EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** **Oxygen mobility and soft mode behaviour in $SrFeO_{2.5+x}$**	**Experiment number**: CH-1925
Beamline: ID18	**Date of experiment**: from: 15.05.05 to: 21.05.05	**Date of report**: 01.09.05
Shifts: 14	**Local contact(s)**: **Dr. Aleksandr Chumakov**	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

We used the technique of nuclear inelastic scattering (NIS) of synchrotron radiation to study the local lattice dynamics of the Fe sites in $SrFeO_{2.5}$ and $SrFeO_3$ by employing the ^{57}Fe resonance. The experiments were performed at the beamline ID18. Only 5 shifts of the beamtime were in 16-bunch mode, then we had to change for the 9 other shifts to the 4-bunch mode with considerably lower intensity. For this reason the experiments had to be performed with an energy resolution of 3 meV (and not with 0.5 meV resolution, as asked for in our proposal). The measuring time per NIS spectrum in the 4-bunch mode took around 6 h. In addition to the NIS spectra we recorded simultaneously nuclear forward scattering (NFS) spectra to monitor the magnetic properties of the samples.

The aim of our studies was to look in $SrFeO_{2.5}$ with the Brownmillerite structure for characteristic dynamic properties connected with the high oxygen mobility observed in related systems of this structure with a variety of potential technological applications, for instance in fuel cells [1]. Our interest in $SrFeO_3$ was twofold, first as a Fe^{4+} reference system with the simple perovskite structure and secondly to look for anomalous changes in the phonon modes connected with the magnetic ordering; such a behaviour was recently reported for a closely related Fe^{4+} system [2].

For these reasons temperature-dependent NIS studies were performed on $SrFeO_3$ in temperature range from 15 K to 295 K and on $SrFeO_{2.5}$ from 15 K to 500 K employing a He flow cryostat and, for $SrFeO_{2.5}$, also a special vacuum oven. The samples were prepared with 30%-enriched ^{57}Fe. The structural and magnetic properties of the samples were carefully characterised by XRD and with conventional ^{57}Fe Mössbauer spectroscopy [3].

Fig. 1 shows local phonon density-of-states (DOS) at the Fe sites, extracted from the recorded ^{57}Fe-NIS spectra for $SrFeO_{2.5}$ and $SrFeO_3$ at various temperatures. The DOS spectra of $SrFeO_{2.5}$ shows characteristic spectral features, resulting from the two different (tetrahedral and octahedral) Fe^{3+} sites. Around 7 meV is a characteristic low-energy mode, which is characteristic for tetrahedral Fe^{3+} sites in the Brownmillerite structure. We attribute, in accordance with similar observations in related systems [4], this soft mode with a collective motion of the FeO_4 tetrahedra, which is responsible for the oxygen diffusion mechanism. We observe no dramatic changes of this structure as function of temperature, but, increasing with temperature, a loss of resolution of all spectral features. We attribute this behaviour to the thermal expansion, connected with anharmonic broadening effects of the phonon modes. The quality of the data is demonstrated by the temperature dependence of the derived elastic and thermodynamic parameters. Some of them, the Lamb-

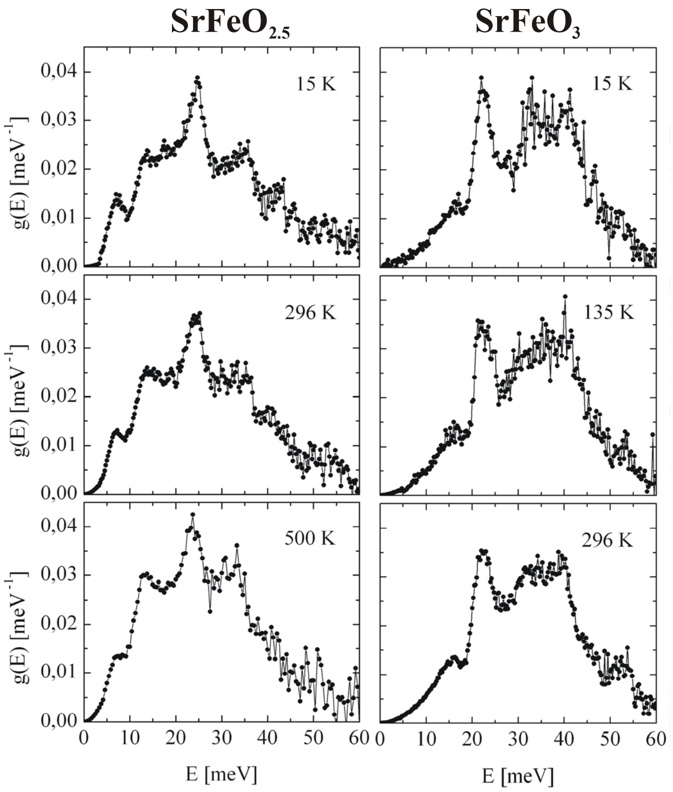

***Fig. 1:** Local [57]Fe density-of-states (DOS) of $SrFeO_{2.5}$ and $SrFeO_3$ at various temperatures.*

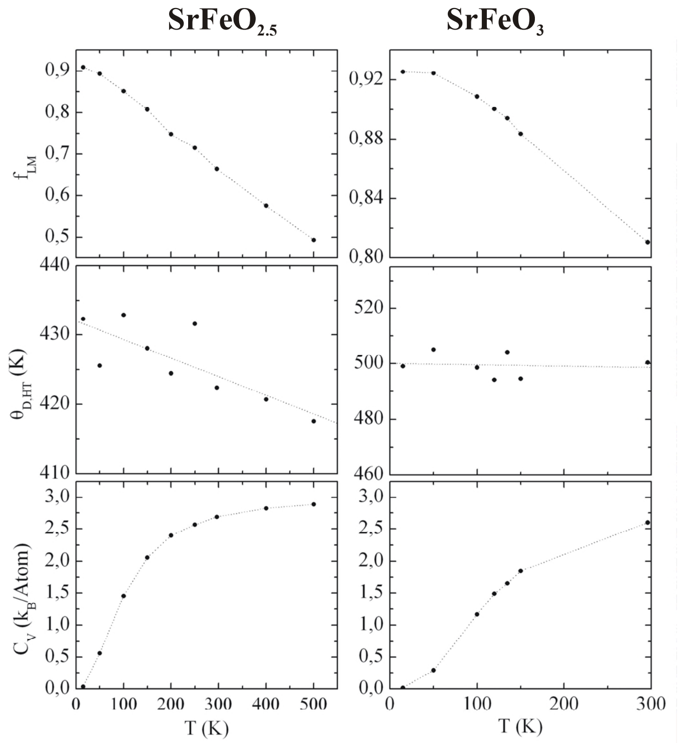

***Fig. 2:** Extracted elastic and thermodynamic parameters derived from the respective DOS: Lamb-Mössbauer factor f_{LM}, high-T Debye temperature $\Theta_{D,HT}$ and specific heat C_v as function of the temperature.*

Mössbauer factor f_{LM}, the high-temperature Debye temperature $\Theta_{D,HT}$ and the specific heat C_v, are shown in Fig.2. Especially the decrease of $\Theta_{D,HT}$ with temperature from 432 K to 418 K reflects nicely the thermal expansion of the lattice. A detailed evaluation of these parameters, especially of the sound velocity, deviating strongly from the Debye model and reflecting the soft-mode behaviour of the tetrahedral sites, is still in progress.

For $SrFeO_3$, the local Fe DOS is quite different from that of $SrFeO_{2.5}$ and exhibited a well resolved (optical) mode at 22 meV, resulting from the high symmetry of Fe^{4+} in the perovskite structure. The DOS spectra exhibit within the temperature range from 15 K to 300 K no spectral changes, as reflected by the constant value of the derived Debye temperature $\Theta_{D,HT}$ = 500 K, expected for Fe^{4+} in octahedral surrounding, which is considerably higher than the ones observed for the Fe^{3+} sites in $SrFeO_{2.5}$. We looked carefully for spectral changes in the DOS around 135 K, the magnetic ordering temperature, and found within 0.5 meV no changes in the spectral features. This is in contrast to the findings on a related system, $Sr_2FeCoO_{6-\delta}$, where from ^{57}Fe-DOS spectra variations as large as 1.5 meV were reported [2].

References:

[1] Z.P. Shao and S.M. Halle, Nature 431, 170 (2004) and references therein.
[2] A.I. Rykov et al., 68, 224401 (2003).
[3] S. Janson and Ch. Urban, Diploma theses, University Paderborn, 2005 (unpublished).
[4] A.I. Rykov et al., Physica B, 350, 287 (2004).