Experimental Report

15/01/2014

Proposal: **4-01-1323** **Council:** 10/2012

Title: Crystal-field excitations in NdFeAsO1-xFx (x = 0, 0.10, 0.18)

This proposal is resubmission of: 4-01-1222

Researh Area: Physics

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Samples: NdFeAsO1-xFx (x = 0, 0.10, 0.18)

Instrument	Req. Days	All. Days	From	To
IN4	4	3	29/04/2013	02/05/2013

Abstract:

We have determined the ordered magnetic moment of Nd in the parent compound NdFeAsO of the high temperature Fe-based (1111)superconductors by studying hyperfine interaction by high resolution back-scattering neutron spectroscopy and found that the magnetic moment of Nd is considerably reduced from the free-ion value. To check the reliability of our newly developed technique we wish to determine the moment reduction by the crystal-field effects. To be able to do this we propose to study crystal-field excitations in NdFeAsO. We also wish to check the evolution of crystal-field excitations in the superconducting state by investigation two F doped samples. We request 4 days of neutron beam time on IN4 and further 3 days on IN6 for the proposed experiment.

Inelastic neutron scattering study of crystal field excitations of Nd^{3+} in NdFeAsO

As a major interaction in rare-earth compounds, the crystalline electric field (CEF) interaction reflects directly the electrical and magnetic potential on the rare-earth site, which is created by neighboring ions [1]. The experimental determination of the structure and parameters of CEF is of a considerable importance in order to get deeper insights into the related energy scale, and therefore to enhance the understanding of the physical properties of rare-earth contained compounds, based on the degeneracy of the CEF states.

The discovery of superconductivity at T_c = 26 K in $LaFeAsO_{1-x}F_x$ has triggered extensive research on the physical properties and the superconducting mechanism of Fe-based superconductors [2, 3]. For the specific case of NdFeAsO, the Fe spin-density-wave (SDW) transition at T_{SDW} = 137 K is found to be preceded by a tetragonal-to-orthorhombic structural phase transition at T_S = 142 K. A spin-reorientation of the Fe magnetic sublattice takes place upon the ordering of the Nd moments at low temperature [4-6]. As the CEF interaction in the NdFeAsO parent phase has to date not been investigated, we have probed the crystal field excitations of Nd^{3+} in NdFeAsO by means of inelastic neutron scattering.

Polycrystalline sample of NdFeAsO was prepared by standard solid state chemistry methods as previously reported.[7] The inelastic neutron scattering measurements were performed, in the temperature range from 1.6 to 200 K, on the direct-geometry thermal-neutron time-of-flight spectrometer IN4C at the Institut Laue Langevin (Grenoble, France). About 7 g of NdFeAsO powder sample was put inside a thin aluminum sample holder that was fixed to the cold tip of the sample stick of a standard orange cryostat. Standard corrections including detector efficiency calibration and background substraction were performed.

Figures 1(a) and 1(b) show the Bose-factor-corrected $S(Q,\omega)$ plots for NdFeAsO at 5 and 160 K, respectively. Above T_{SDW}, both the lattice and CEF excitations contribute to the spectra. Below T_{SDW}, the neutron scattering intensity contains also a contribution of magnon scattering. The integrated cross sections of the Fe spin wave excitations in these materials are relatively small compared to that of phonon and CEF excitations. Therefore, the CEF and lattice (phonon) excitations dominate the neutron spectra while the magnon scattering can be neglected during the data analysis, as presently done. It is known that the phonon scattering intensity generally increases proportional to Q^2. Pure CEF excitations, which are not coupled to propagating modes, are local excitations. They do not possess a characteristic dispersion, and the scattering intensity decreases with Q following a magnetic form factor. By considering the different Q-dependence behaviors of phonon and CEF excitations, the contribution from CEF excitations can be separated by subtracting the high-Q spectra which contain phonon scattering from the low-Q spectra corresponding to both CEF and phonon scattering. Thus, the CEF scattering in NdFeAsO are presently obtained by subtracting the data summed over the high-Q range from the low-angle data, after scaling by a constant factor at each temperature. The obtained CEF excitation spectra at 5 and 160 K are shown in Figs. 2(a) and 2(b) as plots of the energy dependence of the scattering intensity.

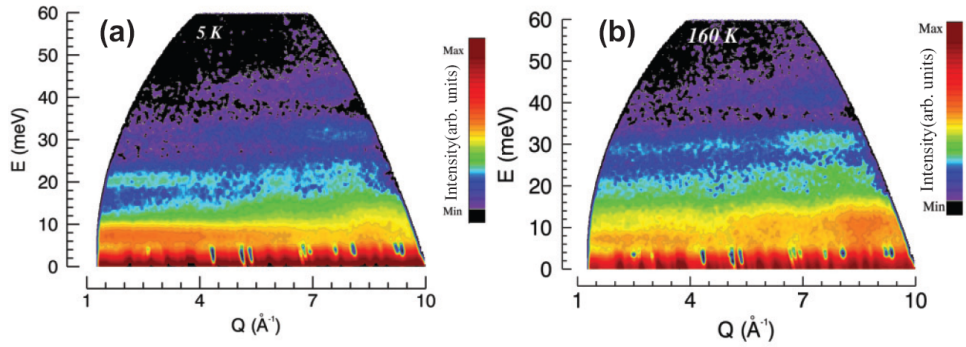

FIG. 1. (a) and (b) The experimental Bose-factor corrected $S(Q,\omega)$ plots for NdFeAsO at 5 and 160 K obtained using an incident neutron wavelength of 1.11 Å. For clarity, a logarithmic representation is used for the intensities.

To interpret the CEF spectra, we analyze the data in the framework of the following ionic CEF model Hamiltonian:

$$\hat{H} = \hat{H}_{\mathrm{CEF}} + 2\mu_B(g_J - 1)B_{\mathrm{mol}}\hat{J},$$

where H_{CEF} represents the crystalline electric field Hamiltonian, which describes the CEF interaction at the Nd^{3+} site in the NdFeAsO compound. The second term is the contribution of a molecular magnetic field coupling to the total angular momentum J of the Nd^{3+} ion. The powder-averaged cross section can be used for a direct comparison with the CEF scattering data obtained using a polycrystalline sample. By taking into account the observed CEF energy positions, transition intensities, and the evolution of the spectra as a function of temperature, a relevant fit is performed allowing us to obtain reliable crystal field parameters that can be used to describe the behavior of the CEF excitations in NdFeAsO. As indicated by the solid lines in Figs. 2(a) and 2(b), the results of the fitting lead to a good agreement with the observed spectra. Two sets of CEF parameters are obtained, at 5 and 160 K. A schematic diagram of the splitting of the Nd^{3+} $^4I_{9/2}$ ground multiplet is presented in Fig. 2(c). Clearly, the ground state at 5 K is a magnetic singlet, whereas the ground state at 160 K is a magnetic doublet. Usually, the different ground states would result in a different quasielastic scattering behavior. The comparison of the neutron spectra at 5 K [Fig. 2(a)] and at 160 K [Fig. 2(b)] highlights the noticeable appearance of a considerable quasielastic peak intensity nearby the resolution limit of the elastic peak. The quasielastic signal can be understood as being due to the spin fluctuations occurring within the degenerate ground state of Nd3+ ions. It favors the multiplet ground state. The strong quasielastic peak observed at 160 K is mainly due to the magnetic doublet ground state, whereas the ground state at 5 K is a magnetic singlet.

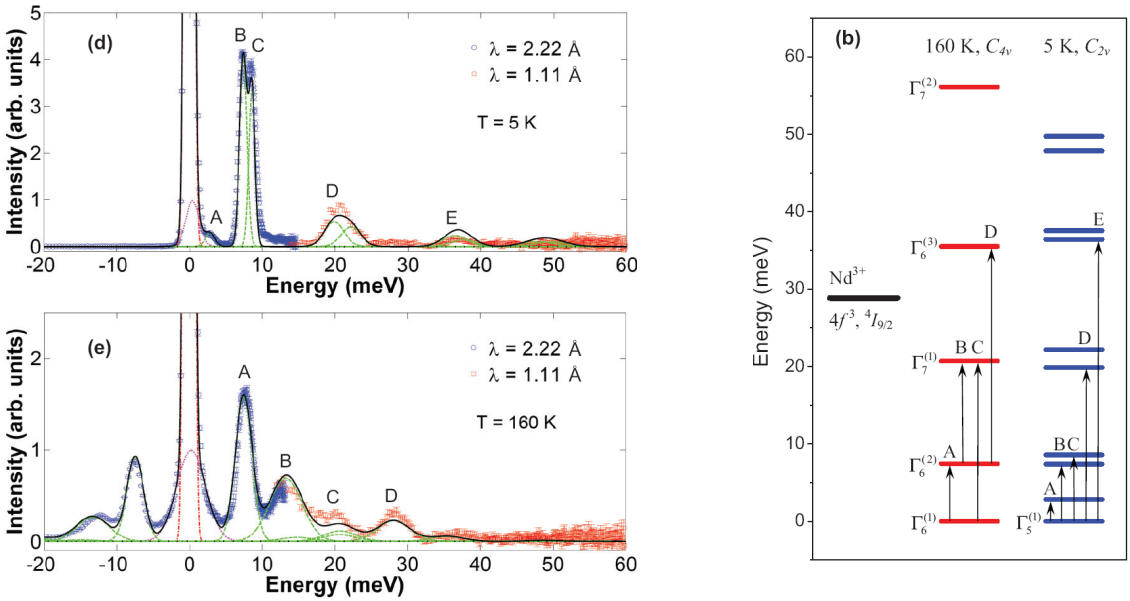

FIG. 2. (a) and (b) Energy spectra of the CEF excitations of NdFeAsO at 5 and 160 K. The dash-dotted lines denote the elastic scattering line, the dotted line denotes the quasielastic scattering line shape fit, the dashed lines represent the fit of individual CEF transitions, and the solid line is a fit of the whole inelastic neutron scattering spectrum. The labeled peaks correspond to the representative CEF transitions marked in (c). (c) Scheme of the energy-levels of Nd^{3+} cations in NdFeAsO for the lowest *J* multiplets under the tetragonal and orthorhombic structural environments. The arrows indicate few representative CEF transitions as extracted from our neutron spectra.

In summary, we have performed temperature-dependent inelastic neutron scattering measurements of the crystal field excitations in NdFeAsO. With decreasing temperature, the crystal field ground state of Nd^{3+} changes from a magnetic doublet to a magnetic singlet state, accompanied by the occurrence of a long-range magnetic ordering of the Fe moments. The crystal field parameters of the Nd^{3+} ions have been determined, for both the high-temperature paramagnetic and the low-temperature antiferromagnetic phases, based on the analysis of the inelastic neutron spectra using a single-ion crystal field model Hamiltonian [8].

References

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