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Magnetic order in CeI_2

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Abstract. CeI_2 is a halide with metallic conductivity according to the formula $(Ce^{3+})(I^-)_2(e^-)$. Magnetic interactions are mediated by the conduction electrons and are significantly stronger than for insulating rare-earth halides. CeI_2 crystallizes in the $MoSi_2$ 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 $\boldsymbol{k}$ vector of (0, 0.2761(1), 1) at 1.5 K. The $\boldsymbol{k}$ vector is temperature-dependent and, as the sublattice magnetization, reaches saturation below 4 K. CeI_2 has one magnetic sublattice with moments parallel to the a axis. The amplitude is sine-modulated along the b axis and amounts to $1.87(1)\,\mu_B$ per Ce^{3+} 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 Ce^{3+}.

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Due to its metallic conductivity, CeI_2 is an especially interesting compound. Its properties lie between those of trivalent, insulating, ionic cerium salts and intermetallic compounds. CeI_2 was first synthesized by Corbett et al. [1], who also established its metallic conductivity. Later on, the room-temperature crystal structure of CeI_2 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. CeI_3 [3], Ce_2I_5 [4] and CeI_2, 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 CeI_2.

1 Experimental

CeI_2 was synthesized from CeI_3 and Ce metal (Johnson&Matthey, ingot, 99.99%). CeI_3 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 CeI_3 was again sealed in a silica ampoule under vacuum and sublimed for purification at 760 °C. High-purity CeI_3 was obtained in the colder part of the ampoule as lustrous yellow needles. CeI_3 is thermochromic and changes its color towards red upon heating. The melting of CeI_3 in a silica ampoule should be avoided to prevent the formation of oxide impurities.

For the CeI_2 synthesis, CeI_3 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. CeI_2 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 ($H_20 < 0.1$ ppm). CeI_3 is very hygroscopic and CeI_2 both hygroscopic and sensitive to oxidation. Exposed to air, CeI_2 immediately changes its appearance from black to colorless and evolves hydrogen from moisture. For neutron-diffraction experiments CeI_2 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 CeI_2 was refined at 15 K in the paramagnetic state from data obtained from a HRPT measurement with $\lambda = 1.8857$ Å. The $MoSi_2$-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* 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 $\boldsymbol{k}$ vector (0, 0.2761(1), 1) at 1.5 K. The tem-

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

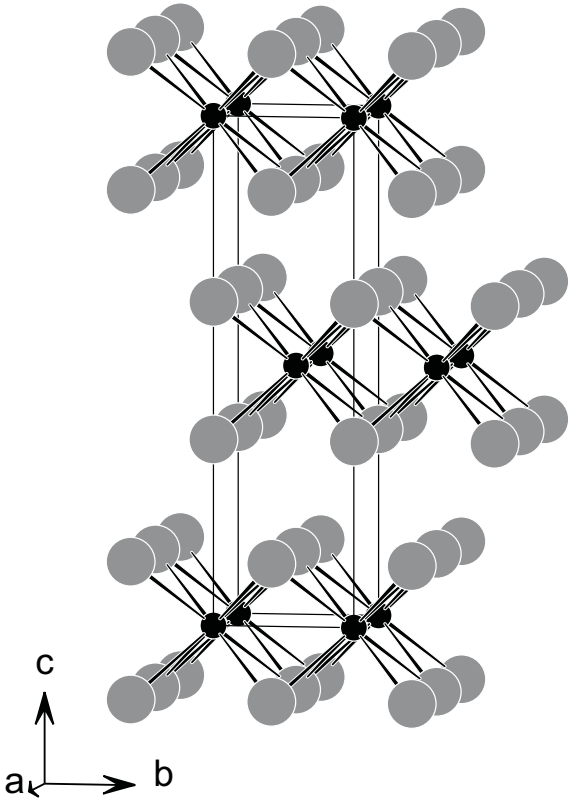

Fig. 1. Perspective view of the crystal structure of CeI_2 along the *a* axis. The Ce^{3+} ions are shown as *black* and the I^- ions as *grey spheres*, respectively

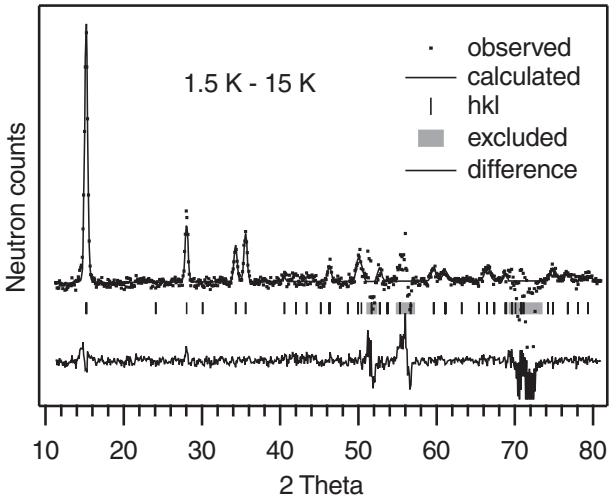

Fig. 2. Difference neutron diffraction diagram at 1.5–15 K of CeI_2 for $\lambda = 2.56$ Å

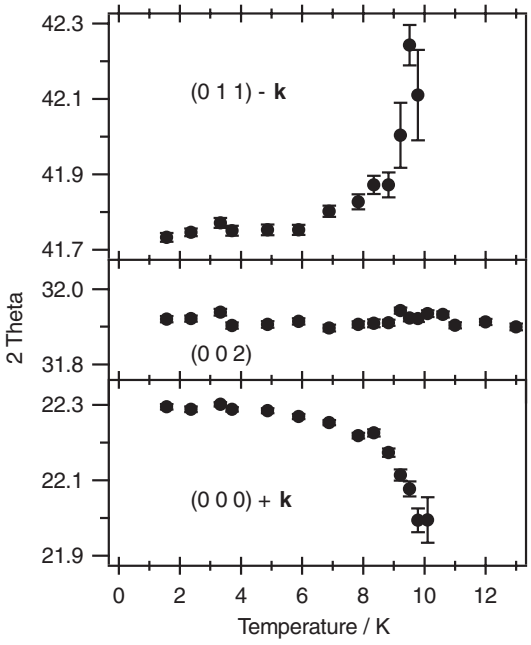

Fig. 3. Temperature dependence of the 2Θ positions of the $(000)+\boldsymbol{k}$ and $(011)-\boldsymbol{k}$ magnetic as well as the (002) nuclear Bragg peaks for $\lambda = 3.8$ Å

perature dependence of the integrated magnetic peak intensity of the $(000)+\boldsymbol{k}$ 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.

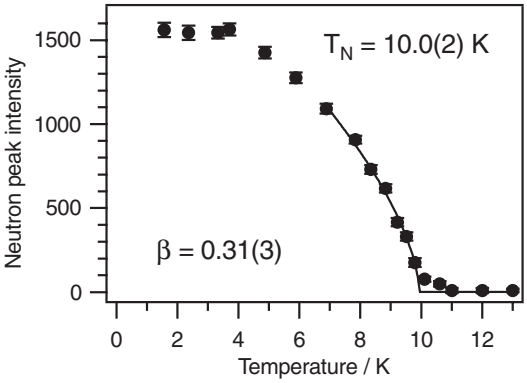

Fig. 4. Temperature dependence of the integrated magnetic peak intensity of the $(000)+\boldsymbol{k}$ reflection. A fit to a power law is added as a *solid line*

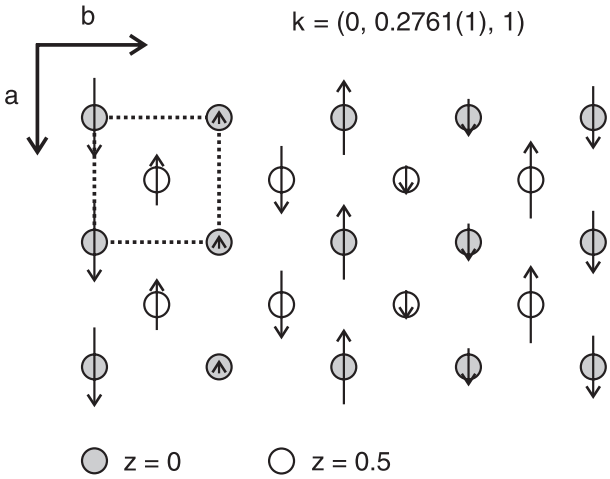

Fig. 5. Magnetic structure of CeI_2 at 1.5 K. The nuclear unit cell is shown as a *dotted line*

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 = Br, 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 $1.87(1)\,\mu_B/Ce^{3+}$ 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 $\boldsymbol{k}_y = 0.2761(1)$ at 1.5 K. Along the c axis the layers are stacked antiferromagnetically in a commensurate $+-$ manner according to $\boldsymbol{k}_z = 1$.

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