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STRUCTURAL STUDIES OF THE LIQUID Rb-RbBr SYSTEMS BY XANES

J.F. JAL, J. DUPUY and A. SADOC

Département de Physique des Matériaux, Université Claude Bernard, F-69622 Villeurbanne Cedex, France
LURE (CNRS, CEA, MEN), Bâtiment 209D, Université Paris-Sud, F-91405 Orsay Cedex, France

Résumé

- Une étude XANES du seuil d’absorption K du brome est reportée pour le système fondu Rb/RbBr en fonction de la concentration.

Abstract

- A XANES study above the Br K absorption edge of the molten Rb/RbBr system is reported versus concentration.

I - INTRODUCTION

A large amount of work has already been devoted to the structural investigation of metal-molten salt solutions. As a matter of fact the molten salt mixture problem provides an excellent testing ground for theories of liquids. Recently, a neutron investigation\(^1\) of the structural order in Rb\(_x\)(Rb\(_{1-x}\)Br) solutions has shown how little the short range correlations of the pure salt are perturbed by the addition of metal, even up to about 40 % metal. On the other hand for the metal rich side, the introduction of small amounts of salt considerably alters the pure metal short range correlations. A different approach is taken here by studying the Rb-RbBr system versus concentration using XANES. A preliminary report\(^2\) has yet been made for Rb\(_{0.8}\)(RbBr)\(_{0.2}\).

II - EXPERIMENT

Rb\(_x\)(RbBr)\(_{1-x}\) samples were prepared for \(x=0, 0.2, 0.4, 0.5, 0.6, 0.8\) by sputter deposition on the windows of a high temperature cell. Silica was chosen for these windows in order to avoid the strong chemical reactivity of the materials and due to its transparency in the X-ray domain.
Each silica window was 0.5 mm thick; this was a compromise for thinner windows have the disastrous tendency to crack during the heating (or even before) and thicker windows absorb more of the X-ray beam.

The experiments were carried out at LURE (DCI) with the EXAFS-1 spectrometer using a Si (220) channel cut monochromator. The EXAFS spectra of RbBr were measured versus temperature from room temperature up to the melting point ($T_m = 692\,^\circ C$). For liquid Rb$_x$(RbBr)$_{1-x}$, the spectra were taken above the melting point ($T_m \sim 631 \, ^\circ C - 670 \, ^\circ C$ for $x$ varying from 0.8 to 0.1). Both the Br (13 475 ev) and Rb (15 201 ev) K-absorption edges were recorded one after another but up to now we have just analyzed the Br edge.

III - DATA ANALYSIS

The normalized $\chi(k)$ oscillations for RbBr are plotted in figure 1 at room temperature and in the liquid state, at 700 °C. The effect of thermal disorder shows up immediately since, at 700 °C, the oscillations decrease very rapidly versus the energy so that they completely disappear about 150 - 200 eV above the edge. Therefore a XANES (X-ray Absorption near Edge Structure) study was necessary for these liquid systems.

The Fourier transforms (FT) of the $k\chi(k)$ spectra were done using the same window (10-190 eV) for all the concentrations (figure 2). They exhibit mainly one peak. intensity and position of which do not vary much in all the domain of concentrations (0.1 - 0.8). Therefore the local order around a Br atom appears almost identical whatever the concentration may be. This corroborates the neutron diffraction study.

![Figure 1. Experimental XANES and EXAFS spectra above the Br edge in RbBr compared (a) in the solid state at room temperature and (b) in the liquid state at 700 °C](image-url)
A detailed analysis of the main peak has been done for liquid RbBr and Rb$_{0.8}$(RbBr)$_{0.2}$. The peak was isolated and backtransformed into k space where the inverse FT was fitted using the single scattering formula. The room temperature spectrum of pure RbBr was used as a reference to extract experimental amplitudes and phase shifts and to determine the relative value of the disorder parameter $\sigma$.

The main peak was found to be due to Rb backscatters at similar distance in liquid RbBr and Rb$_{0.8}$(RbBr)$_{0.2}$. The number of Rb neighbours can be evaluated roughly to be about 6 ± 0.5 in the pure salt ($\Delta\sigma = 0.20 \pm 0.03$ Å) and 4 ± 0.5 in the mixture ($\Delta\sigma = 0.11 \pm 0.03$ Å). As $k_m$ is about 1.5 Å$^{-1}$ and $\sigma$ about 0.25 Å, the criterion $k_m\sigma<1$ is fulfilled ($k_m\sigma \approx 0.37$). This criterion estimates the minimum accessible photoelectron k value for which the determination of the first shell is allowed in highly disordered materials without taking into account any multiple scattering effect.

We are now analyzing the Rb edge in order to study the effect of the salt addition to the metal structure.
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