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No Van Vleck-Type Paramagnetism in In_2ZrBr_6

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Abstract: The synthesis of In_2ZrBr_6 has been repeated via an alternative route, and by using thoroughly purified starting materials. These samples are diamagnetic ($\chi_{mol} = -2.27\ [10^{-4}$ emu/mol]). Thus, previous claims that In_2ZrBr_6 would show a van Vleck-type paramagnetism are disproved. Based on structural data of better accuracy (single-crystal structure analysis: $P4/mnc$, 495 reflections, $R_1 = 0.037$) density functional band structure calculations were performed, which give no evidence for indirect coupling of In and Zr, mediated by bromine.

Introduction

In a recent paper, R. Dronskowski[1] reports on the discovery of an new type of van Vleck paramagnetism in In_2ZrBr_6. As experimental evidence for the findings, magnetic susceptibility data were presented, and the conclusions were backed by band structure calculations. As these results have appeared rather unusual to us, we have undertaken a reinvestigation.

Results and Discussion

In_2ZrBr_6 has been synthesized by an alternative route. Thoroughly purified InBr and $ZrBr_4$ (molar ratio 2:1) were reacted in the solid state at mild temperatures, and in a sealed DURAN glass tube. The reaction product consisted of pale yellow, transparent untwinned crystals of the room temperature modification of In_2ZrBr_6. The formerly given crystallographic data are confirmed, in principle (Table 1). While the lattice constants, as derived from an X-ray powder diffractogram, agree within the limits of experimental error, the positional parameters, as determined by single crystal work, differ by about 10 times (x and y coordinate of Br(1)) or even by 20 times (z of Br(2)) the esd's given, and the precision is improved by 2 orders of magnitude (Table 2). While the anisotropic thermal parameters of the bromine atoms can be traced back to the motion of a rigid $ZrBr_6$ octahedron, those of In are slightly enlarged, which is in accordance with previous findings on related compounds, and which seems to reflect the "floppy" nature of the In^+ ion.[2]

Measuring the magnetic susceptibilities clearly reveals that our samples of In_2ZrBr_6 are diamagnetic (Figure 1). The experimental value ($\chi_{mol}^{exptl} = -2.27\ [10^{-4}$ emu/mol]) is in good agreement with the sum of the increments of the constituting ions[3] ($\chi_{mol}^{cal} = -2.64\ [10^{-4}$ emu/mol]). As the X-ray data do not leave any doubt about the identity of the phases under consideration, one has to assume that the samples, which were investigated by R. Dronskowski, contained magnetic impurities, and that the claim of a special type of van Vleck paramagnetism was based on an artifact. Thus, all respective conclusions are obsolete.

Density functional band structure calculations with the TB-LMTO-ASA method[4] show an insulator with a band gap of 1.85 eV. The bands below the fermi level (−6.2 eV) are mainly built from Br-4p and In-5s orbitals. The projected density of states of In-5s has its maximum at the lower end of the valence bands. Above the fermi level, in the region between −4.4 and 0 eV, there are bands either built from Zr-4d, mixed with Br-4p, or In-5p bands.

Table 1. Crystal Data and Structure Refinement for In_2ZrBr_6

formula	In_2ZrBr_6
formula wt	800.32
temp	293(2) K
wavelength	0.71073 Å
cryst syst	tetragonal
space group	$P4/mnc$
unit cell dimens	$a = 7.413(2)$ Å $c = 10.740(2)$ Å
vol, Z	590.2(3) $Å^3$, 2
density (calcd)	4.503 g/cm^3
abs coeff	24.985 mm^{-1}
$F(000)$	696
crystal size	0.13 × 0.23 × 0.39 mm
θ range	3.34−37.33°
limiting indices	$-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-17 \leq l \leq 13$
no. of colld reflns	5692
no. of indep reflns	495 ($R_{int} = 0.064$)
abs correction	numerical on optimized crystal shape[7]
refinement method	full-matrix least-squares on F^2
goodness-of-fit on F^2	1.096
final R indices [$F_o > 4\sigma(F_o)$]	$R_1 = 0.037$, $wR_2 = 0.073$
R indices (all data)	$R_1 = 0.051$, $wR_2 = 0.079$
largest diff peak and hole	1.387 and −0.894 e $Å^{-3}$

Slight mixing of other orbitals to the bands described above has to be attributed to numerical effects of the method, e.g. to large differences of the MT-radii (In, 5.0 bohr; Br, 2.7 bohr; Zr, 3.0 bohr) and to the large empty spheres at 000 and $^1/_2$, $^1/_2$, $^1/_2$ (3.2 bohr). These effects cannot be used to interpret physical properties. Overall, the band structure shows no surprising features.

Experimental Section

Synthesis of In_2ZrBr_6. All preparative work was performed in an strictly inert atmosphere using Schlenk techniques. The starting materials were used as purchased (In 99.9999%, Zr >99.8%, Heraeus,

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(1) Dronskowski, R. *J. Am. Chem. Soc.* **1995**, *117*, 1991−1995.

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(3) Selwood, P. W. *Magnetochemistry,* 2nd ed.; Interscience Publishers: New York, 1956.

(4) Krier, G.; van Schiffgaarde, M.; Daxton, T. A.; Jensen, O.; Andersen, O. K. *TB-LMTO-ASA Program, Version 4.6*; Max-Planck-Institut für Festkörperforschung: Stuttgart, Germany, 1994.

10.1021/ja9927117 CCC: $19.00

Table 2. Positional and Anisotropic Displacement Parameters for In_2ZrBr_6

atom	site	x	y	z	$U_{11}{}^a$	$U_{22}{}^a$	$U_{33}{}^a$	$U_{12}{}^a$	$U_{13}{}^a$	$U_{23}{}^a$
Zr	2b	0	0	0.5	0.0290(4)	0.0290(4)	0.0264(6)	0	0	0
In	4d	0	0.5	0.75	0.1072(8)	0.1072(8)	0.0874(9)	−0.0318(9)	0	0
Br(1)	8h	0.2820(1)	0.2105(1)	0.5	0.0387(4)	0.0434(4)	0.0734(6)	−0.0150(3)	0	0
Br(2)	4e	0	0	0.2566(1)	0.0792(6)	0.0792(6)	0.0259(5)	0	0	0

[a] The U_{ij} are defined as $\exp\{-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{23}klb^*c^*)\}$.

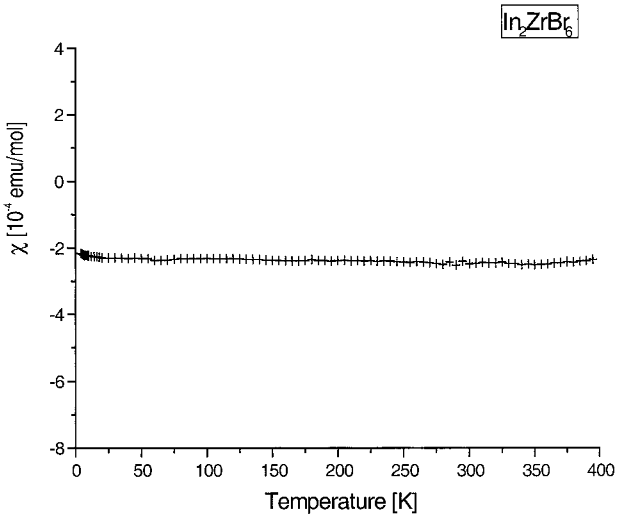

Figure 1. Molar susceptibility as a function of temperature for In_2ZrBr_6 (H = 1 T).

Hanau, Germany) or purified by distillation (Br_2, distilled from finely divided dry KBr). In a first step, $InBr_3$ and $ZrBr_4$ were prepared from the elements, and purified by sublimation according to prescriptions as taken from Brauer's handbook of preparative inorganic chemistry.[5,6] Subsequently, $InBr_3$ was reduced by an excess of metallic In. The raw InBr was purified by sublimation. In a second step mixtures of InBr and $ZrBr_4$ (molar ratio 2:1) were reacted at 300 °C for 31 days in a sealed DURAN glass tube to form crystalline In_2ZrBr_6.

Magnetic Analysis. Magnetic measurements (field strengths: 1, 3, and 5 T; temperature range: 3−400 K; sample weight: 16.8 mg) were carried out on a Superconducting Quantum Interference Device (Quantum Design, San Diego (USA)).

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Supporting Information Available: Complete crystallographic data for In_2ZrBr_6 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[5] Brauer, G. *Handbuch der Präparativen Anorganischen Chemie Board II*; Ferdinand Enke Verlag: Stuttgart, Germany, 1978; p 870.

[6] Brauer, G. *Handbuch der Präparativen Anorganischen Chemie Board II*; Ferdinand Enke Verlag: Stuttgart, Germany, 1978; p 1359.

[7] Herrendorf, W. Dissertation, University of Karlsruhe, Germany, 1993.