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Abstract

L_{III}-XANES measurements of Sm in an inert Ar-matrix show a continuous increase of the Sm valence with increasing Sm concentration. A sharp transition region is observed near $c = 1:100$ where the valence steeply rises from 2.05 to a breakpoint $v = 2.6$. Tempering of a matrix results in a rise of the valence. There is strong evidence that the Sm-Sm interaction in small clusters is responsible for the valence change.

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1. Introduction

From X-Ray Absorption Near Edge Structure (XANES)-measurements of pure Sm at the L_{III}-edge Materlik et al. (1) have shown that bivalent (atomic) and trivalent (solid) states of Sm can easily be distinguished by the white line shift of ∿ 7 eV. This fact can be used to determine the valence in mixed-valence systems by evaluating the peak heights or peak areas of the corresponding white lines. Up to now, valence changes in Rare Earths have been performed by changing the chemical environment, by inducing high pressure to force a phase transition or by temperature changes.

In this paper we describe a novel approach to mixed-valence systems by trapping Sm atoms in a chemical inert Ar-matrix with Sm concentrations from 1:15 to about 1:500. Because Ar has no chemical reaction with Sm, the results can only be due to Sm-Sm interactions or cage effects. It is shown that every valence between 2.0 and 2.8 can be produced in this range of concentrations. Furthermore, irreversible changes of the original valence in a matrix sample occur by tempering the matrix to temperatures near the boiloff-point of Ar.

2. Description of the experiment

The absorption measurements have been performed at the EXAFS II beam line of the Hamburg Synchrotron Radiation Laboratory HASYLAB. Details of the beam line are described by Malzfeldt et al. (2).

A Si111 double-crystal monochromator was used with an energy resolution of ∿ 2 eV at 6.7 keV. Using three ionization chambers in a row with two sample chambers placed between them the absorption measurements of the matrix and of a reference sample are done simultaneously. The reference sample (Sm_2O_3) is needed for an exact energy calibration which is independent of varying beam conditions.

The matrix is prepared in a UHV sample chamber at a residual pressure $p = 10^{-8}$ Torr. On a thin (∿ 1000 Ångström) Aluminium foil cooled down to 5 K by a liquid Helium cryostat Ar and Sm are co-deposited with constant deposition rates which are monitored by a quartz crystal (for Sm) and by the Ar-pressure in the sample chamber. Typical parameters are 0.2 Ångström/sec for the Sm rate and an Ar-pressure of 10^{-4} - 10^{-5} Torr which corresponds to ∿20 Ångström/sec. Various concentrations M/R (=matrix/radical) are produced by changing the Ar-pressure. The deposition rates are calibrated by comparing absorption measurements with known cross-sections. In a typical preparation time of 3 h a Sm thickness of 1500 Ångström is achieved.

Every sample has been tempered at a series of distinct temperatures converging to the boiloff-temperature of Ar. Each temper stage had a duration of 5 min., and afterwards the sample was cooled down again to avoid additional effects by the heat load of the x-ray beam.

3. Results

Figure 1 shows the L_{III}-absorption spectra of atomic Sm (from Ref. (1)) and of various concentrations M/R at the original temperature 5 K. For comparison, a spectrum of solid Sm is added. The energy is calibrated to 6.716 keV at the maximum of the L_{III}-white line of the reference sample Sm_2O_3. An appropriate background polynomial has been subtacted from the original data.

Using a least squares technique, the valence of each matrix is easily computed by fitting a linear combination of atomic and solid Sm spectra to the data. The accuracy of this procedure is estimated to be better than $\Delta v = 0.05$.

In figure 2 the Sm valence of the original samples at 5 K is drawn versus the concentration on a logarithmic scale. At low Sm concentrations (M/R = 400) a nearly bivalent behaviour is observed. The Sm valence increases monotonically with increasing concentration. In the vicinity of M/R = 140 a sharp rise of the valence from 2.05 to 2.6 is observed within a concentration range of factor 2. The steep rise of the valence ends at M/R = 100 reaching a breakpoint v = 2.6. At higher concentrations, the valence shows a slow increase but does not reach the value of 3 at M/R = 6. The breakpoint v = 2.6 agrees with the valence which is associated to a first order volume collapse at ∿7.5 kbar by high pressure experiments in SmS by Röhler et al. (3). The valence transition in the M/R range 100-200 occurs at those concentrations where Moskovits and Hulse (4) observed efficient small-cluster production (2-5 atoms) by optical spectroscopy of Cu in Ar. As there are general trends for cluster formation in matrices as a function of impurity concentration similar cluster aggregation is expected in the case of Sm. Nonmetal-to-metal

transitions in matrices occur at much higher concentrations (∿ 3:1) as shown by Berggren et al. (5). If Sm atoms are trapped into a Ne matrix, the observed absorption spectra are nearly identical to those of Sm in Ar.

Additional effects are visible by tempering a sample. In figure 3 the absorption of a sample with M/R = 200 is shown at different temper stages in parts a - d. The following spectra e - h are due to a M/R = 130 sample. Note, that with two samples only, the valence range from 2.05 to 2.8 is scanned by temper effects.

As there are drastic valence changes of Sm in one matrix due to the temperature rise we argue that cage effects which have been observed e.g. in the case of Ni in Ar by Breithaupt et al. (6) are of minor importance. The Sm-Sm interactions in small Sm-clusters are believed to be responsible for the observed valence changes.

Although it is nowadays possible to calculate the atomic-to-solid L-level shifts of the Rare Earth elements (see, e.g., J. Herbst (7)) and the X-ray absorption at simple conditions, e.g. the 3d→4f absorption of Ce at zero temperature (Gunnarson and Schönhammer (8)), to our knowledge nothing is known about the absorption properties of Rare Earth clusters. These measurements reveal the necessity of reliable calculations of cluster properties of Rare Earth elements.

Acknowledgement

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Figure Captions

Fig. 1 L_{III}-absorption $\mu \cdot d$ of a) atomic (from Ref. 1) and h) solid Sm and of Sm in Ar with the following concentrations: b) 440:1, c) 200:1, d) 130:1, e) 120:1, f) 55:1 and g) 6:1.

Fig. 2 Sm-valence as a function of the concentration M/R in an Ar-matrix at T = 5 K.

Fig. 3 L_{III}-absorption $\mu \cdot d$ for two matrices at various temper stages: a) 5K, b) 26 K, c) 29 K and d) 34 K for a sample with M/R = 200:1; e) 5 K, f) 29K, g) 34 K and h) 38 K for a sample with M/R = 130:1.

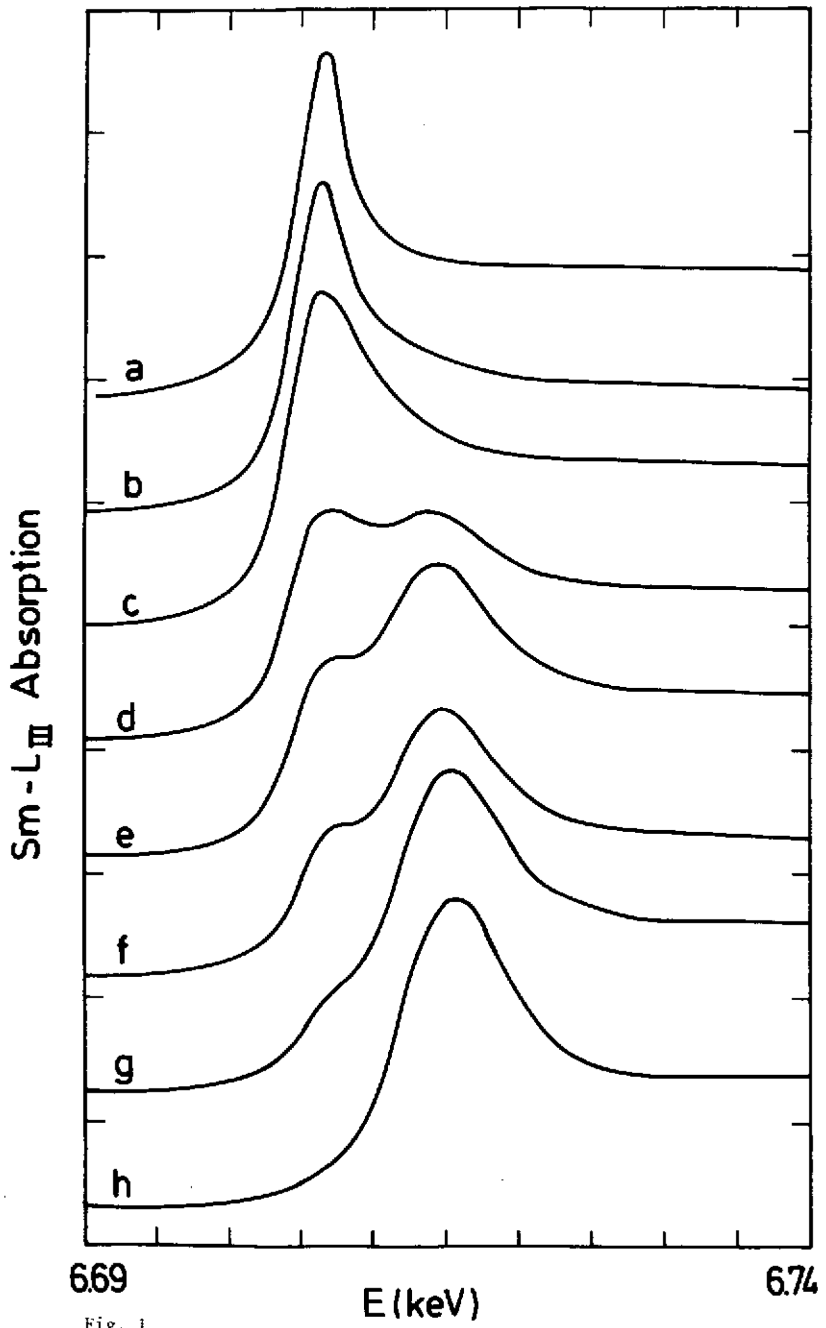

Fig. 1

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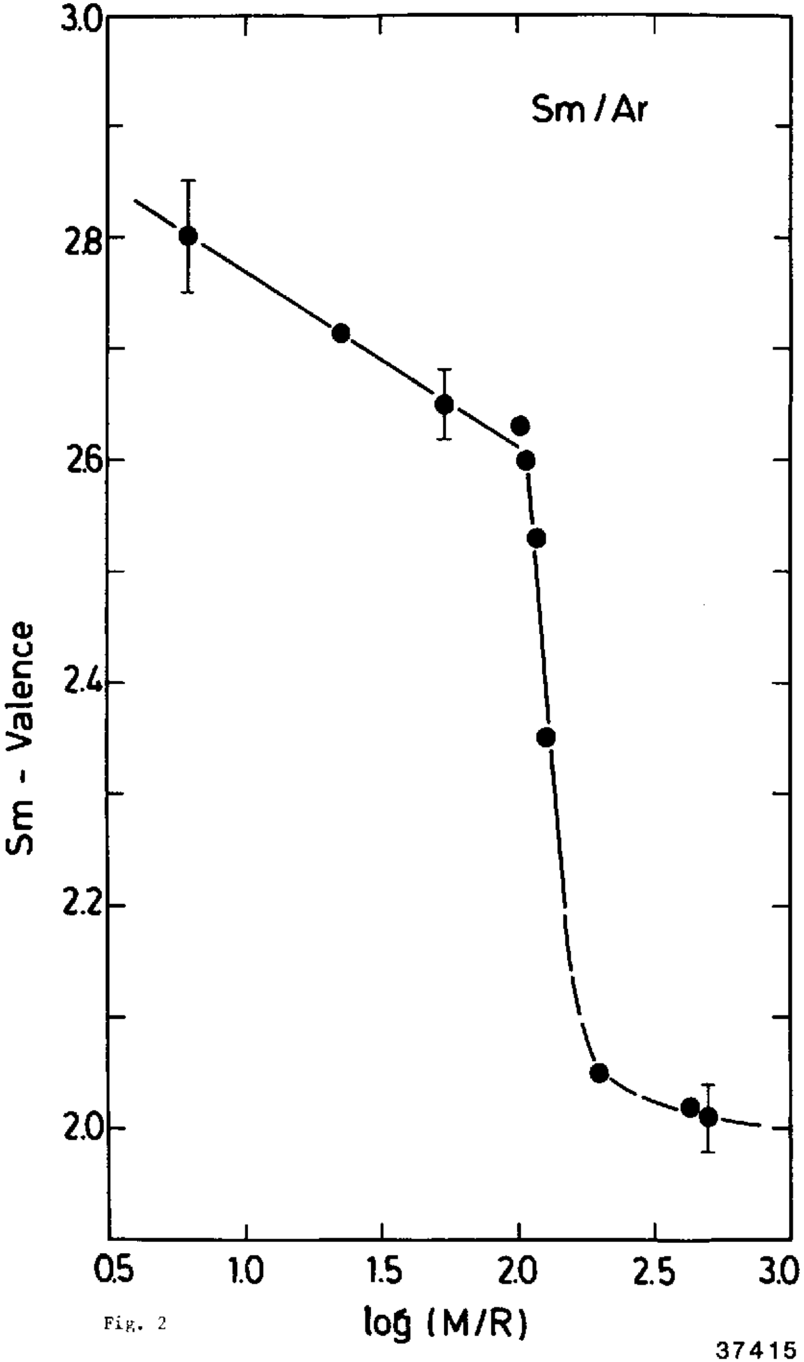

Fig. 2

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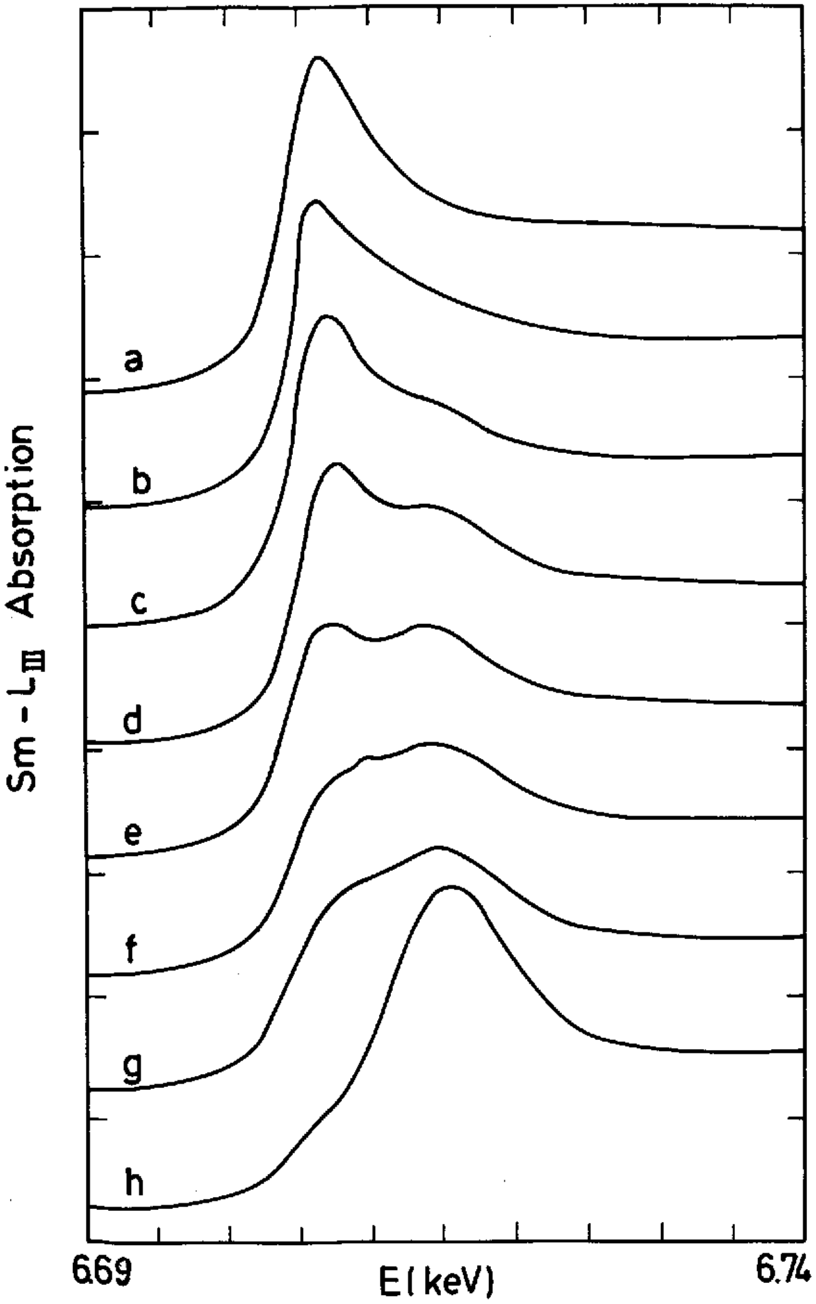

Fig. 3

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