

Magnetic order in CeI₂

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Abstract. CeI₂ is a halide with metallic conductivity according to the formula (Ce³⁺)(I⁻)₂(e⁻). Magnetic interactions are mediated by the conduction electrons and are significantly stronger than for insulating rare-earth halides. CeI₂ crystallizes in the MoSi₂ layer-type structure with space group I4/mmm and lattice parameters $a = 3.87212(5)$ Å and $c = 13.8646(2)$ Å at 15 K. At $T_N = 10.0(2)$ K, a phase transition to a 3D antiferromagnetically ordered state occurs with an incommensurate \mathbf{k} vector of (0, 0.2761(1), 1) at 1.5 K. The \mathbf{k} vector is temperature-dependent and, as the sublattice magnetization, reaches saturation below 4 K. CeI₂ has one magnetic sublattice with moments parallel to the a axis. The amplitude is sine-modulated along the b axis and amounts to 1.87(1) μ_B per Ce³⁺ ion. The crystal-field splitting reduces the ordered moment slightly below the ²F_{5/2} free-ion value of $g \cdot J = 15/7$ for Ce³⁺.

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Due to its metallic conductivity, CeI₂ is an especially interesting compound. Its properties lie between those of trivalent, insulating, ionic cerium salts and intermetallic compounds. CeI₂ was first synthesized by Corbett et al. [1], who also established its metallic conductivity. Later on, the room-temperature crystal structure of CeI₂ was determined by X-ray diffraction [2]. In the course of our investigations of magnetic properties of rare-earth halides, we became interested in this compound. The whole series of binary cerium iodides, i.e. CeI₃ [3], Ce₂I₅ [4] and CeI₂, was synthesized and investigations of their magnetic structures by neutron diffraction are in progress. Here we report the magnetic phase transition and magnetic structure of CeI₂.

1 Experimental

CeI₂ was synthesized from CeI₃ and Ce metal (Johnson&Matthey, ingot, 99.99%). CeI₃ was prepared from Ce metal and iodine (Merck, 99.5%) in an evacuated and sealed

silica ampoule. The ampoule was heated in a tubular furnace in such a way that its bottom was situated in the middle and its tip 1 cm outside the furnace. The temperature was kept at 200 °C for three days until the reaction was almost completed. Then the temperature was raised slowly to 750 °C. After cooling to room temperature the ampoule was opened and excess iodine removed under vacuum. The crude CeI₃ was again sealed in a silica ampoule under vacuum and sublimed for purification at 760 °C. High-purity CeI₃ was obtained in the colder part of the ampoule as lustrous yellow needles. CeI₃ is thermochromic and changes its color towards red upon heating. The melting of CeI₃ in a silica ampoule should be avoided to prevent the formation of oxide impurities.

For the CeI₂ synthesis, CeI₃ and Ce metal were filled into a tantalum ampoule and sealed off under helium by arc welding. The tantalum ampoule was covered in a silica ampoule under vacuum, heated to 820 °C for one day, to 680 °C for three days and slowly cooled to room temperature. CeI₂ was obtained as a black solid with metallic luster. All steps of the synthesis were done under strictly dry and oxygen-free conditions in closed ampoules or glove boxes (H₂O < 0.1 ppm). CeI₃ is very hygroscopic and CeI₂ both hygroscopic and sensitive to oxidation. Exposed to air, CeI₂ immediately changes its appearance from black to colorless and evolves hydrogen from moisture. For neutron-diffraction experiments CeI₂ was ground to a fine powder and enclosed under helium in an indium-sealed vanadium can of 50-mm length and 8-mm diameter. The neutron experiments were performed on the HRPT and DMC diffractometers of the continuous spallation neutron source SINQ at the Paul Scherrer Institute. The sample was cooled to 1.4 K in an ILL-type helium cryostat. Powder-diffraction patterns were corrected for the measured absorption of $\mu \cdot r = 0.0636$ at $\lambda = 2.56$ Å and evaluated by the program FULLPROF [5].

2 Results and discussion

The crystal structure of CeI₂ was refined at 15 K in the paramagnetic state from data obtained from a HRPT measurement with $\lambda = 1.8857$ Å. The MoSi₂-type layer structure was confirmed. Lattice parameters and atomic distances are in good

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agreement with previous measurements at room temperature. The final fit resulted in agreement factors of $R_p = 2.7\%$, $R_{wp} = 3.5\%$, $R_{exp} = 2.1\%$ and $R_{Bragg} = 2.3\%$. Important parameter values are summarized in Table 1 and interatomic distances in Table 2. A perspective view of the crystal structure along the a axis is shown in Fig. 1. Ce^{3+} ions are coordinated by eight I^- ions in the shape of a tetragonal prism. Compared to a cube, the prism is slightly compressed along the c

Table 1. Crystallographic data of CeI_2 at 15 K

Space group: I4/mmm (No. 139)					
Lattice parameters: $a = 3.87212(5)$ Å, $c = 13.8646(2)$ Å					
Atom	Site	x/a	y/b	z/c	B (Å ²)
Ce	2a	0	0	0	0.32(3)
I	4e	0	0	0.36479(5)	0.09(2)

Table 2. Interatomic distances in CeI_2 at 15 K

Atoms	Distances (Å)	
Ce–I	3.3183(4) (8×)	
Ce–Ce	3.8721(1) (4×)	in-plane
	7.4534(2) (8×)	inter-plane
I–I	3.7493(2)	c
	3.8721(1) (4×)	a
	4.1986(7) (4×)	inter-plane

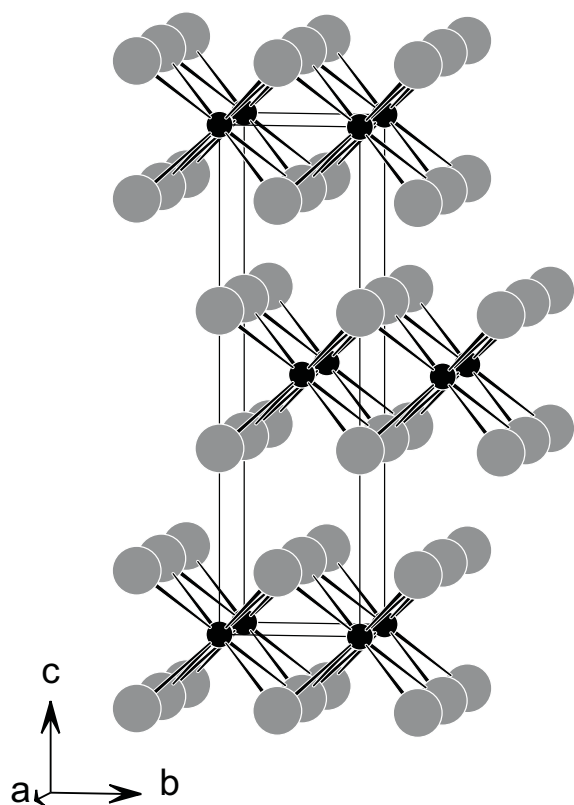


Fig. 1. Perspective view of the crystal structure of CeI_2 along the a axis. The Ce^{3+} ions are shown as *black* and the I^- ions as *grey spheres*, respectively

axis. The prisms are connected via all rectangular faces and form layers perpendicular to the c axis. The layers are stacked along the c axis and held together by van der Waals forces.

Upon cooling, a transition from the paramagnetic to an antiferromagnetically ordered state takes place. Due to the 3D order additional magnetic Bragg peaks occur. A difference diagram between the magnetically saturated state at 1.5 K and the paramagnetic state at 15 K separates the magnetic contributions from the nuclear ones, see Fig. 2. The areas around 52° , 56° and 72° 2θ had to be excluded due to shifts of strong nuclear peaks between 15 and 1.5 K and an instrumental artefact, respectively. The magnetic peak positions are incommensurate with the nuclear unit cell. Their positions are temperature-dependent, as shown in Fig. 3, and they are indexed by the k vector (0, 0.2761(1), 1) at 1.5 K. The tem-

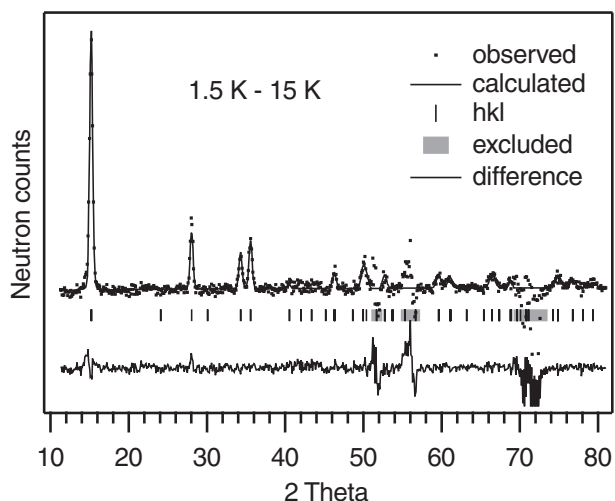


Fig. 2. Difference neutron diffraction diagram at 1.5–15 K of CeI_2 for $\lambda = 2.56$ Å

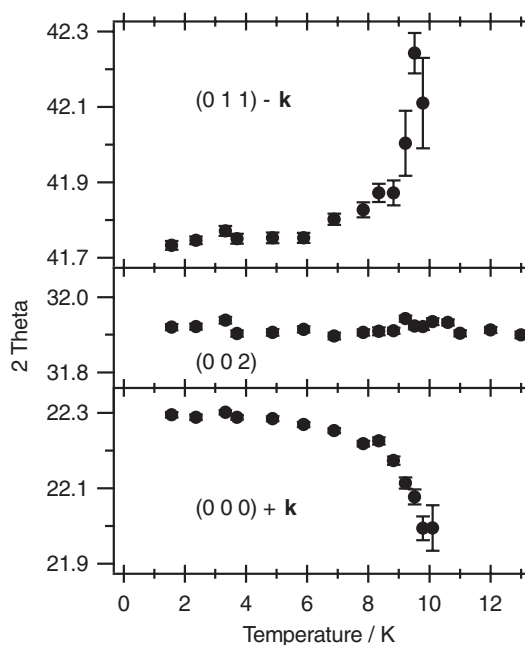


Fig. 3. Temperature dependence of the 2θ positions of the (000) + k and (011) – k magnetic as well as the (002) nuclear Bragg peaks for $\lambda = 3.8$ Å

perature dependence of the integrated magnetic peak intensity of the $(000) + \mathbf{k}$ reflection results in an ordering temperature of $T_N = 10.0(2)$ K, see Fig. 4. A fit of a power law to the data between 7 and 10 K yields the critical exponent $\beta = 0.31(3)$, which is close to those for 3D Ising or Heisenberg systems.

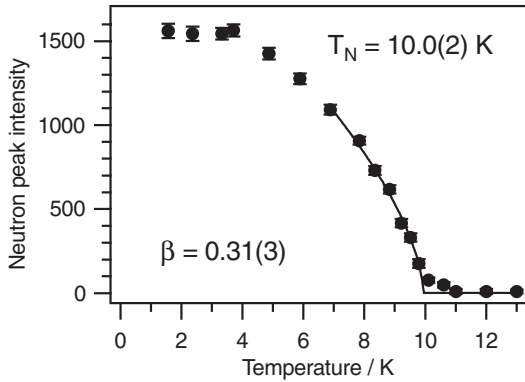


Fig. 4. Temperature dependence of the integrated magnetic peak intensity of the $(000) + \mathbf{k}$ reflection. A fit to a power law is added as a solid line

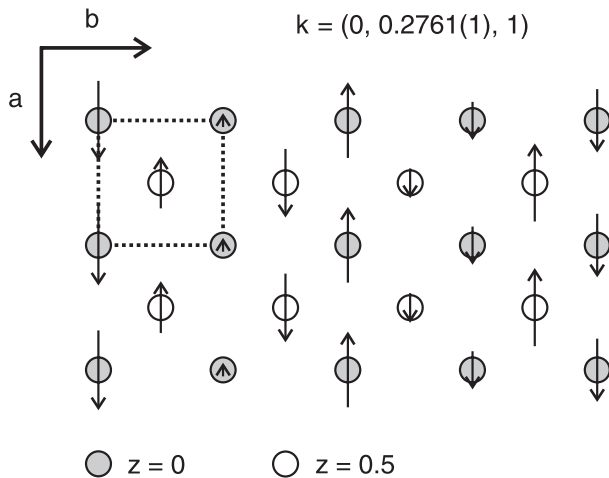


Fig. 5. Magnetic structure of CeI_2 at 1.5 K. The nuclear unit cell is shown as a dotted line

The critical exponent and the ordering temperature point towards the crucial role of the conduction electrons for the magnetic order in CeI_2 . For insulating, layer-type, rare-earth compounds, usually smaller critical exponents are observed that are indicative of predominantly 2D magnetic interactions, e.g. $\beta = 0.23$ for ErCl_3 [6]. In such compounds magnetic order typically occurs below 1 K due to the strong shielding of the unpaired $4f$ electrons. In CeI_2 the delocalized 3D nature of the conduction electrons overcomes the quasi-2D crystal structure and mediates the magnetic interactions between the Ce^{3+} ions. Similar behavior was observed for Pr_2X_5 ($X = \text{Br}, \text{I}$) [7] with ordering temperatures as high as 50 K for Pr_2Br_5 .

The magnetic structure of CeI_2 is shown in Fig. 5. It consists of one magnetic sublattice with Ce^{3+} ions at the crystallographic positions $0, 0, 0$ and $0.5, 0.5, 0.5$. The final fit, see Fig. 2, resulted in agreement factors of $R_p = 2.2\%$, $R_{wp} = 2.8\%$, $R_{exp} = 2.2\%$ and $R_{mag} = 9.1\%$. The ordered magnetic moment amounts to $1.87(1) \mu_B/\text{Ce}^{3+}$ at saturation and is slightly reduced below the free-ion value of $g \cdot J = 15/7$ by the crystal-field splitting. The moments are aligned parallel to the a axis and their amplitude is sine-modulated along the b axis according to $k_y = 0.2761(1)$ at 1.5 K. Along the c axis the layers are stacked antiferromagnetically in a commensurate $+-$ manner according to $k_z = 1$.

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