Research Article

Inelastic Neutron Scattering Studies on the Crystal Field Excitations in Superconducting NdFeAsO$_{0.85}$F$_{0.15}$

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Inelastic neutron scattering experiments were performed on polycrystalline samples of NdFeAsO$_{0.85}$F$_{0.15}$ over a wide temperature range (3 K–250 K). Based on the analysis of the experimental data, a Nd^{3+} CF energy level scheme is proposed to give a consistent explanation about the observed CF transitions. The observed extra ground-state CF transitions could not be simply explained by the transitions between five Kramers doublets split from the Nd^{3+} $^4I_{9/2}$ ground state in the C_{4v} point symmetry. A reliable explanation would be a superposition of crystal fields due to different local symmetries around the Nd^{3+} ions induced by the fluorine doping.

1. Introduction

For materials with rare-earth (R) elements, the interactions between f-electrons and the crystal field potentials produced by local lattice environment play important roles in determining the electronic ground state of R ions, as well as in understanding the magnetic and thermodynamic properties of these compounds. Inelastic neutron scattering has been widely accepted as the most reliable technique in determining the crystal field potentials in rare-earth based materials. Particularly, for superconducting materials, in either high-T_c cuprates or other R based heavy fermion superconductors, important research progress has been made in investigating the neutron spectroscopy of the CF excitations [1, 2].

The discovery of Fe-based superconductor LaFe AsO$_{1-x}$F$_x$ has caused a tremendous upsurge of scientific interest since 2008 [3]. Shortly after the report of 26 K superconductivity in LaFeAsO$_{1-x}$F$_x$, through the substitution of La by other R elements with f-electrons (such as Ce, Pr, Nd, and Sm), superconducting critical temperature T_c above 50 K could be observed in RFeAsO$_{1-x}$F$_x$ [4–6]. So far, these so-called FeAs-1111 compounds mark the highest T_c in all Fe-based superconductors, which also provided a unique opportunity in studying the correlation between CF

excitations and physical properties in these exotic superconducting families. Up to now, there have been several publications about crystal field studies in FeAs-1111 compounds through inelastic neutron scattering technique. For example, in CeFeAsO$_{1-x}$F$_x$ (x = 0, 0.16), the Ce CF levels were determined and the intrinsic linewidth Γ of 18.7 meV was found to have a clear anomaly at T_c [7]; inelastic neutron scattering measurements of CF transitions in RFeAsO$_{1-x}$F$_x$ (RE = Pr, Nd) provided evidences that there were two distinct charge environments around the RE ions arising from a random distribution of fluorine ions [8]. The CF level structures for both paramagnetic phase and antiferromagnetic phase of NdFeAsO were constructed by Xiao et al. [9]. However, for NdFeAsO$_{1-x}$F$_x$, there are still insufficient neutron scattering data on the CF transitions and the CF energy level scheme of Nd ion is still not clear.

In this paper, we report inelastic neutron scattering studies on superconducting NdFeAsO$_{0.85}$F$_{0.15}$ samples. Based on the analysis of inelastic neutron scattering spectra at different temperatures, we propose a crystal field energy level scheme for Nd ion, which could explain the CF transitions observed in the experimental data. The additional CF transitions beyond the requirements of C_{4v} point symmetry indicate the superposition of crystal field

and inhomogeneous ligand environments around the rare-earth ions in $NdFeAsO_{0.85}F_{0.15}$.

2. Experimental Results and Discussions

About 20 grams of $NdFeAsO_{0.85}F_{0.15}$ polycrystalline samples were synthesized using the solid state reaction method. Resistivity measurements show that the onset superconducting transition temperature of our samples is about 47 K while the state of zero resistivity is reached at about 43 K, as shown in the inset of Figure 1(a). Inelastic neutron scattering measurements on $NdFeAsO_{0.85}F_{0.15}$ were carried out on thermal triple-axis spectrometer TAIPAN at the Australian research reactor OPAL [10]. The final neutron energy E_f was set to be 14.7 meV, with pyrolytic graphite (PG) as the monochromator and analyzer. The collimation was $48'$-$40'$-$40'$-$120'$.

Figure 1 shows the raw data of the inelastic neutron spectra for $NdFeAsO_{0.85}F_{0.15}$ at different temperatures. From 3 K to 250 K, constant-Q scans were performed every 50 Kelvin. The momentum transfer Q was fixed to be 3.1 Å in the whole measurements. First of all, the strong peaks at about 45 meV and 40 meV (marked with red stars) could be easily distinguished as the spurious peaks, which originated from the 2λ elastic neutron scattering. (The best energy windows for PG filter are 14.7 meV and 13.5 meV. In our experimental setup, E_f was fixed to be 14.7 meV; when E_i = 58.8 meV and 54 meV, the energy transfers of 2λ neutron (14.7 meV and 13.5 meV) were corresponding to the strong elastic scattering signals. That is the origin of the spurious peaks at the energy transfers equaling 44.1 meV and 40.5 meV.) At below 30 meV plenty of CF excitation peaks could be clearly observed in the spectra at 3 K (marked with green arrows). With increasing temperature, the intensities of these peaks gradually decreased, which indicates that the corresponding CF excitations are ground-state excitations. In high temperature regions, some new CF peaks gradually emerge at around 11 meV and their absolute intensities got higher with increasing temperature. So these peaks should correspond to the excitations between excited CF states.

In order to fit and carefully analyze the CF peaks, after subtracting the spurious peaks, the next thing needed is to clarify the phonon contributions from the inelastic neutron spectrum. From both experimental data and theoretical calculations, it is known that the phonon spectra are almost the same for both parent compound and F-doped superconductors in FeAs-1111 system [11–13]. So with the generalized phonon density of states (GDOS) of NdFeAsO in reference paper [9], after transformation with Bose factor and the neutron cross section equation [14, 15]

$$\frac{d^2\sigma}{d\Omega\,dE} = N\frac{k_f}{k_i}\frac{(\gamma r_0)^2}{4}g_J^2 S(Q,E), \qquad (1)$$

we can finally calculate the phonon background for each temperature in our inelastic neutron spectra. The results calculated for T = 3 K are shown in Figure 1(f) (red hollow scatters).

After subtracting phonons, we noticed that the spectrum at 3 K almost overlaps with the spectrum at high temperatures in energy transfer above 36 meV except for notable additional intensity contributions between 40 meV and 48 meV. These additional neutron intensities gradually disappeared with increasing temperatures, which indicates the existence of ground-state CF excitations in this energy range. So it is reasonable to choose the spectrum above 36 meV at high temperature as instrument background because these intensities could not come from CF excitations and most likely result from the 2λ neutron contributions. After subtracting both the phonon and instrument background, the spectrum obtained at 3 K could be well fitted by seven CF excitation peaks with the method of Gaussian fitting, as shown in Figure 2(a) (labelled as A–G, resp.). The similar crystal field excitations at energy transfer below 30 meV were also observed by Goremychkin et al. [8]. Because our data included higher energy transfer region, we could observe the CF excitations at 41.5 meV and 44.5 meV. From both Figures 1 and 2(b), it can be seen that the intensities of all these seven CF peaks decrease with increasing temperatures, which is clearly the characteristic of ground-state excitations.

Therefore based on our inelastic neutron data, we proposed a Nd^{3+} CF energy level scheme for $NdFeAsO_{0.85}F_{0.15}$, which is illustrated in Figure 3. The crystal field energy levels of NdFeAsO were obtained from another publication [9]. As shown in Figure 3, under crystal field with the C_{4v} point symmetry, the Nd^{3+} $^4I_{9/2}$ ground state splits into five doublets in NdFeAsO at temperatures above the antiferromagnetic and structural phase transition [9]. For $NdFeAsO_{0.85}F_{0.15}$, the ground-state CF transitions marked as "A" to "G" in Figure 3 were observed in the inelastic neutron spectra as shown in both Figures 1 and 2(a). From the comparison between the 150 K and 3 K data in Figure 2(b), we could also notice that, in high temperature neutron spectra, there were some new CF peaks emerging at around 11 meV and 26 meV. These new CF peaks were corresponding to the excitations between excited states, as illustrated in Figure 3 (i.e., transitions "H" and "I"). The consistence between the observed CF transitions and the CF energy level scheme proved the validity of our CF model proposed in this paper.

It is clear that the CF level scheme of $NdFeAsO_{0.85}F_{0.15}$ is significantly different from that of tetragonal NdFeAsO. In order to understand this difference, first of all we need to check whether there were CF states splitting caused by magnetic phase transitions. In the inset of Figure 1(a), the typical temperature dependence of resistances was measured on our samples. There were no traces of phase transitions because there was no anomaly in the normal state resistance which should be the typical features in the samples with structural or magnetic phase transitions. The resistance measurements were also performed in different batches of our samples which show similar features. Also based on our previous neutron measurements on samples with similar doping [16], we could safely rule out the possibility of structural or magnetic phases transitions induced additional CF states.

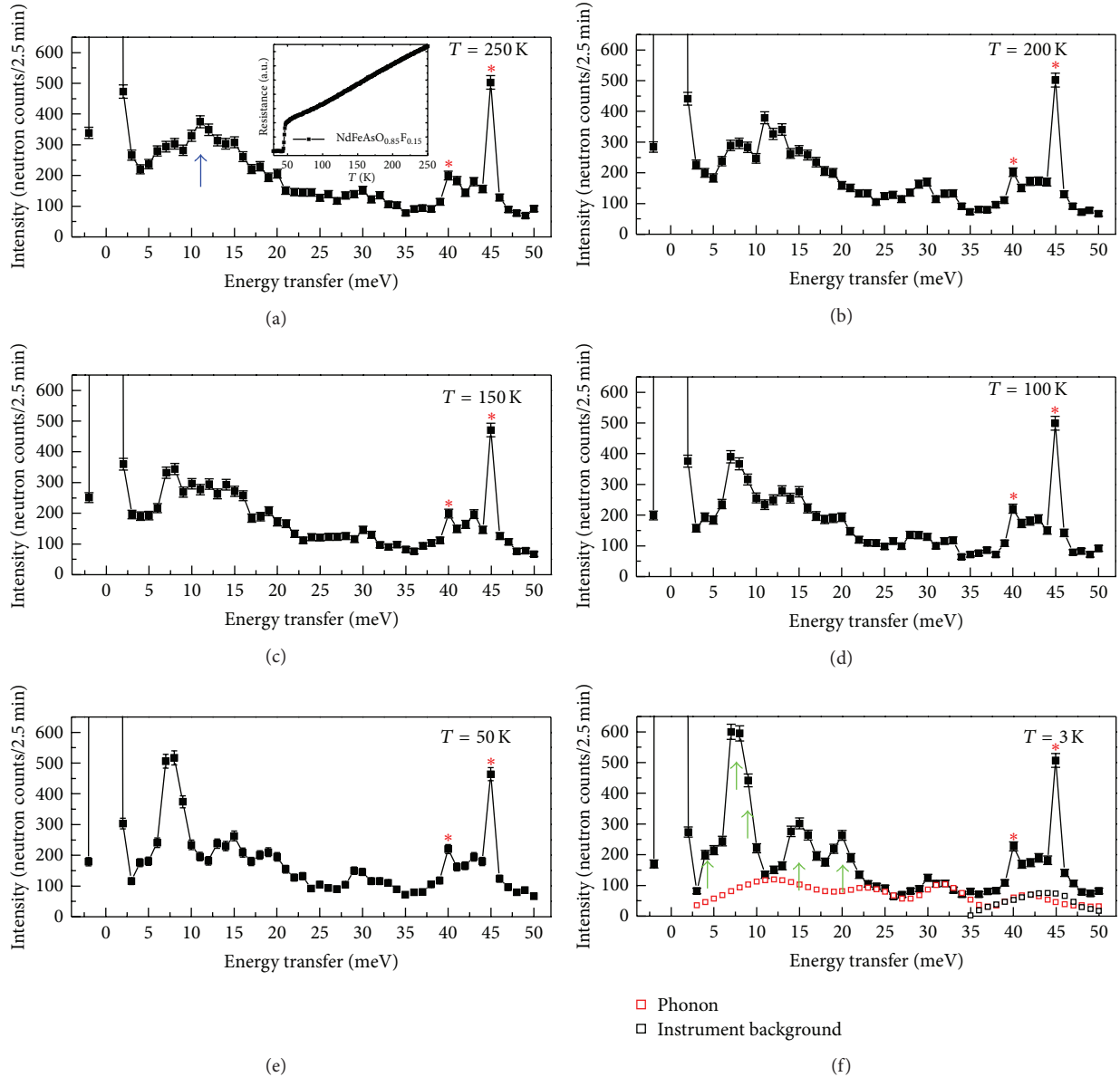All the CF peaks should correspond to certain transitions of Nd f-electrons between different CF states. In

FIGURE 1: Inelastic neutron scattering spectra of NdFeAsO$_{0.85}$F$_{0.15}$ were measured with fixed E_f = 14.7 meV and Q = 3.1 Å. The energy scans were carried out at temperatures from 3 K to 250 K as marked on each figure. The solid lines are guides to the eye. The red stars marked the spurious peaks caused by the instrument setup. In the inset of Figure 1(a), the temperature dependence of resistance data of our samples is shown.

the weak crystal field approximation, which applies well to the R elements, the multiplets of different J's (total angular moment) are well separated in energy compared to the intra-multiplet splittings; therefore, the interactions between multiplets can be ignored. In such a case, the crystal field states can be considered based solely on the ground-state splitting [17].

According to Hund's rules, the ground state of Nd^{3+} ion, which contains three f-electrons, is $^4I_{9/2}$. The splitting of CF levels is directly related to the local lattice symmetry. NdFeAsO$_{0.85}$F$_{0.15}$ samples have a tetragonal crystal structure with P4/nmm space group. The Nd atoms are located at the $2c$ crystallographic site therefore having C_{4v}

point symmetry. This gives the crystal field Hamiltonian as follows:

$$H_{\text{CEF}}\left(C_{4v}\right) = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^4 O_4^4 + B_6^4 O_6^4, \quad (2)$$

where B_n^m are the CF parameters and O_n^m are Steven's operator equivalents. This CF symmetry splits the $^4I_{9/2}$ ground-state multiplet of the Nd^{3+} ion into five Kramers doublets.

However, suppose the CF peaks at T = 3 K in our NdFeAsO$_{0.85}$F$_{0.15}$ samples all came from the transitions between the five doublets as in the high temperature tetragonal phase of NdFeAsO [9]; then the number of ground-state excitation peaks should be at most four. According to
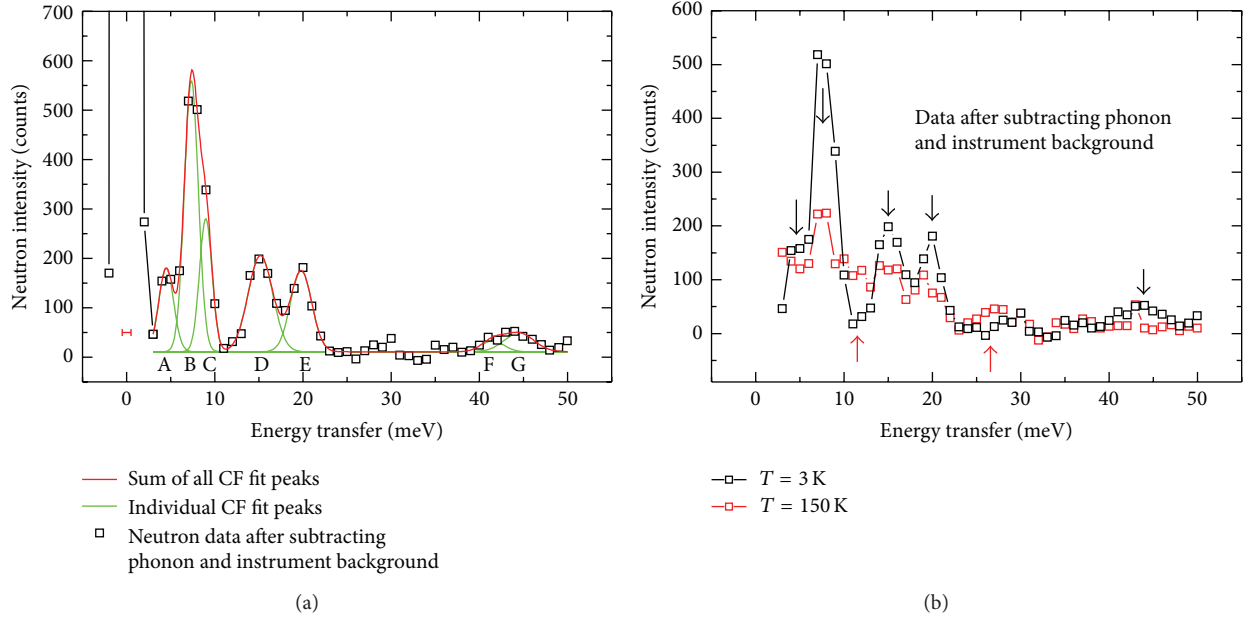
(a)

(b)

FIGURE 2: (a) Energy spectra of CF excitations in NdFeAsO$_{0.85}$F$_{0.15}$ at T = 3 K after subtracting the phonon and instrument background. The spectra were well fitted by seven Gaussian peaks. The instrumental energy resolution is 0.98 meV at elastic position (horizontal bar). (b) Comparison of the energy spectra of CF excitations between T = 3 K and T = 150 K after subtracting the phonon and instrument background. The black lines are guides to the eye.
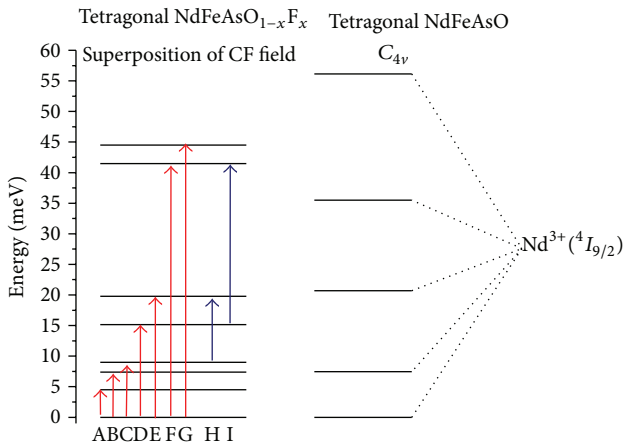

FIGURE 3: The Nd^{3+} CF energy level schemes for both NdFeAsO and NdFeAsO$_{0.85}$F$_{0.15}$ are shown. The values of energies of Nd^{3+} in NdFeAsO$_{0.85}$F$_{0.15}$ are sorted in increasing order: 0, 4.49, 7.34, 8.97, 15.17, 19.79, 41.50, and 44.51 meV. The energies of CF levels of NdFeAsO were obtained from another paper [9].

our data, the observed CF transitions for NdFeAsO$_{0.85}$F$_{0.15}$ outnumbered the transitions allowed for Nd^{3+} with C_{4v} point symmetry. Therefore the Hamiltonian in (2) is insufficient to describe the CF states in F-doped samples.

A reliable interpretation of the experimental data would be the occurrence of a superposition of crystal fields due to different local symmetries around the Nd^{3+} ions induced by the fluorine doping, similar to the case of oxygen defects in the R compounds RBa$_2$Cu$_3$O$_x$ [18] and RCoO$_x$ [19]. There are

four nearest-neighboring oxygen ions around the Nd^{3+} ion; the ways of substitution of fluorine for oxygen could not all be the same. So different local charge environments and CF potentials around Nd^{3+} ions are expected. As in the analysis of RCoO$_x$ [19], in this situation because of the lowered point symmetry, additional terms are needed to enter the Hamiltonian in (2) which would produce more CF states as in our experimental data. Although it is difficult to give a parameterization in terms of the current complex CF Hamiltonian based on our data, the clear observation of seven ground-state CF transitions would provide strong evidence for the above analysis.

Besides NdFeAsO$_{0.85}$F$_{0.15}$, the additional CF states induced by F-doping were also observed in PrFeAsO$_{0.87}$F$_{0.13}$ [8]. However it is interesting to mention that, for another typical FeAs-1111 compound CeFeAs(O,F) [7], there is not much difference between the CF states in tetragonal CeFeAsO phase and PrFeAsO$_{0.86}$F$_{0.14}$ phase. The reason could be that the line widths of major CF transitions in the Ce compounds are of the order of 10 meV, which is significantly larger than that in Nd compounds (mainly below 3 meV). So the presumably small effect of fluorine doping could not be detected.

3. Concluding Remarks

Inelastic neutron scattering measurements were carried out on polycrystalline samples of NdFeAsO$_{0.85}$F$_{0.15}$ at different temperatures. Through the analysis of inelastic neutron spectra, up to seven ground-state CF excitations were identified. A crystal field energy level scheme for Nd^{3+} was proposed

which shows quite different features comparing with that in tetragonal NdFeAsO phase. This indicates the occurrence of superposition of crystal fields due to the inhomogeneous ligand charge environments and lowered local point symmetries around the Nd^{3+} upon fluorine doping.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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