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High-temperature EXAFS study of solid and liquid rhodium

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Accurate EXAFS spectra of solid and liquid rhodium at very high temperature were recorded at the E.S.R.F. (BM29, Grenoble) The short range $g(r)$ was determined using reliable EXAFS data-analysis methods based on *ab-initio* multiple scattering calculations. Experimental results were compared with molecular-dynamics (MD) calculations. The first neighbor distribution departs from a simple Gaussian model, even at moderate temperatures in the solid phase.

Keywords: XAFS; GNXAS; ANHARMONICITY; LIQUID; METALS.

1. Introduction

Recently developed advanced data-analysis methods of the x-ray absorption fine structure (XAFS) using *ab-initio* multiple scattering calculations showed to give reliable information on the local structure of ordered and disordered systems (GNXAS, see ref. Filipponi *et al.*, 1995 and Filipponi & Di Cicco, 1995). In particular XAFS is a powerful technique to determine the shape of the first peak of the pair distribution function which is directly related to the short range part of the interatomic potential. Here, we report about structural results of solid and liquid rhodium. These results are compared with those obtained by MD simulations. The MD simulations are performed by using realistic expressions for the interatomic potentials based on pair functional (Carlsson, 1990) developed in recent years for transition metals. Two different functional forms containing a square-root (1/2Ros) (Cleri & Rosato, 1993) or a 2/3 dependence (Guevara *et al.*, 1995) from the effective coordination were used. Two different 2/3 models have been proposed, hereafter labeled as 2/3Gue-f1 and 2/3Gue-f2. The first-neighbor distribution in liquid Rh, never measured before, was accurately reconstructed from EXAFS data and compared with the one provided by MD simulation of liquid Rh at 2500 K.

2. Experimental and data analysis

X-ray absorption measurements near the Rh K-edge were performed in transmission mode using ionization chambers at the E.S.R.F. beamline BM29. BM29 offers numerous advantages (Filipponi *et al.*, 1998) as an excellent flux and energy resolution due to the high brilliance of the source. BM29 is equipped with a double-crystal Si (311) fixed exit monochromator, which allows to obtain an energy resolution of about 0.5 eV at 23 KeV. Suitable samples of Rh were prepared mixing and pressing into pellets ammonium-hexachlororhodate fine powder (99.999 %) with different inert matrices (Filipponi & Di Cicco, 1994): in particular, pure liquid rhodium was successfully measured using an HfO_2 matrix and a W crucible at 2240 K. Afterwards, the Rh salt was decomposed and reduced by an *in-situ* heat treatment into micrometric size metallic grains. Low noise EXAFS spectra as a function of temperature are reported in Fig. 1, starting from room temperature (298 K) up to 2240 K, above the melting point. EXAFS spectra of Rh at various temperatures were analyzed using multiple-scattering (MS) calculations in the framework of an *ab initio* data-analysis method (GNXAS) (Filipponi *et al.*, 1995 and Filipponi & Di Cicco, 1995). GNXAS is based on an n-body expansion of the x-ray absorption cross-section where only the lower terms are retained. In fact, we considered only two-body ($\gamma^{(2)}$) and three-body ($\gamma^{(3)}$) MS contributions. Data analysis was performed taking into account into the atomic background the opening of the [1s4p], [1s3d] and [1s3p] double-electron excitation channels. They occur at about 65, 340 and 520 eV above the edge respectively (Filipponi & Di Cicco, 1995). Using the GNXAS method, the structural analysis is performed by optimizing the agreement between a model absorption and the experimental signals.

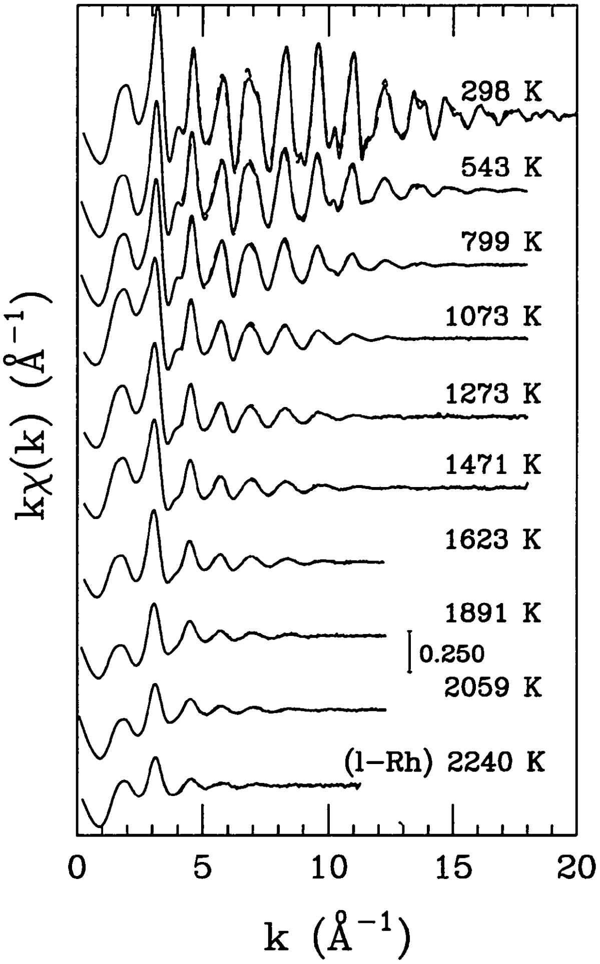

Figure 1
Best fit (dashed) of experimental EXAFS data (solid line) of solid (at temperatures ranging from 298 K up to 2059 K) and liquid (at 2240 K) rhodium using model model signals obtained from *ab initio* calculation based on multiple scattering theory. An excellent agreement between experimental and calculated signals can be observed at all temperatures.

In Fig. 1 we report the comparison between best-fit multiple scattering calculations and raw EXAFS $k\chi(k)$ structural signals in the whole temperature range of the experiment. The agreement is excellent and only at 298 K a small difference between theoretical and experimental signals can be appreciated.

3. Results

Refinement of the model signals permits an accurate determination of first-neighbor average distances R, bond variances σ^2 and skewness β. In Fig. 2, we report R, σ^2, β for the first shell obtained from MD simulation of solid rhodium compared with XAFS experimental results (data with error bars).

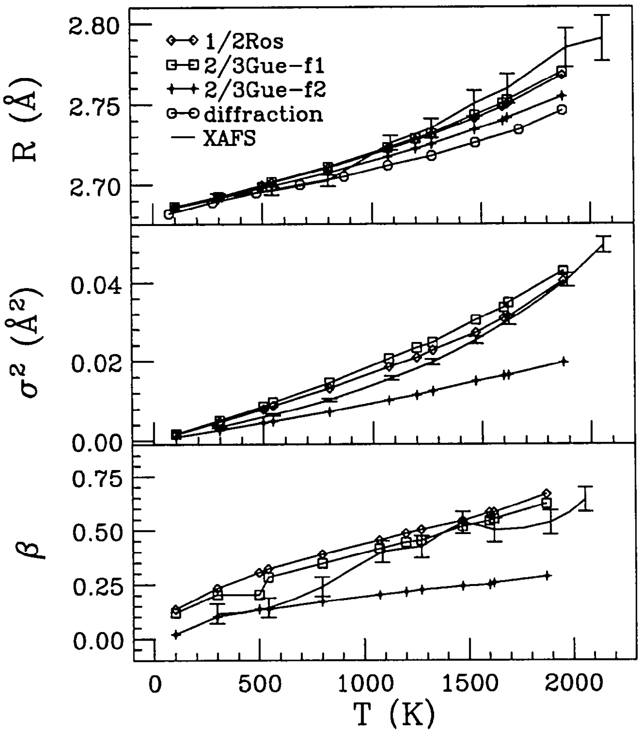

Figure 2
First-shell distance R, variance σ^2 and skewness β of solid Rh as a function of temperature obtained from XAFS data analysis (data with error bars) compared with those determined from MD simulations and measured by diffraction.

The elongation of the average distance with respect to the cell parameter $a = \sqrt{2}R$, measured by diffraction, as a function of the temperature, is a normal effect. In fact, XAFS measures the interatomic distance including the vibrations perpendicular to the bond direction and the same structural quantity has been computed by MD simulations. The first-neighbor variance at high temperature is in a quite good agreement with MD results, using 1/2Ros and 2/3Gue-f1 models. The vibrational amplitudes are highly underestimated by using 2/3Gue-f2 potential. This is also confirmed looking at the parameter β vs. temperature, which is connected to the anharmonic character of the atomic vibrations. β starts to be substantially different from zero for temperatures greater than 500 K.

In Fig. 3, we report the first peak of the $g(r)$ as a function of temperature. The broadening of the first peak of the pair distribution function is related to the increase of structural disorder, and with the low degree of correlations between atoms.

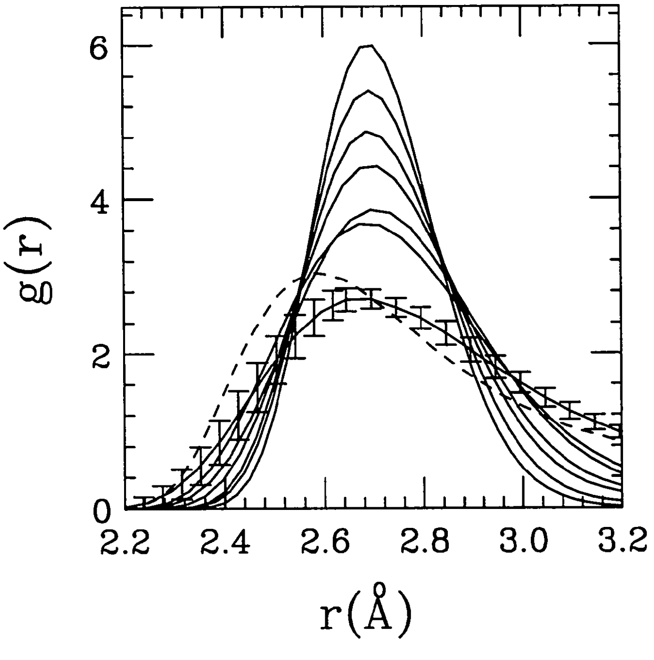

Figure 3
First peak of $g(r)$ of solid Rh at temperatures from 1073 K up to 2240 K reconstructed by XAFS (solid lines). First peak of $g(r)$ of pure liquid Rh at 2240 K (data with error bars) compared with that obtained from MD simulation (dashed curve).

We also report the $g(r)$ of pure liquid Rh (with error bars) compared with that obtained from MD simulation performed at 2500 K (dashed curve). Note the shift toward longer distances ($\approx$ 0.1 Å) of the first peak with respect to MD results. Full report of the experiment on liquid Rh will be given elsewhere (Di Cicco *et al.*, 1998).

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