Crystalline electric field study in the pyrochlore Nd$_2$Ir$_2$O$_7$ with metal-insulator transition

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Abstract. We carried out inelastic neutron scattering measurements to identify crystalline electric field (CEF) states of Nd$^{3+}$ (a total angular momentum $J = 9/2$) in Nd$_2$Ir$_2$O$_7$, which exhibits a metal-insulator transition at $T_{\text{MI}} = 36$ K. Excitation peaks observed around 26 and 41 meV are interpreted as CEF excitations within five Kramers doublets. It is notable that splitting of the ground doublet by 1.3 meV was microscopically observed at 3 K for the first time, indicating emergence of magnetic long-range order despite geometrical frustration. The splitting width decreases with increasing the temperature towards $T_{\text{MI}}$ like an order parameter of the transition. We discuss the results in light of Nd-Ir interactions.

1. Introduction

Geometrical frustration has attracted much attention. A pyrochlore $A_2B_2O_7$ is the representative system, in which both $A$ and $B$ sites form pyrochlore sublattices. Recently, the interesting transport properties were discovered, e.g. metal-insulator (MI) transition in Hg$_2$Ru$_2$O$_7$ and Cd$_2$Os$_2$O$_7$, superconductivity in Cd$_2$Re$_2$O$_7$ and anomalous Hall effect in Nd$_2$Mo$_2$O$_7$ [1; 4].

Nd$_2$Ir$_2$O$_7$ with magnetic ions Nd$^{3+}$ and Ir$^{4+}$ exhibits an MI transition at $T_{\text{MI}} = 36$ K [5]. In magnetic susceptibility measurements, zero-field-cooling and field-cooling curves do not trace each other below $T_{\text{MI}}$, indicating magnetic ordering/freezing at $T_{\text{MI}}$ [6]. In specific heat measurements, magnetic entropy of Nd$^{3+}$ was estimated to be $R \ln 2$ at $T_{\text{MI}}$ ($R$: the gas constant), meaning that the crystalline-electric-field (CEF) ground state is a doublet [6]. Schottky anomaly was also observed at around 5 K, suggesting that the doublet splits by 1.2 meV below $T_{\text{MI}}$ [6]. This splitting probably comes from a static internal magnetic field at Nd sites, induced by the magnetic anomaly.

In this paper, we study the magnetic state with MI transition in light of CEF by inelastic neutron scattering. The ground doublet splitting is microscopically verified for the first time, indicating the emergence of magnetic long-range order despite the expected geometrical frustration. A model of CEF level scheme is also proposed.
2. Experiments

Powder samples of Nd$_2$Ir$_2$O$_7$ and Y$_2$Ir$_2$O$_7$ were synthesized by K. Matsuhira, as described in Ref. [5]. The 4.5 g Nd$_2$Ir$_2$O$_7$ sample and the 4.2 g Y$_2$Ir$_2$O$_7$ one were enclosed in thin aluminium foils, and were shaped to hollow cylinders with 0.7 mm thickness in order to diminish an effect of the strong neutron absorption of Ir nuclei as low as possible. Then the cylinder was set in an aluminium container, which was placed under a cold head in a $^3$He closed-cycle refrigerator.

Inelastic neutron scattering experiments were performed using the triple axis spectrometers HER installed at the cold-neutron guide of JRR-3, JAEA, Tokai, Japan and TOPAN installed at the thermal beam hole of the same reactor. On HER, the final energy of the neutrons was fixed at $E_f = 3.6$ meV. Higher-order contamination was eliminated by a pyrolytic graphite (PG) filter or a cooled Be filter before a sample and another Be filter after it. The horizontal collimation sequence was guide-blank-radial collimator (with 2 blades)-blank. The scattered neutrons were merged by a horizontal focusing analyzer in 5 degrees scattering angle. The energy resolution (full width at half maximum FWHM) was 0.13 meV at the elastic condition. On TOPAN, $E_f = 13.5$ meV was selected. A sapphire filter and a PG filter cut the fast and higher-order neutrons. The collimation was blank-100'-100'-blank. The energy resolution was 1.5 meV.

3. Results

Figures 1(a) and 1(b) show the constant-$Q$ scan data on Nd$_2$Ir$_2$O$_7$ and Y$_2$Ir$_2$O$_7$, respectively. Nd$_2$Ir$_2$O$_7$ shows a clear peak at around 1.3 meV at 3 K, as shown in Fig. 1(a), which coincides with the splitting width estimated from the Schottky anomaly [6]. As the temperature increases, both the excitation energy and the intensity decrease towards $T$ like order parameters of the transition. In contrast, Y$_2$Ir$_2$O$_7$ shows no distinct excitation down to 5 K, as shown in Fig. 1(b). Therefore, the former excitations most likely correspond to be the ground doublet splitting of Nd$^{3+}$. Below 21 K, a weak broad signal is also observed in the lower energy side of the main peak even at 3 K (Fig. 1(a)).

In order to shed further light on the magnetic state, we performed measurements in higher energy transfer where the CEF levels can be detected. Figure 2(a) shows the constant-$Q$ scan data measured at 3.1, 3.5 and 3.9 Å$^{-1}$ at 4 K, and Fig. 2(b) shows that measured at 3.5 Å$^{-1}$ at 40 K. The Y$_2$Ir$_2$O$_7$ data, measured with the same experimental conditions, was subtracted from the Nd$_2$Ir$_2$O$_7$ data to eliminate phonon contribution and background. Around 26 and 41 meV, appreciable peaks are observed for all the $Q$’s below and above $T_{MI}$, which are identified as higher-energy CEF excitations of Nd$^{3+}$.

![Figure 1](image-url)  

**Figure 1.** Constant-$Q$ scan data of Nd$_2$Ir$_2$O$_7$ (a) and Y$_2$Ir$_2$O$_7$ (b). $Q$ is the magnitude of scattering vector and $E$ is the energy transfer.
Figure 2. Constant-Q scan data in a high-energy region measured at 3.1, 3.5 and 3.9 Å⁻¹ at 4 K (a) and that measured at 3.5 Å⁻¹ at 40 K (b). The solid curves show calculated results (See the text).

4. Analyses
Within a CEF level scheme of Nd³⁺ (a total angular momentum \( J = 9/2 \)), we simultaneously analyzed the spectra with the 26-meV and 41-meV excitations and the magnetic susceptibility data [6]. The CEF Hamiltonian \( \hat{H}_{CEF} \) with trigonal symmetry (\( D_3 \)) is described by

\[
\hat{H}_{CEF} = \sum_{n,m} B_n^m \hat{O}_n^m = B_2^0 \hat{O}_2^0 + B_4^0 \hat{O}_4^0 + B_4^1 \hat{O}_4^1 + B_6^0 \hat{O}_6^0 + B_6^3 \hat{O}_6^3 + B_6^6 \hat{O}_6^6,
\]

where the quantisation z axis is along the [111] three-fold axis, \( B_n^m \) are coefficients to determine scale of the CEF eigenenergy \( \hat{E}_i \) and order of the eigenstate \( \hat{\Gamma}_i \), and \( \hat{O}_n^m \) are Stevens’ operators, e.g. \( \hat{O}_2^0 = \hat{J}_z^2 - J(J+1) \) [7; 8]. The internal magnetic field generating splitting of ground doublet (~1 meV) is ignored, since it is too small to be resolved from the present thermal neutron scattering data.

By using the \( \hat{E}_i \) and \( \hat{\Gamma}_i \) obtained by numerically diagonalising Eq. (1), inelastic neutron scattering cross section for a transition from \( \hat{\Gamma}_i \) to \( \hat{\Gamma}_j \) in a non-interacting ion can be calculated by

\[
\frac{d^2\sigma}{d\Omega dE} = C_0 \frac{k_f}{k_i} \exp\left[-E_i/k_BT\right] \frac{\left|\langle \hat{\Gamma}_i \mid \hat{J}_\perp \mid \hat{\Gamma}_j \rangle \right|^2}{Z \Gamma_i^0} R(E_i - E_j + E),
\]

where \( C_0 \) is a constant, \( k_i \) and \( k_f \) are wave numbers of incident and final neutrons, respectively, \( T \) is temperature, and \( Z \) is the CEF partition function [9]. The matrix element \( \left|\langle \hat{\Gamma}_i \mid \hat{J}_\perp \mid \hat{\Gamma}_j \rangle \right|^2 \) is represented by \((2/3) \sum_{\alpha=1}^3 \left|\langle \hat{\Gamma}_i \mid \hat{J}_\alpha \mid \hat{\Gamma}_j \rangle \right|^2 \) for a powder sample, where \( \hat{J}_\alpha \) is a total angular momentum operator and \( \alpha \) means the components of the Cartesian coordinate [10]. The function \( R \) is an instrumental energy resolution, for which we assumed a Lorentzian with FWHM estimated by the Cooper-Nathans formula [11]. Then, based on the above \( \hat{H}_{CEF} \), the powder-averaged magnetic susceptibility is evaluated by

\[
\tilde{\chi}_{CEF} = \frac{N g_J \mu_B}{H} \sum_{\alpha=1}^3 \exp\left[-E_i^{(\alpha)}/k_BT\right] \frac{\left|\langle \hat{\Gamma}_i^{(\alpha)} \mid \hat{J}_\alpha \mid \hat{\Gamma}_j^{(\alpha)} \rangle \right|^2}{Z^{(\alpha)}},
\]

where \( N \) is number of Nd³⁺ in a sample, \( \hat{\Gamma}_i^{(\alpha)} \) and \( E_i^{(\alpha)} \) are eigenstate and eigenenergy of another Hamiltonian \( \hat{H}_{CEF}' = \hat{H}_{CEF} - g_J \mu_B \hat{J}_\perp \hat{H} \), respectively, \( Z^{(\alpha)} \) is the partition function, \( g_J \) is the Landé’s \( g \)-factor, and \( H \) is magnitude of an applied magnetic field [12].
We carried out a fitting procedure of the CEF parameters $B_n$ for the experimental data using Eqs. (1) to (3). Figures 2(a) and 2(b) show the calculated curves of scattering intensity for a found model, which are in good agreement with the experimental data. Figure 3 shows the calculated lines of $\tilde{\chi}_{CEF}$ and $\tilde{\chi}_{CEF}^{-1}$ for $H = 0.1$ T, which are also in good agreement with the experimental data [6]. Table 1 summarizes the obtained CEF parameters, eigenenergies and eigenstates. The $J = 9/2$ decatet splits into five Kramers doublets. The ground doublet exhibits a highly anisotropic magnetic dipole moment $g_J \langle \vec{J} \rangle = (0, 0, \pm 2.37) \mu_B$ per ion.

![Figure 3](image)

**Figure 3.** Magnetic susceptibility and the inverse one. Open squares and circles indicate experimental data [6], and solid curves show calculated results.

**Table 1.** Calculated CEF parameters, eigenenergies and eigenstates for Nd$^{3+}$ ($J = 9/2$). Ten coefficients with respect to $|J_z\rangle$ are given for each eigenstates.

| CEF parameters [meV] | $B_2^0$ | $B_4^0$ | $B_4^4$ | $B_6^0$ | $B_6^4$ | $B_6^6$ |
|----------------------|---------|---------|---------|---------|---------|---------|
| $-0.28(0)$           | $-0.95(9) \times 10^{-2}$ | $-0.33(9)$ | $-0.44(3) \times 10^{-4}$ | $0.17(7) \times 10^{-2}$ | $-0.45(7) \times 10^{-2}$ |

| eigenenergies [meV] and eigenstates | $E_i$ | $1\cdot 9/2\rangle$ | $1\cdot 7/2\rangle$ | $1\cdot 5/2\rangle$ | $1\cdot 3/2\rangle$ | $1\cdot 1/2\rangle$ | $1\cdot 1/2\rangle$ | $1\cdot 3/2\rangle$ | $1\cdot 5/2\rangle$ | $1\cdot 7/2\rangle$ | $1\cdot 9/2\rangle$ |
|-------------------------------------|-------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| 123                                | 0     | 0                 | 0.375             | 0                 | 0.533             | 0                 | 0                 | -0.758            | 0                 | 0                 |
| 123                                | 0     | 0                 | 0.758             | 0                 | -0.533            | 0                 | 0                 | 0.375             | 0                 | 0                 |
| 57                                 | 0.135 | 0                 | 0                 | -0.289            | 0                 | 0                 | -0.772            | 0                 | 0                 | 0.550             |
| 57                                 | 0.550 | 0                 | 0.772             | 0                 | -0.289            | 0                 | 0                 | 0                 | 0                 | -0.135            |
| 42                                 | 0     | 0                 | -0.439            | 0                 | 0                 | -0.617            | 0                 | 0                 | -0.653            | 0                 |
| 42                                 | 0     | 0                 | 0.653             | 0                 | -0.617            | 0                 | 0                 | 0.439             | 0                 | 0                 |
| 26                                 | 0     | 0                 | 0.816             | 0                 | 0                 | -0.578            | 0                 | 0                 | -0.003            | 0                 |
| 26                                 | 0     | 0                 | 0.003             | 0                 | 0                 | -0.578            | 0                 | 0                 | -0.816            | 0                 |
| 0                                  | -0.057| 0                 | 0                 | -0.286            | 0                 | -0.489            | 0                 | 0                 | -0.822            | 0                 |
| 0                                  | -0.822| 0                 | 0                 | 0.489             | 0                 | 0                 | -0.286            | 0                 | 0                 | 0.057             |

5. Discussion
We succeeded in microscopically verifying the splitting of ground doublet below $T_{MI}$ (Fig. 1(a)), indicating an appearance of static internal magnetic field at Nd sites. The energy spectrum shows a single sharp peak at 1.3 meV at 3 K, suggesting that the internal field is almost equivalent at all Nd sites. Therefore magnetic long-range order seems to uniformly occur despite geometrical frustration.
On the other hand, a weak broad signal is also observed in the spectrum, suggesting the coexistence of an additional random-field component like short-range order. Thus it was revealed that frustration is predominantly relieved below $T_{MI}$.

The coexistence of long-range order and short-range order is observed in frustrated spinel insulators $A\text{Cr}_2\text{O}_4$ ($A = \text{Mn, Co}$) with magnetic $A^{2+}$ and Cr$^{3+}$, in which $A$ sites form a non-frustrated diamond lattice and Cr sites form a frustrated pyrochlore lattice [13; 14]. In lowest temperature phases the chromates exhibit a conical spin structure, resolved into an Ising-type ferrimagnetic long-range component and a spiral short-range one. This partially frustrated state is interpreted as a result of the Cr-site frustration suppressed by $A$-Cr exchange interactions [13; 15]. In analogy with the chromates, the coexistence of two components in $\text{Nd}_2\text{Ir}_2\text{O}_7$ would be also due to Ir-site frustration suppressed by Nd-Ir exchange interactions.

The internal field at Nd sites might also come from these interactions. In fact, the value $1.3 \text{ meV} (~15 \text{ K})$ is too large for dipole-dipole interaction energy with $2.37 \mu_B$, and interactions between well-localized $4f$ moments of Nd$^{3+}$ can be normally neglected in an insulator without RKKY interactions.

6. Conclusions
We studied CEF states of Nd$^{3+}$ in $\text{Nd}_2\text{Ir}_2\text{O}_7$ by powder inelastic neutron scattering. A CEF model with five Kramers doublets was proposed. The ground-doublet splitting below $T_{MI}$ was microscopically verified for the first time, indicating emergence of magnetic long-range order with static internal field at Nd sites despite geometrical frustration. The internal field can be interpreted as Nd-Ir exchange field, which probably relieves frustration and causes the magnetic ordering. Further experimental and theoretical works will be needed to elucidate the magnetic state and MI transition.

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