Ba$_2$YIrO$_6$ : A cubic double perovskite material with Ir$^{5+}$ ions

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Abstract

Materials with a 5$d^4$ electronic configuration are generally considered to have a nonmagnetic ground state ($J = 0$). Interestingly, Sr$_2$YIrO$_6$ (Ir$^{5+}$ having 5$d^4$ electronic configuration) was recently reported to exhibit long-range magnetic order at low temperature and the distorted IrO$_6$ octahedra were discussed to cause the magnetism in this material. Hence, a comparison of structurally distorted Sr$_2$YIrO$_6$ with cubic Ba$_2$YIrO$_6$ may shed light on the source of magnetism in such Ir$^{5+}$ materials with 5$d^4$ configuration. Besides, Ir$^{5+}$ materials having 5$d^4$ are also interesting in the context of recently predicted excitonic types of magnetism. Here we report a single-crystal-based analysis of the structural, magnetic, and thermodynamic properties of Ba$_2$YIrO$_6$. We observe that in Ba$_2$YIrO$_6$ for temperatures down to 0.4 K, long-range magnetic order is absent but at the same time correlated magnetic moments are present. We show that these moments are absent in fully relativistic $ab$ initio band-structure calculations; hence, their origin is presently unclear.

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I. INTRODUCTION

The iridates have become an interesting playground for material researchers as they show novel ground states due to competing interactions between the crystal field (CF), the Coulomb interaction ($U$) and the spin-orbit coupling (SOC) $[1]$. To name a few examples, (Sr/Ba)$_2$IrO$_4$ $[2,3]$, Sr$_3$Ir$_2$O$_7$ $[4,5]$, (Na/Li)$_2$IrO$_3$ $[6,7]$ have been studied intensively in recent times, both experimentally and theoretically.

In all the above mentioned compounds, the iridium ion is magnetic with a formal oxidation state +4 (5$d^4$). In contrast, materials with a 4$d^4$ or 5$d^4$ electronic configuration (such as Re$^{4+}$, Ru$^{4+}$, Os$^{4+}$, Ir$^{5+}$) are believed to be in a Van Vleck-type non-magnetic band insulating ground state with a completely filled $J = 3/2$ manifold having a total angular momentum $J = 0$ $[8]$. Such a nonmagnetic ground state is realized in NaIrO$_3$ $[9,10]$.

However, recently two independent theoretical studies proposed that the interplay between $U$ and SOC in some of these materials may lead to novel magnetism governed by gapped singlet-triplet excitations $[11,12]$, although the ground states obtained in these two studies are different. Meetei et al. $[12]$ proposed a magnetic phase diagram for the 4$d$ Mott insulators which consists of a nonmagnetic ($J = 0$) and two different ferromagnetic phases ($J = 2$ and $J = 1$). The authors have identified the double perovskite materials as good candidates to observe such novel magnetic states.

Recently, in the double perovskite material Sr$_2$YIrO$_6$ with Ir$^{5+}$ ions, a transition to an antiferromagnetic long-range order was observed below 1.3 K $[21]$. Cao et al. $[21]$ assigned the structural distortion of Sr$_2$YIrO$_6$ originating in the monoclinic structure (space group $P2_1/n$) with highly distorted IrO$_6$ octahedra as the driving force for the long-range magnetic order in this compound. Hence, the motivation to study the Ba analog Ba$_2$YIrO$_6$ is twofold: (i) the investigation of other Ir$^{5+}$ materials in general to verify or discard the theoretically predicted excitonic magnetism in the Van Vleck-type $d^4$ Mott insulators $[13,21]$, and (ii) the investigation of cubic analogs with Ir$^{5+}$ to shed light on the impact of noncubic symmetry on the magnetism in such systems.

The crystal structure of Ba$_2$YIrO$_6$ has been described using a cubic symmetry (space group $Fm\overline{3}m$) $[22,24]$ as well as a monoclinic symmetry (space group $P2_1/n$) with $\beta = 90.039^\circ$ (Ref. $[25]$). The monoclinic description with $\beta \sim 90^\circ$ closely matches with the cubic description. In any case, since all previous studies are based on polycrystalline samples, it is important to revisit the crystal structure of Ba$_2$YIrO$_6$ using single crystals and in particular shedding light on the magnetic properties of this material.

In this work, we report the growth of Ba$_2$YIrO$_6$ single crystals and the details of their structural, magnetic, thermal, and electrical transport properties. Ba$_2$YIrO$_6$ clearly crystallizes in a cubic double perovskite-type (space group $Fm\overline{3}m$) structure, as demonstrated by our single-crystal and powder (on crushed single crystals) x-
II. EXPERIMENTAL DETAILS

Single crystals of Ba$_2$YIrO$_6$ were grown using high-purity starting materials BaCO$_3$ (Alpha Aesar 99.997%), IrO$_2$ (Alpha Aesar 99.99%), and Y$_2$O$_3$ (Alpha Aesar 99.999%). Ultra-dry BaCl$_2$ (Alpha Aesar 99.5%) was used as flux. The stoichiometric mixture of the starting materials and the flux were put inside a platinum crucible covered with a platinum lid to reduce flux evaporation. The mixture was heated to 1250 – 1300°C, held at this temperature for 24 h and then slowly cooled to 950°C. After that it was cooled to room temperature very fast by switching off the furnace. Cubic-size single crystals (typical dimensions 0.3 × 0.3 × 0.3 mm$^3$, also compare Fig. 1) were precipitated at the bottom of the platinum crucible. After dissolving the flux in water, the single crystals were collected and used for further characterization.

Single-crystal x-ray diffraction (XRD) data of Ba$_2$YIrO$_6$ were collected on a Bruker AXS Kappa APEX diffractometer with graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073\text{Å}$) using the complete sphere mode.
Table I: Crystal data for Ba$_2$YIrO$_6$ from single-crystal diffractometry.

| Parameter                        | Value                  |
|----------------------------------|------------------------|
| Temperature (K)                  | 198(2)                 |
| Crystal (for XRD) size (mm$^3$) | 0.15 × 0.16 × 0.19     |
| Space group                      | $Fm\overline{3}m$ (No. 225) |
| $a$ (Å)                          | 8.3387(8)              |
| $V$ (Å$^3$)                      | 579.8(2)               |
| $Z$                              | 4                      |
| $\rho_{\text{calc}}$ (g cm$^{-3}$) | 7.467                 |
| $\rho_{\text{calc}}$ (g mm$^{-3}$) | 46.149               |
| Multiscan absorption correction  | 0.041 ≤ $T$ ≤ 0.055    |
| $\theta$ range (°)              | 0.95 – 45.1            |
| Collected reflections            | 12012                  |
| Independent reflections          | 162($R_{\text{int}} = 0.0486$) |
| Observed reflections             | 162[$I \geq 2\sigma(I)$] |
| Refined parameters              | 8                      |
| $R$                              | 0.0096                 |
| $wR^2$                           | 0.0270[$I > 2\sigma(I)$] |
| Max residual electron density (eÅ$^{-3}$) | 1.459             |
| Min residual electron density (eÅ$^{-3}$) | −0.559             |
| Goodness of fit                  | 1.350                  |

Table II: Atomic positions and thermal parameters for a Ba$_2$YIrO$_6$ single crystal at 198(2) K.

| Atoms  | Site | x    | y    | z    | Site occ. | $U_{\text{iso}}$ |
|--------|------|------|------|------|-----------|-----------------|
| Ba(1)  | 8c   | 0.25 | 0.25 | 0.25 | 1         | 1.0675          |
| Y(1)   | 4a   | 0    | 0    | 0    | 1         | 0.75687         |
| Ir(1)  | 4b   | 0.5  | 0.5  | 0.5  | 1         | 0.81458         |
| O(1)   | 24e  | 0.25944(2) | 0   | 0    | 1         | 0.51547         |

at 198(2) K. The following programs were used to collect and analyze the data: the data collection was done with APEX2 [28], the data reduction with ‘SAINT’ [27], the numerical absorption correction was applied using SADABS [28], the structure solution was obtained with SHELXS-97 [29], and the structure refinement was performed by full-matrix least-squares against $F^2$ using SHELXL-97 [28]. CSD 427064 contains the supplementary crystallographic data for this work. Room temperature powder XRD patterns were obtained using a Stoe Stadi-P diffractometer with Mo-Kα1 radiation equipped with a curved Ge(111) primary monochromator and a Dectris Mythen 1 K detector. Our data were analyzed with the Rietveld method using the FULLPROF program [30]. The homogeneity and the chemical composition of the crystals were analyzed using energy-dispersive x-ray (EDX) analysis with a scanning electron microscope (SEM Philips XL 30).

Magnetization measurements were performed as a function of temperature ($T$) and magnetic field ($H$) on randomly oriented single crystals of a total mass ~ 57 mg in a Quantum Design MPMS in the temperature range 0.43 – 300 K using the $^3$He option below 1.8 K. Heat capacity measurements ($C_p$) were performed on 10 – 12 crystals (mass ~ 2 mg) in the temperature range 0.4 – 10 K using the $^3$He option of a Quantum Design PPMS. The resistivity was measured as a function of temperature in the range 4.2 – 300 K in a homemade device. The contacts on the sample were made using graphite epoxy in the four-point contact geometry.

III. RESULTS AND DISCUSSIONS

A. Microstructure analysis

Figure 1 exemplarily shows an as-grown Ba$_2$YIrO$_6$ single crystal (left panel). The middle panel of Fig. 1 shows the SEM image of a single crystal in backscattered electron (BSE) mode. Our SEM analysis suggests that the composition is homogeneous over the crystals. However, we cannot exclude the possibility of a certain amount of off-stoichiometry, e.g., Ba$_2$Y$_{1+4}$Ir$_{1-d}$O$_{6-d}$.

B. XRD and crystal structure

Single-crystal XRD measurements (shown in the right panel of Fig. 1) performed on several pieces from different preparation batches showed a high quality of the crystals, proven by the good internal consistency of the data collected using the full-sphere mode and an extremely low $R$ factor (less than 1%). These measurements confirm that Ba$_2$YIrO$_6$ crystallizes in a cubic double perovskite structure with space group $Fm\overline{3}m$ (No. 225), similar to results as reported in Refs. [22, 23] based on XRD measurements on polycrystalline samples. The results of the structural refinement of the single-crystal XRD measurements at 198(2) K are summarized in Table III. The atomic positions and thermal parameters are listed in Table III.

Furthermore, we have measured powder XRD on

Figure 4: Resistivity ($\rho$) as a function of temperature for a single-crystal piece of Ba$_2$YIrO$_6$. Inset: Arrhenius plot of the resistivity.

$\rho$ = 221 meV

$T$ = 57 mg

$R$ = 0.95 – 45.1

$\theta$ range (°)

Collected reflections

Independent reflections

Observed reflections

Refined parameters

$R$

$wR^2$

Max residual electron density (eÅ$^{-3}$)

Min residual electron density (eÅ$^{-3}$)

Goodness of fit

$[30]$
crushed single crystals. The resulting XRD pattern is shown in Fig. 2. Traces of unreacted Y\textsubscript{2}O\textsubscript{3} (∼ 2%) are found in the XRD pattern with the main peak corresponding to Y\textsubscript{2}O\textsubscript{3} marked by an arrow along with small amounts of Pt from the crucible that are contaminating the surfaces of the crystal. All the major peaks in the powder XRD pattern are indexed with space group \textit{Fm\textoverline{3}m} as shown in Fig. 2. The double-phase Rietveld refinement of the powder XRD pattern (shown in Fig. 2) using space group \textit{Fm\textoverline{3}m} for Ba\textsubscript{2}YIrO\textsubscript{6} and \textit{I\textoverline{6}}\text{3} for Y\textsubscript{2}O\textsubscript{3} results in refinement parameters \(R_p = 2.54\) and \(R_{wp} = 3.88\). The lattice constants obtained from single-crystal XRD and powder XRD on crushed crystals are consistent with earlier reports \[22–25\]. We find no signature of any structural transition of the crystals from room temperature (powder XRD) down to 198(2) K (single-crystal XRD). Also, no anomaly is seen in our magnetic susceptibility and heat capacity measurement (discussed later), which suggests the absence of any structural transition down to 0.4 K.

The crystal structure of Ba\textsubscript{2}YIrO\textsubscript{6} based on our refinement results is shown in Fig. 3. An alternating arrangement of IrO\textsubscript{6} (pink) and YO\textsubscript{6} (light blue) octahedra, with the Ba atoms (yellow) placed in between, form the crystal structure. Please note that the Ir\textsuperscript{5+} ions in this structure build up a face-centered cubic (fcc) network. Attempts to allow site disorder in the refinement were not leading to better fit results; hence, we concluded that site disorder does not play a role here. This is consistent with the ionic size of Y\textsuperscript{3+} and Ir\textsuperscript{5+} ions being very different, rendering site disorder rather unlikely. The same arguments hold for off-stoichiometry. The distortion of IrO\textsubscript{6} octahedra as present in the monoclinic Sr\textsubscript{2}YIrO\textsubscript{6} is absent in the cubic Ba\textsubscript{2}YIrO\textsubscript{6}.

C. Resistivity

Figure 4 shows the semiconductor-type resistivity of a Ba\textsubscript{2}YIrO\textsubscript{6} single crystal as a function of temperature. The measurement was done at a constant current of \(I = 5\ \mu\text{A}\). The resistivity at room temperature is \(\rho(300\text{K}) = 40\ \text{m}\Omega\text{cm}\) and increases exponentially with decreasing temperature. At temperatures lower than \(\sim 170\ \text{K}\), the resistivity increases to very high values, hindering a correct measurement with our device. The inset of Fig. 4 shows the Arrhenius plot of the resistivity data. From room temperature down to 160 K, \(\ln(\rho)\) is inversely proportional to the temperature, i.e., \(\rho \propto \exp(\Delta/2k_B T)\). Our analysis yields an energy gap of \(\Delta \approx 221\ \text{meV}\). It should be noted that the geometrical error of the contacts is quite high due to the small sample size. This may influence the accuracy of the absolute value of the resistivity; however, the overall temperature
dependence and therefore the energy gap is unaffected.

## D. Magnetization

Since the magnetization of the material is expected to be small, we have taken special care to increase the sample mass and to subtract the background signal of the sample holder. Figure 3 shows the zero-field-cooled susceptibility data as a function of temperature in an external magnetic field of 5 kOe for our as-grown single crystals. No signature of any long-range magnetic order is found in the measured temperature range 0.43 K ≤ T ≤ 300 K. Moreover, no splitting between zero-field-cooled (ZFC) and field-cooled (FC) susceptibilities are observed 300 K. The inverse susceptibility (after subtracting χ₀) is plotted on the right axis of the figure. Below ~15 K, deviations from the CW fitting occur, which probably stem from even larger antiferromagnetic spin correlations in the low-temperature regime, or from a small temperature-dependent contribution to the Van Vleck susceptibility, which has not been taken into account in the fit but which has been observed, e.g., for Eu³⁺.

Since materials with 5d⁴ electronic configuration are expected to be Van Vleck-type nonmagnetic, it is interesting to extract the Van Vleck part in the susceptibility for this material. For insulating materials one can consider χ₀ = χ_{core} + χ_{vv}, where χ_{core} is the core diamagnetic susceptibility and χ_{vv} is Van Vleck paramagnetic susceptibility. In case of Ba₂YIrO₆, χ_{core} = -1.68 × 10⁻⁴ cm³K/mol (obtained by adding the core diamagnetic susceptibility for individual ions [33]), which results in χ_{vv} = 7.51 × 10⁻⁴ cm³K/mol. This value is of the same order of magnitude as for other Ir⁵⁺ (5d⁴) materials (see Table III).

The effective magnetic moment (μ_{eff} = 0.44 μ_B/Ir) is unusual for an expected J = 0 material. The simplest explanation for the magnetic response could be the presence of a few percent of Ir⁴⁺ ions (which are known to be

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**Figure 8:** Partial density of states (pDOS) for Ir and O atoms: (a) LDA scheme, (b) LDA+SOC scheme, (c) LDA+SOC+U scheme, (d) total density of states, calculated in the frame of LDA, LDA+SOC, LDA+SOC+U.
magnetic) caused by oxygen deficiency. To verify or discard the presence of oxygen vacancies, we have annealed the as-grown crystals under 700 bar oxygen pressure at 500°C for 2 days. Magnetization measurements on these oxygen-annealed crystals yield identical results compared with those of the as-grown crystals. This probably suggests that there are no oxygen vacancies in the as-grown crystals.

Another possibility for the presence of Ir⁴⁺ ions is a partial substitution of Y³⁺ by Ir⁴⁺ ions, as it was seen in the cubic double perovskite material Ba₂(Y₀.67Ir₀.33)O₆ with the formal oxidation state of Ir +4.5 [34]. The small Curie constant of Ba₂YIrO₆ and Weiss temperature could result from the presence of a few percent of Ir⁴⁺ ions (~5% of J = 1/2 spins). A third scenario accounts for Ir⁶⁺ ions created due to the intermixing and/or off-stoichiometry. For double perovskite materials with Ir⁶⁺ ions, μ_eff is reported to be more than 3 μ_B/Ir [35]. Hence, the presence of a small amount of Ir⁶⁺ ions can result in the observed μ_eff = 0.44 μ_B/Ir.

To understand the origin of the magnetic moments, we further analyzed the isothermal magnetization data M(H) at 480 mK as shown in Fig. 6. We were able to fit our data with a modified Brillouin function M(H) = χ₀H + fNₐμ_BJ_B(jμ_BH/k_BT), where f, Nₐ, g, and k_B represent a scaling factor to account for a finite number of paramagnetic impurities, the Avogadro constant, the Landé g factor, and the Boltzmann constant, respectively (see Fig. 6). The first linear term χ₀H describes the core plus the Van Vleck contributions (see above), while the second term, the Brillouin function B_J, represents the behavior of paramagnetic spins as a function of a magnetic field at a particular temperature.

Our analysis suggests the presence of ~2 % of J = 1/2 spins in the material and a g factor of 2.14. This result matches quite well with the estimate from the CW fitting assuming g = 2.14. We also tried to vary the J value according to the different scenarios outlined above, but the fitting result depicted in Fig. 6 is very robust. However, the fitted g value is decreasing from 2.14 to 1.2 for J = 1/2 to J = 3/2, respectively.

While the temperature-independent susceptibility contribution from the CW fitting yields χ₀ = 5.83 × 10⁻⁴ cm³/mol, we obtain a larger value of χ₀ = 15.0 × 10⁻⁴ cm³/mol from the field dependence of the magnetization. This mismatch probably arises from non-negligible antiferromagnetic spin correlations in Ba₂YIrO₆ which have not been taken into account in the Brillouin function. Further detailed investigations are planned in order to shed light on the nature of the magnetic correlations in Ba₂YIrO₆, which seem to increase at low temperatures.

E. Heat capacity

The low-temperature specific heat (C_P) data for zero field is shown on the left axis of Fig. 7. Our specific heat data is qualitatively similar to that of Sr₂YIrO₆ [21]. We do not find any signature of magnetic ordering down to 0.4 K in Ba₂YIrO₆, and no anomaly is resolved even in the dC_P/dT vs T plot, which is shown on the right axis of Fig. 7 in contrast to what has been reported for Sr₂YIrO₆.

F. Ground state in DFT theory

To understand the origin of the insulating ground state in Ba₂YIrO₆ we performed density functional theory (DFT) calculations of the electronic structure. Our calculations were carried out within the local (spin) density approximation [L(S)DA] using the Full Potential Local Orbital band-structure package (FPLO) [35, 37]. A k-mesh of 12 × 12 × 12 k-points in the whole Brillouin zone was employed. To take correlation effects in the Ir 5d shell into account we adopted the L(S)DA+U scheme. Due to the rather sizable spin-orbit interaction of the Ir atoms, the full relativistic four-component Dirac scheme was used.

Similar to other iridates, the DFT results suggest a metallic state for Ba₂YIrO₆ as indicated by a finite density of states (DOS) at the Fermi level E_F [Fig. 8(a)]. The Ir 5d and O 2p states have strong hybridization due to strong metal-ligand covalency. The Ir 5d electrons give
Table III: A comparison of the Van Vleck susceptibility ($\chi_{vv}$), effective magnetic moment ($\mu_{\text{eff}}$) and Curie-Weiss temperature ($\theta_{\text{CW}}$) of different 5$d$ materials.

| Material     | Electronic config. | $\chi_{vv}$ (cm$^3$/K/mol) | $\mu_{\text{eff}}$ (µB/Ir) | $\theta_{\text{CW}}$ (K) | Reference |
|--------------|--------------------|---------------------------|-----------------------------|--------------------------|-----------|
| Ba$_2$YIrO$_6$ | 5$d^1$             | $7.51 \times 10^{-4}$     | 0.44                        | $-8.9$                   | This work |
| Sr$_2$YIrO$_6$ | 5$d^2$             | $10.11 \times 10^{-4}$    | 0.91                        | $-229$                   | [21]      |
| NaIrO$_3$    | 5$d^1$             | $19 \times 10^{-4}$       | 0.28                        | $-2.2$                   | [17]      |

a contribution to the total density of states in three energy windows: from $-6.5$ eV to $-4.5$ eV, from $-1$ eV to $0.5$ eV, and from $2.5$ eV to $4.5$ eV. From Fig. 8 one can see that the $t_{2g}$ and $e_g$ states are well separated. The spin-orbit interaction [Fig. 8(b)] considerably changes the bands near the Fermi level, but still the DOS at the Fermi level remains finite. Analyzing the partial density of states, one can identify a splitting of the 5$d$ states into single-particle 5$d_{3/2}$ and 5$d_{5/2}$ contributions. To obtain an insulating ground state one needs to take into account strong correlations in the mean-field approxima-
tion (LDA+U). We introduce a Hubbard $U \approx 1.4$ eV and Hund’s $J = 0.5$ eV for the Ir 5$d$ shell. These values of $U$ and $J$ give a magnetic solution for the system with the magnetic moment of the order of $2\mu_B$ in the absence of the spin-orbit interaction. But with the spin-orbit inter-
action the magnetic solution becomes unstable and instead we find, at a configuration with an effective single particle, $J_s = S_z = 0$, as one can see from Figs. 8(c) and 8. The presence of a moderate $U$ opens a gap $\Delta = 0.2$ eV, pushing up one of the bands of predominantly 5$d_{5/2}$ character. This value for the gap is close to one that we have found experimentally from the resistivity measurements. From this we conclude that the insulating state has a similar origin as in other iridates: the interplay of spin-orbit interaction and correlations.

IV. CONCLUSIONS

Single crystals of the double perovskite Ba$_2$YIrO$_6$ were grown by the flux method. Our XRD measurements on single and crushed crystals unambiguously reveal that this material crystallizes in a cubic double perovskite structure. In contrast to the general expectation, we found that Ba$_2$YIrO$_6$ is paramagnetic from our bulk suscept-

ceptibility measurements. The susceptibility data is fit-
ted well with the CW formula and results in an effective magnetic moment $\mu_{\text{eff}} = 0.44$ µB/Ir and a Weiss temperature $\theta_{\text{CW}} = -8.9$ K. However, it is not clear at the moment if this is the manifestation of proposed gapped excitonic magnetism [19, 20] in $d^4$ materials or caused by chemical disorder and/or off-stoichiometry (the presence of Ir$^{4+}$ or Ir$^{6+}$ ions). Density-functional-based electronic structure calculations show that in the LDA+U approach a magnetic ground state is stable for physical values of the Hubbard $U$ and Hund’s rule exchange $J$, but only if relativistic effects are treated on a scalar relativistic level (no spin-orbit coupling). In fully relativistic calculations we find that the spin-orbit coupling drives the system into a Mott insulator with a value of the gap close to the experimental value. However, at the same time the system becomes nonmagnetic. This calls for further in-
vestigations of the origin of the unexpected magnetism in this material and suggests that the origin of the observed magnetic moments is related to electronic many-body ef-
fekts, the theoretical description of which likely stretches beyond the reach of effective mean-field approaches such as LDA+U.

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