, 80,$ and $100\%$ of Rh in Pt-Rh alloy) at temperatures ranging from $T = 300K$ to $T = 1500K$ with $200K$ increments. In contrast to static lattice sums, molecular dynamics inherently takes into account the anharmonic effects in computed physical properties.

In the following, we present the expressions specific to these many-body potentials which are used in the computations. The many-body force on atom $i$ along a direction $a(= x, y, z)$ is given as:

$$F_{ai} = -\frac{D}{2}(\sum_j^* u'(r)\frac{r_{ija}}{r_{ij}} - \frac{c_i}{2}\frac{\sum_j^* \phi'(r)\frac{r_{ija}}{r_{ij}}}{\rho_i}),$$

where $'$ denotes $\frac{\partial}{\partial r}$ and $*$ signifies the exclusion of $i = j$ from the sums. The anisotropic stress tensor including the contribution from the many-body potential is calculated from

$$\Omega P_{ab} = \sum_i \frac{p_{ia}p_{ib}}{m_i} - \frac{D}{2}\sum_i(\sum_j^* u'(r)\frac{r_{ija}r_{ijb}}{r_{ij}} - \frac{c_i}{2}\frac{\sum_j^* \phi'(r)\frac{r_{ija}r_{ijb}}{r_{ij}}}{\rho_i}),$$

The potential energy contribution to the elastic constants, the hypervirial tensor $\chi_{abcd}$, is given as

$$
\begin{aligned}
\Omega\chi_{abcd} \quad = \quad & \frac{D}{2}\sum_i(\sum_j^*(u'' - \frac{u'}{r_{ij}})\frac{r_{ija}r_{ijb}r_{ijc}r_{ijd}}{r_{ij}^2} \\
& -\frac{c_i}{2}\frac{\sum_j^*(\phi'' - \frac{\phi'}{r_{ij}})\frac{r_{ija}r_{ijb}r_{ijc}r_{ijd}}{r_{ij}^2}}{\rho_i} \\
& +\frac{c_i}{4}\frac{(\sum_j^* \phi'\frac{r_{ija}r_{ijb}}{r_{ij}})(\sum_k^* \phi'\frac{r_{ikc}r_{ikd}}{r_{ik}})}{\rho_i^3}).
\end{aligned}
$$

In our computations at each concentration and at each temperature we have first determined the zero strain state, $h_o$, of the system by performing constant-temperature and constant-stress simulations (NPT) at zero stress. This yields the reference shape and size matrix, $h_o$ in the Parrinello-Rahman (1980) formalism. In determining the elastic constants, this reference state is used in constant-temperature and constant-volume simulations (NVE) of

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50000 steps for each state point. The elastic constants are evaluated using the following statistical fluctuation formulas (Çağın and Ray 1988)

$$C^T_{abcd} = -\frac{\Omega_o}{k_B T}(< P_{ab}P_{cd} > - < P_{ab} >< P_{cd} >)$$
$$+\frac{2Nk_B T(\delta_{ac}\delta_{bd} + \delta_{ad}\delta_{bc})}{\Omega_o} + < \chi_{abcd} >$$

where $<>$ denotes the averaging over time and $\Omega_o = det h_o$ is the reference volume for the model system.

We use the program Simulator developed by Çağın that employs the state of the art MD algorithms based on extended Hamiltonian formalisms emerging from the works of Anderson(1980), Parrinello and Rahman(1980), Nosé(1984), Hoover(1985) and Çağın and Pettitt(1991a,1991b). We used a 500-atom cubic system and the simulation started with atoms randomly distributed on a fcc lattice. The system is thermalized starting from 1K to the target temperature using constant-enthalpy and constant-pressure (NHP) ensemble by slowly heating while scaling velocities to increment the temperature of 1K/step over the specific number of steps depending on the target temperature. This is followed by strict velocity scaling at each target temperature. We then performed NPT dynamics at this temperature for 20000 steps to calculate the volume, density and enthalpy of the system for each concentration. The resulting zero-strain averaged matrix $< h_0 >$ is used in calculating elastic constants over 50000 steps of NVE dynamics. A fifth-order Gear predictor-corrector algorithm is used with $\Delta t = 2$ fs. The Parrinello-Rahman piston mass parameter is chosen as W=400 and in NPT runs the Nosé-Hoover parameter is set to Q=100.

## 3. Results and Discussion

Here we present molecular simulation results obtained for the Pt-Rh alloy. We calculated the density and volume of 500 atoms and enthalpy of mixing for Pt-Rh alloy as a function of percent of atomic concentration of rhodium. We have done the simulation under isothermal-isobaric condition (NPT) at temperatures ranging from 300K to 1500K with 200K increments.

In Figure 1, the density and enthalpy at six different atomic concentration values $0, 20, 40, 60, 80, 100\%$ of Rh in Pt-Rh alloy are given. At the end points we found the density for Rh and Pt to be $12.3g/cm^3$ and $21.2g/cm^3$, respectively, at 300K. These values show approximately 1.5% deviation from the experimental values $12.45g/cm^3$ and $21.50g/cm^3$. In Figure 2 we have drawn the calculated enthalpy of mixing with respect to atomic concentration of Rh in Pt-Rh alloy at two temperature values of 300K and 1500K.

We also studied the thermal expansion behaviour of the Sutton-Chen potential that we use. The percent change in the lattice parameter at each temperature (the lattice parameter at 300K is used as the reference) are given in Table 2. Comparison with the experiment indicate that for Pt the theoretical thermal expansion coefficient is approximately twice that of the experimental value while for Rh it is around 1.3 higher.

In Figure 3 the elastic constants of Pt-Rh alloy at six different concentration values are shown. In order to see the effect of temperature, we repeated the drawing at three different temperatures (300K, 900K, 1500K). Thermal softening of the alloy is observed as the temperature increases. In Figure 4 the calculated bulk modulus values at the same temperatures are shown.

In our calculations at each concentration and at each temperature we have first determined the zero-strain state of the system by performing constant-temperature and constant-stress simulations. In determining the elastic constants this reference state is used in constant-temperature, constant-volume simulations of 50000 steps for each state point. Comparison with experimental results is possible only at the end points where Pt or Rh is pure. This we have done in Table 3. The static results of Sutton and Chen(1990) are also given to facilitate comparison.

To summarize, the potentials used in the present dynamic simulations take account of the anharmonic effects and give reasonably accurate description of the thermodynamic properties and the elastic constants of Pt-Rh alloys. The system is quite stable and the sign of the enthalpy of mixing is correct at all concentration values. For the concentrations and temperatures at which we performed our simulations we found that mixing is enthalpically favourable.

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Table 1: The interaction potential parameters for Pt and Rh.

| a ($\mathring{A}$) | $D$ ($10^{-2}$ eV) | c | m | n | metal |
|---|---|---|---|---|---|
| 3.92 | 1.98330 | 34.428 | 8 | 10 | Pt |
| 3.80 | 0.49371 | 145.658 | 6 | 12 | Rh |

Table 2: The percent change in the lattice parameter from simulation and experiment. The changes are computed using the 300K lattice parameters from simulation and experiment as reference, respectively.

| T (K) | Pt | | Rh | |
|---|---|---|---|---|
| | This work | Experiment | This work | Experiment |
| 500 | 0.35 | 0.18 | 0.26 | 0.18 |
| 700 | 0.73 | 0.38 | 0.54 | 0.39 |
| 750 | 0.83 | 0.42 | 0.61 | 0.46 |
| 900 | 1.14 | 0.59 | 0.83 | 0.61 |
| 1000 | 1.36 | 0.70 | 0.98 | 0.73 |
| 1100 | 1.59 | 0.81 | 1.13 | 0.84 |
| 1300 | 2.10 | 1.04 | 1.46 | 1.11 |
| 1500 | 2.72 | 1.29 | 1.80 | 1.38 |

Table 3: Elastic constants and bulk modulus of Pt and Rh. All values are in units of eV A$^{-3}$. At each entry, the first number gives the molecular dynamics simulation result at 300K. The second number in round brackets is the corresponding experimental value at 0K, while the third number in square brackets is the statically calculated value from Sutton and Chen (1990) at 0K.

| | $C_{11}$ | $C_{12}$ | $C_{44}$ | $B$ |
|----|----------|----------|----------|-----|
| Pt | 1.81(2.23)[1.96] | 1.50(1.59)[1.61] | 0.41(0.48)[0.46] | 1.60(1.80)[1.73] |
| Rh | 2.01(2.63)[2.12] | 1.39(1.20)[1.45] | 0.82(1.21)[0.89] | 1.60(1.68)[1.68] |



(a)
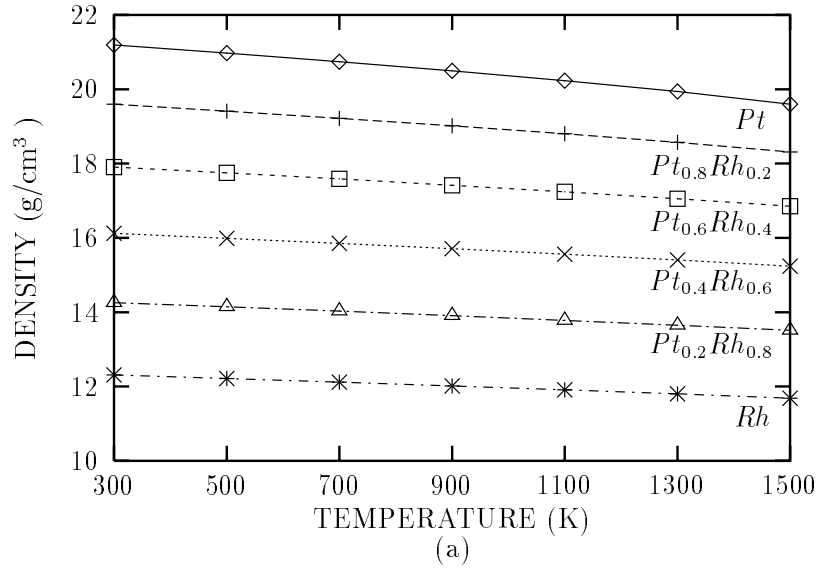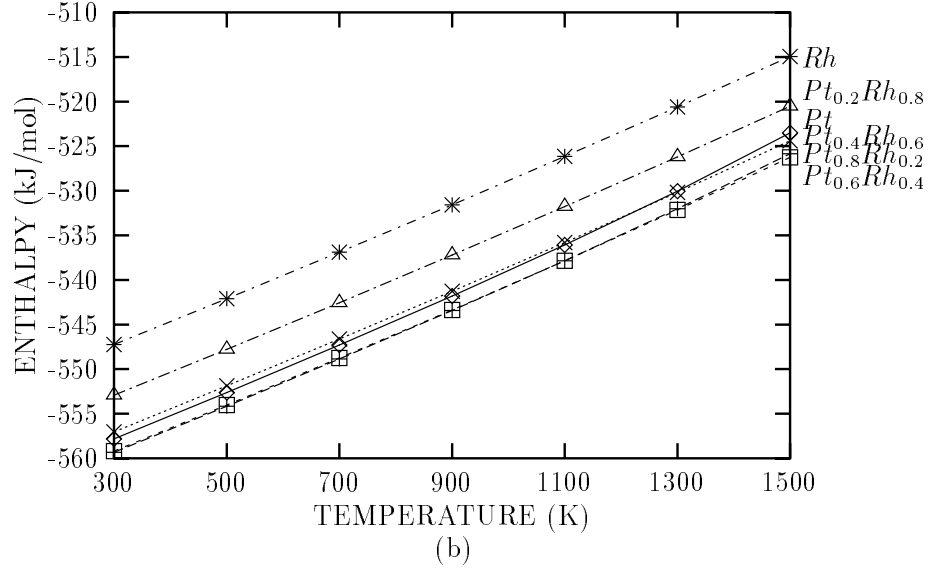
Figure 1: (a) Density and (b) enthalpy as a function of temperature at different atomic concentrations of Rh in Pt-Rh alloy.
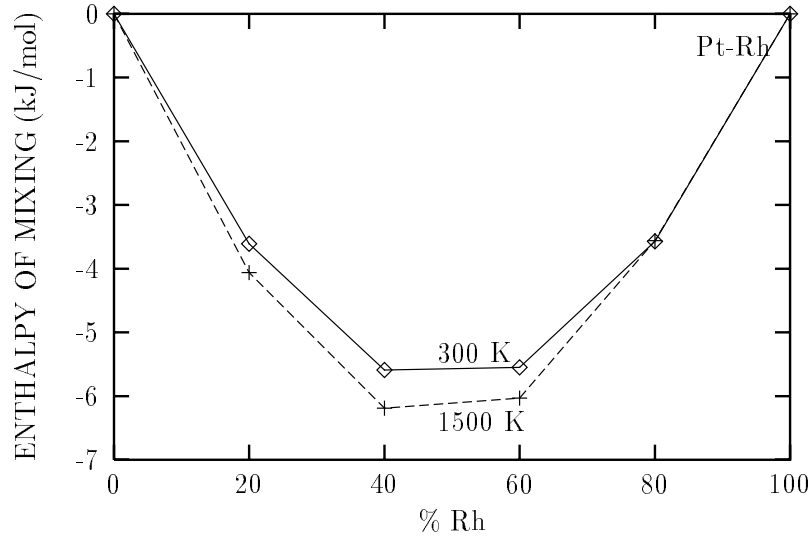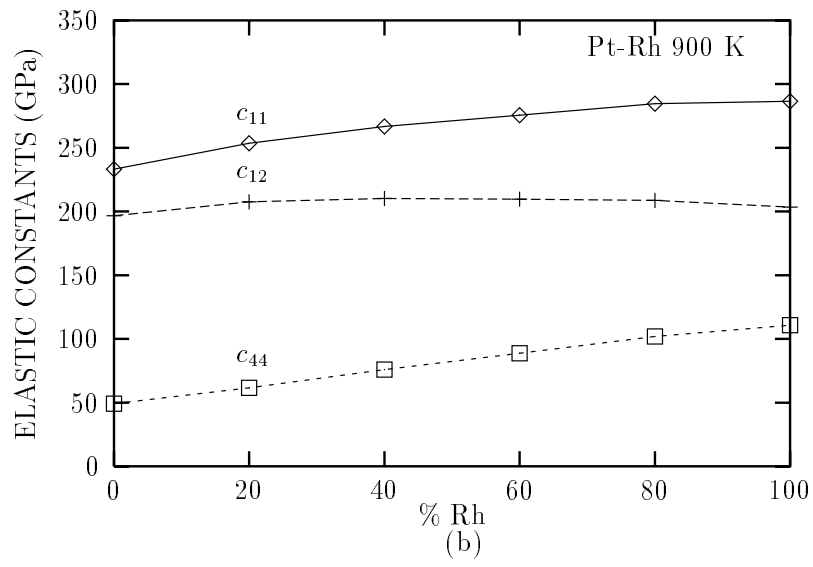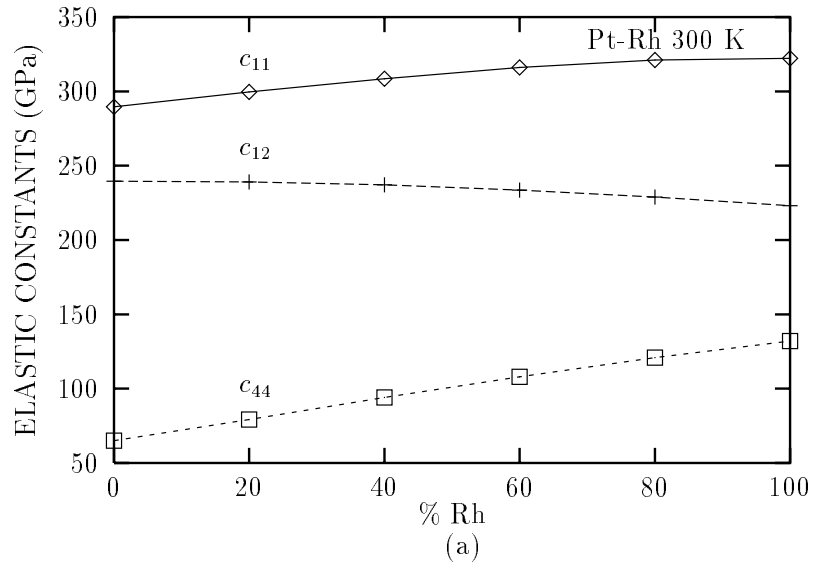


Figure 2: Enthalpy of mixing as a function of atomic concentration of Rh in Pt-Rh alloy at two different temperatures.
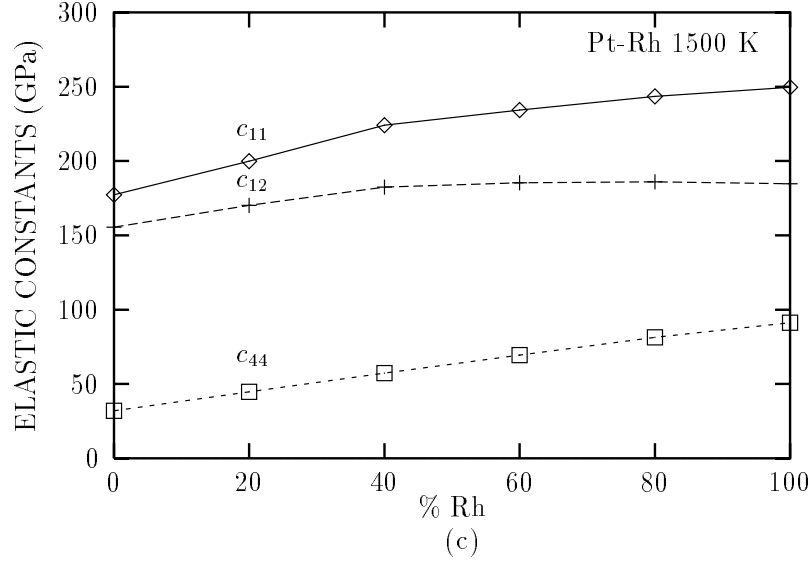
(a)



(b)

Figure 3: (a)-(b)-(c) Elastic constants as a function of atomic concentration of Rh in Pt-Rh alloy at three different temperatures
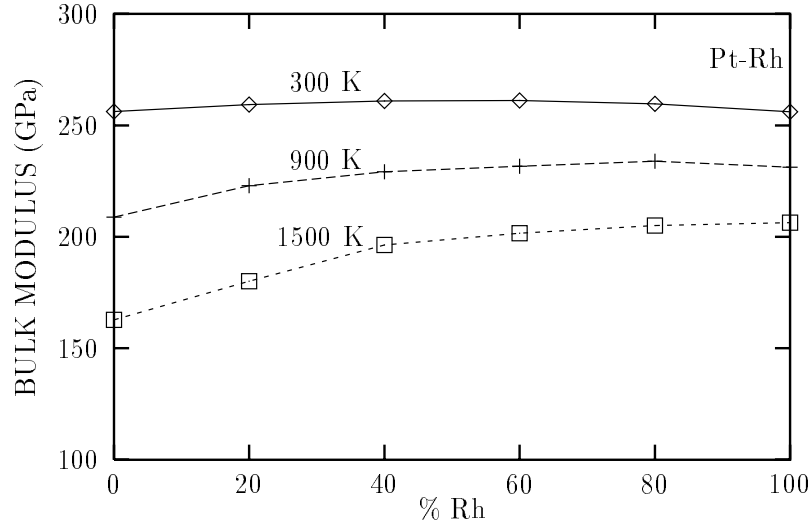


Figure 4: Bulk modulus as a function of atomic concentration of Rh in Pt-Rh alloy at three different temperatures.

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