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Report:

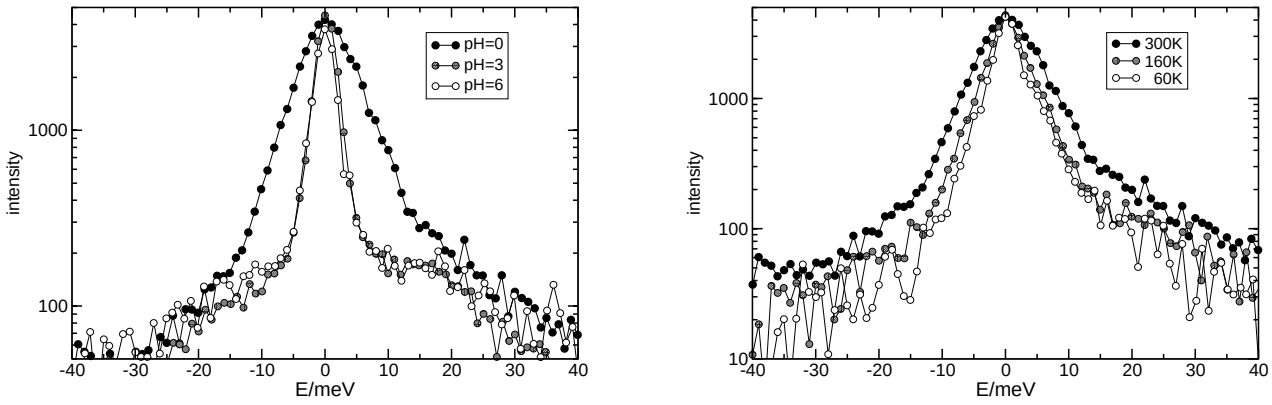
The aim of this proposal was twofold: first, to investigate the diffusion of iron ions in zeolites having one-dimensional channels in order to find, if possible, deviations from normal bulk diffusion, using nuclear inelastic absorption (NIA); second, to attempt a determination of the effective diffusing mass and hence the coordination number of the iron atom via a precise measurement of the recoil shift in the NIA spectra.

For investigations of the scaling behaviour of diffusion in reduced dimensions – similar to the case of investigations of glass dynamics in confined geometry [1] – it is important to minimize the strength and range of the interaction between the diffusing particle and the surrounding matrix so that geometrical constraints prevail over adsorption or chemical bonding effects. Hence, the best choice turns out to be ferrocene, a neutral, almost spherical molecule, rather than polar iron salts, which would adsorb at the inner surface of the zeolite. However, it turned out that samples consisting of large-pore zeolites loaded with a large quantity of enriched ferrocene were not available for the experiment. Therefore, we have chosen another system that has previously been investigated by NIA at room temperature only [2,3], namely aqueous iron salt solutions. Our aims were now:

1. to tackle the second issue of the proposal, by varying the pH of the solution it is possible to influence the degree of aggregation of the solvated Fe ions and hence the effective diffusing mass;
2. to undercool an acid solution down to various temperatures and to investigate whether the data can be described by a simple diffusive model.

The experiment was carried out at the new beamline ID22N at the European Synchrotron Radiation Facility, using two undulators, a standard Si(111) high-heat load monochromator with LN_2 cooling and a 3.5 meV four-bounce high-resolution monochromator. The samples were enriched $^{57}FeCl_3$ solutions in hydrochloric acid buffered with $NaHCO_3$. The liquid samples were filled into small Teflon vessels having a thin bottom of only 0.2 mm thickness to minimize photoabsorption of the incoherently emitted 6.4 keV X-rays. In order to avoid evaporation of the samples during cooling down of the closed-cycle Helium cryostat, they were quenched using LN_2 before pumping the vacuum chamber.

Fig. 1 (left) shows the raw NIA spectra of samples having various pH. The position of the elastic peak in the present data can not be determined with sufficiently high precision owing to lack of counting statistics. However, it is easily seen that the acid sample shows an elastic line that is strongly broadened by fast quasielastic processes, but that already at pH=3, which according to chemistry textbooks does not yet imply a complete aggregation into poly-iron clusters, the inelastic spectrum shows a mainly solid- or cluster-like behaviour with a phonon DOS clearly separated from the elastic line, which does not change essentially on further raising the pH. Fig. 1 (right) shows NIA spectra of the acid sample having pH=0 at three different temperatures. Obviously, the width of the quasielastic peak decreases only slightly on cooling. The diffusion coefficients obtained by fitting a simple Lorentzian-type diffusion curve (broadened by the instrumental function) to the data were $1.0{\cdot}10^{-5}\,cm^2/s$, $0.6{\cdot}10^{-5}\,cm^2/s$ and $0.4{\cdot}10^{-5}\,cm^2/s$, for 300 K, 160 K and 60 K, respectively. For a frozen-in sample, the latter two values seem too high. A more sophisticated model, which takes into account the possible formation of a glassy phase (no Bragg peaks could be detected for the undercooled solutions), needs to be developed for a deeper understanding of the results.



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