The vibrational properties of Eu_2O_3 nanoparticles as studied by nuclear inelastic absorption

T. Asthalter[1], V. Krishnan[1], O. Leupold[2], H.-C. Wille[2], L. Pasquini[3], E. Bauer[4], P. Müller-Buschbaum[4]

1: Institut für Physikalische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D–70569 Stuttgart, Germany
4: E13 Experimentalphysik, TU München, James-Franck-Str. 1, D–85747 Garching, Germany
3: Dipartimento di Fisica, Università di Bologna e I.N.F.M., I-40127 Bologna, Italy
2: ESRF, B.P. 220, F–38043 Grenoble, France

Motivation

The physical and chemical properties of nanostructured ceramic oxide materials are both of fundamental and technological importance. In particular, the optical properties of rare-earth complexes in sol-gel matrices and of nanosized oxide clusters have been intensively studied, since their luminescence may be used for markers in medical diagnostics [1–3], optical sensors [4], flat-panel displays [5] and many more. The energetically sharp 4f—4f transitions, with wavelengths in the visible range, are particularly suited for that purpose.

It is well known [6] that the luminescence quantum yield of Eu^{3+} complexes is strongly influenced by the chemical environment of the rare-earth ion, since e.g. the presence of O–H oscillators may decrease the lifetime of the excited state by vibronic coupling to the $^5D_0$ — $^7F_2$ transition [7].

Recently, the synthesis of surface-capped cubic Eu_2O_3 nanocrystals was reported, whose luminescence quantum yield increased with decreasing size [8] although the electronic transition is strongly localized on the Eu^{3+} ion and therefore should not be very susceptible to quantum size effects. It was speculated that the surface coating would passivate defects in the crystal wandering from the interior to the surface [8]. Whether such defects are important or not may be successfully investigated by vibrational spectroscopy: in particular by a technique that is sensitive to the only, excluding any matrix or coating vibrations. The novel technique of NIA (nuclear inelastic absorption) fulfills just this requirement.

We have investigated the vibrational density of states (VDOS) of the europium atoms in bulk Eu_2O_3, uncoated n-Eu_2O_3 having an average diametre of 58 nm and coated n-Eu_2O_3 having diametres around 15 nm, respectively.

Moreover, NIA gives access to the VDOS of soft phonons in nanostructured systems, which is of fundamental importance for the understanding of their thermodynamical properties.

The issue of this study was

- to assess the effect of confinement on the VDOS,
- to separate this effect, if possible, from surface effects owing to organic coating,
- to find out whether n-Eu_2O_3 behaves like a harmonic solid with static disorder or whether there are anharmonic effects similar to those in glasses.

The experiment was carried out at the beamline ID22N, working at 21.542 keV primary energy [9]. Data processing was carried out using the program PHOENIX [10].

References

[1] D. Parker, P. Kanthi-Senanayake, J.A.G. Williams, *J. Chem. Soc. Perkin Trans.* 2, 2129 (1998)

[2] B. Alpha, J.-M. Lehn, G. Mehtis, *Angew. Chem. Int. Ed. Engl.* 26, 1266 (1987)

[3] D. Parker, *Coord. Chem. Rev.* 205, 109 (2000)

[4] J.-C.G. Banzli, G.R. Choppin (Eds.): *Lanthanide probes in Life, Chemical and Earth Sciences*, Elsevier, New York 1989

[5] N.A.H. Male, O.V. Salata, V. Christou, *Synth. Met.* 126, 7 (2002)

[6] B.R. Judd, *Phys. Rev.* 127, 750 (1962)

[7] R. Reisfeld, T. Saraidarov, M. Pietraszkewicz, S. Lis, *Chem. Phys. Lett* 349, 266 (2001)

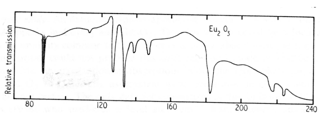
[8] G. Wakefield, H.A. Keron, P.J. Dobson, J.L. Hutchison, *J. Colloid Interf. Sci.* 215, 179 (1999)

[9] O. Leupold, J. Pollmann, E. Gerdau, H.D. Rüter, G. Faigel, M. Tegze, G. Bortel, R. Rüffer, A.I. Chumakov, A.Q.R. Baron, *Europhys. Lett.* 35, 671 (1996)

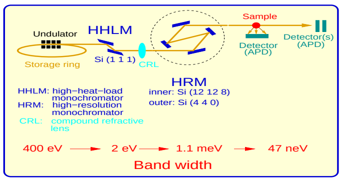
[10] W. Sturhahn, *Hyperf. Int.* 125, 149 (2000)

FIR absorption spectrum of bulk eurpoium oxide

(D.Bloor, J.R.Dean, J.Phys.C: Solid State Phys. 5, 1237 (1972)



Experimental setup for NIA



The formalism

The normalized absorption probability can be decomposed in a multiphonon expansion:

$$W(E) = f_{LM}\left(\delta(E) + \sum_{n=1}^{\infty} S_n(E)\right)$$

The one-phonon term is given by

$$S_1(E) = \frac{E_R \cdot g(E)}{E \cdot (1 - e^{-\beta E})}$$

The multi-phonon terms are given by

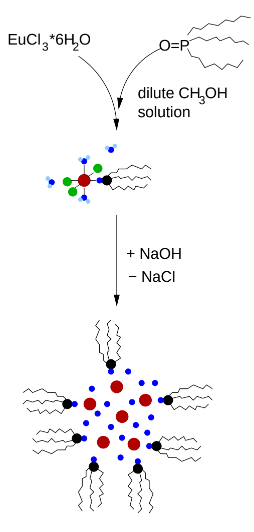
$$S_n(E) = \frac{1}{n}\int_{-\infty}^{\infty} S_1(E')S_{n-1}(E-E')\,dE'$$

g(E) is the normalized density of phonon states:

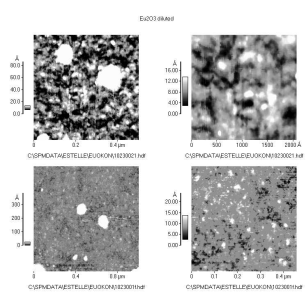
$$g(E) = \frac{V_0}{(2\pi)^3}\sum_j \int d\vec{q}\,\delta\left[E - \hbar\omega_j(\vec{q})\right]$$

β: $k_B T$
k_B: Boltzmann constant
T: temperature
E_R: recoil energy of a free Fe nucleus
V_0: volume of the unit cell
j: index of phonon branch
$\vec{q}$: phonon momentum

Wet−chemical synthesis (after [8])

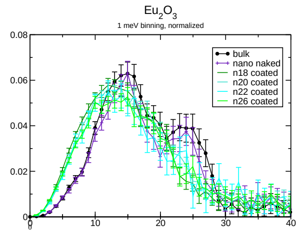


AFM in tapping mode

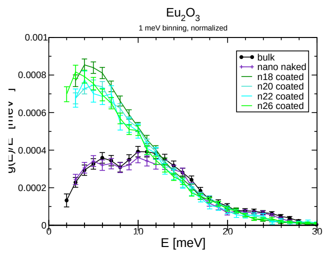


Experimental Results, T = 100 K

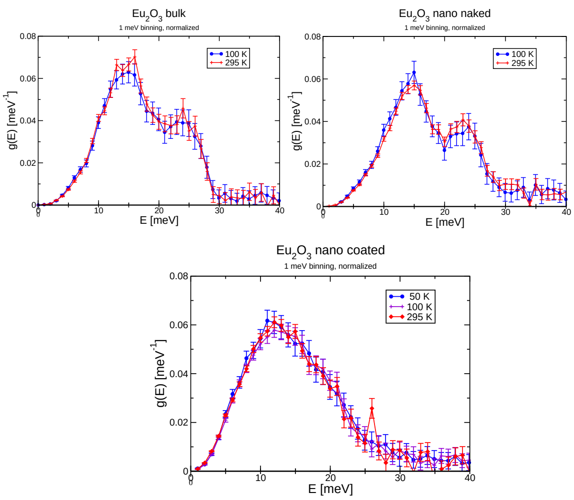
Comparison of bulk and nano VDOS



Reduced VDOS for bulk and nano



Temperature dependence of the VDOS



Conclusion

- 58 nm-confinement does not alter the Eu VDOS significantly – still mostly bulk behaviour
- Suppression of the high-energy bands in favour of soft modes in the coated particles
- VDOS in all investigated systems is entirely independent on temperature: harmonic behaviour even in organically coated nanoparticles
- "Boson peak" that appears in coated nanoparticles is probably connected to static disorder