Crystal field excitations in electron superconductors

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Abstract. We have measured the complete crystalline electric field (CEF) spectrum of Nd^{3+} in superconducting $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ and $\text{Nd}_2\text{CuO}_{3.7}\text{F}_{0.3}$, and in the non-superconducting parent compound, Nd_2CuO_4 , by neutron inelastic scattering. The best description of the ground-state excitations for both compounds is achieved by the addition of a molecular field parameter to the CEF hamiltonian that takes account of exchange interactions from Nd or Cu spin ordering.

Keywords. Neutron scattering (inelastic); crystal field; magnetic interactions; $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$.

1. Introduction

Earlier this year it was announced (Tokura *et al* 1989) that a new family of high-temperature superconductors had been discovered with the Nd_2CuO_4 structure where Nd can be replaced with Pr or Sm. When these compounds are doped with Ce on the rare earth site or F on the oxygen site they provide the first examples of high-temperature superconductors with *n*-type rather than *p*-type conductivity.

Structurally, Nd_2CuO_4 differs from La_2CuO_4 , a parent compound of some of the hole-doped superconductors, in the arrangement of oxygen around the copper ion. In the latter material the copper is octahedrally coordinated, whereas it is in a square-planar environment in Nd_2CuO_4 . In contrast to the Sr-doped La_2CuO_4 superconductors, the new electron-doped materials have *magnetic* rare-earth ions situated above and below the CuO planes, and this provides us with an excellent opportunity to compare, by means of the crystalline electric field (CEF) excitations, the electronic and magnetic interactions at the rare-earth site in the superconductor and non-superconductor.

In this paper we report on measurements and analysis of the CEF spectra for superconducting $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ and $\text{Nd}_2\text{CuO}_{3.7}\text{F}_{0.3}$ and for their parent compound, Nd_2CuO_4 . Earlier predictions for the crystal field levels from susceptibility data (Saez-Puche *et al* 1983; Seaman *et al* 1989) assumed a cubic environment for the rare-earth ion, and found a first-excited state either 40 or 70 meV above the ground state, and a second state 100 meV higher. Our measurements reveal a very different crystal-field scheme, whose description requires the full tetragonal symmetry of the rare-earth site, and which is modified by magnetic interactions.

2. Experimental

The polycrystalline samples used for these experiments were prepared by solid-state reaction. Appropriate quantities of Nd_2O_3 , CuO, CeO_2 and NdF_3 were mixed together and then reacted, with intermittent regrindings. The powders were pressed into

cylindrical pellets of diameter 16 mm and thickness 3 mm, sintered, and then annealed. Processing temperatures for the undoped and Ce-doped compounds are published elsewhere (Boothroyd *et al* 1989); the F-doped material was reacted and sintered at 900°C before annealing in nitrogen at the same temperature. X-ray powder diffraction patterns showed that the products were single phase, and superconductivity was observed in the doped samples by a.c. susceptibility.

For the neutron scattering measurements the sample was constructed of 20 to 30 pellets, stacked in an approximately square array with the cylinder axes perpendicular to the incident neutron beam. The pellets were separated by cadmium strips to prevent neutrons scattered in one pellet from travelling into adjacent pellets and being rescattered. The neutron measurements were made on the high energy transfer (HET) spectrometer at the ISIS pulsed neutron source of the Rutherford-Appleton Laboratory.

3. Analysis and results

In elementary crystal field theory it is usual to assume that the admixture of states within different J -levels can be neglected. With the crystallographic c -axis as the quantization direction, the crystal field hamiltonian for the tetragonal symmetry of the rare-earth site in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ is then given by

$$H_{\text{CEF}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^4 O_4^4 + B_6^4 O_6^4, \quad (1)$$

where the B_{2n}^{2m} are the CEF parameters, and the O_{2n}^{2m} are the corresponding Stevens' operators (Furrer *et al* 1988). The Hund's Rule ground state of Nd^{3+} has $J = \frac{9}{2}$ and, in general, the Hamiltonian (1) causes a splitting of the ten-fold degenerate J -multiplet into five doublets.

The neutron spectra measured at the lowest temperature with incident energies of 40 meV, are shown for Nd_2CuO_4 in figure 1, for $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ in figure 2 and for $\text{Nd}_2\text{CuO}_{3.7}\text{F}_{0.3}$ in figure 3. All three compounds have well-defined peaks at about

Figure 1. Crystal field transitions of Nd_2CuO_4 at 1.6 K.

Figure 2. Crystal field transitions of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ at 1.9 K.

Figure 3. Crystal field transitions of $\text{Nd}_2\text{CuO}_{3.7}\text{F}_{0.3}$ at 1.9 K.

21, 27 and 93 meV, but in the doped samples an extra peak is seen at 10 to 12 meV. These excitations were identified as magnetic in origin from the decrease in their intensity with increasing Q . The obvious similarities between the ground state excitations of the two compounds suggest that in Nd_2CuO_4 there exists a CEF level below 21 meV but with a very small transition probability from the ground state. Indeed, such a level may be inferred from the presence of a peak at about 11 meV in the spectrum of Nd_2CuO_4 (not shown) measured at 200 K. This extra peak at high temperatures arises from transitions between the thermally-populated first-excited level and one of either the 21 or 27 meV levels.

The starting parameters of the fit were the set of B-coefficients calculated from a point-charge model with the known geometrical coordination of the Nd^{3+} ion in the Nd_2CuO_4 structure; the CEF parameters were then allowed to vary independently in order to achieve the best fit. In this way sets of parameters were found which agreed well with the neutron spectra of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ and $\text{Nd}_2\text{CuO}_{3.7}\text{F}_{0.3}$. A set of parameters was found for Nd_2CuO_4 , though having poorer agreement with the measured intensities, that corresponded to a scheme with the first excited CEF level at 16 meV.

Whilst the above analysis in terms of the CEF Hamiltonian (1) represented a reasonable description of the data, some disturbing discrepancies between the calculated and measured spectra remained, especially for the Nd_2CuO_4 sample. In particular, the calculated values of peak intensities did not match the measured intensities. The crystal field Hamiltonian (1), only includes interactions between the rare-earth magnetic moment and the crystal *electric* field. Additional perturbations on the energy levels may be caused by interactions with *magnetic* fields, which in Nd_2CuO_4 can arise from magnetic ordering of the Nd and Cu moments. Muon spin rotation measurements (Luke *et al* 1989) show that the Cu moments order at about 300 K in Nd_2CuO_4 , but that no static magnetic order exists above 4 K in the superconducting, Ce-doped compound. The nature of the ordering in Nd_2CuO_4 has been examined recently in neutron diffraction experiments from single crystals (Endoh *et al* 1989; Skanthakumar *et al* 1989) and from a powder (Rosseinsky *et al* 1989). The copper spins adopt a simple antiferromagnetic arrangement in the planes, but undergo reorientation transitions at about 80 K and 30 K in which the relative configurations of spins in adjacent layers change. Below 30 K the Cu spins return to the high-temperature structure and begin to couple to the Nd spins. Long-range order of the Nd spins sets in below 4 K, with the same magnetic structure as the Cu spins.

The simplest approximation to account for the effects of magnetic ordering on the crystal field levels is to add to the Hamiltonian (1) a term that represents the energy of a Nd moment in a mean molecular field, $\mathbf{H}_{\text{mf}}$. In the present analysis the spins are taken to lie parallel to [110], in which case the additional term may be simplified to

$$H = H_{\text{CEF}} - h_{\text{mf}}(\hat{J}_x + \hat{J}_y)/\sqrt{2}, \quad (2)$$

where h_{mf} is the molecular field parameter in energy units. A repeat of the fitting procedure with the mean field term gave significantly better agreement with the measured transitions than before, especially for Nd_2CuO_4 , and enabled all the ground-state and excited-state transitions to be calculated correctly to within the uncertainty on the measurements. The calculated sets of CEF and molecular field

Table 1. Crystal field parameters (in meV).

Parameter	Nd_2CuO_4	$\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$	$\text{Nd}_2\text{CuO}_{3.7}\text{F}_{0.3}$
B_2^0	0.912 ± 0.006	0.887 ± 0.004	0.960 ± 0.03
B_4^0	$(1.25 \pm 0.02) \times 10^{-2}$	$(1.37 \pm 0.05) \times 10^{-2}$	$(1.36 \pm 0.03) \times 10^{-2}$
B_6^0	$(2.09 \pm 0.04) \times 10^{-4}$	$(1.91 \pm 0.01) \times 10^{-4}$	$(1.06 \pm 0.06) \times 10^{-4}$
B_4^4	$(-2.82 \pm 0.04) \times 10^{-2}$	$(-2.43 \pm 0.03) \times 10^{-2}$	$(-3.71 \pm 0.05) \times 10^{-2}$
B_6^4	$(-2.77 \pm 0.05) \times 10^{-3}$	$(-2.82 \pm 0.02) \times 10^{-3}$	$(-2.76 \pm 0.06) \times 10^{-3}$
h_{mf}	0.31 ± 0.04	0.15 ± 0.02	0.86 ± 0.07

parameters are listed in table 1. In view of the alternative suggestions for the Cu spin arrangement, we also analysed the data with a molecular field parallel to [100], but found no significant differences from the results described below. From this result we conclude that the crystal field spectra are relatively insensitive to the field direction in the plane. A more detailed discussion of the fitting procedure can be found in Boothroyd *et al* (1989).

4. Conclusions

The main effect of applying a molecular field is to cause a small splitting of each of the five doublets. Such a splitting in a Kramer's ion cannot be produced by a lowering of the symmetry through a small structural distortion. The magnitude of this splitting varies from peak to peak, and whilst the two components of the peaks are not resolved in the neutron measurement it is perhaps significant that for Nd_2CuO_4 the splitting of the 27 meV peak is predicted to be twice that of the 20 meV peak, which is consistent with the observed linewidths of the two peaks.

One can only speculate as to the origin of the molecular field in the two compounds. At the lowest temperature where measurements were made it is possible that the Nd spins were ordered in the Nd_2CuO_4 sample, but this is unlikely with the superconducting samples. The non-zero values of h_{mf} for $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ and $\text{Nd}_2\text{CuO}_{3.7}\text{F}_{0.3}$ are rather puzzling, therefore, since there has been no evidence to date for static magnetic ordering of the Cu spins in the superconducting phase of a high-temperature superconductor. On the other hand, whilst the existence of a magnetic interaction at the Nd site requires an exchange coupling, it does not necessarily imply long-range magnetic order. It is possible that coupling between the Nd and Cu spins produces a form of short-range order, brought on by frustration effects, with an exchange energy much greater than the thermal energies available at low temperatures. Such order may persist over a timescale sufficiently long to cause a splitting of the crystal field levels. The observations of powder diffraction peaks persisting above the apparent ordering temperature of Nd_2CuO_4 may be evidence for this effect. It is tempting to identify this proposed short-range order with the two-dimensional magnetic fluctuations of the Cu moments included in several current theories of the mechanism of high temperature superconductivity.

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