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2001 J. Phys.: Condens. Matter 13 8007

(http://iopscience.iop.org/0953-8984/13/35/308)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **13** (2001) 8007–8014 PII: S0953-8984(01)22334-0

Magnetic structure of $HoPd_2Si_2$ redefined on the basis of new neutron diffraction data

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Received 27 February 2001, in final form 4 June 2001
Published 16 August 2001
Online at stacks.iop.org/JPhysCM/13/8007

Abstract

A new sample of $HoPd_2Si_2$ ($ThCr_2Si_2$-type structure, space group $I4/mmm$) has been prepared and investigated. Magnetic susceptibility and magnetization data indicate antiferromagnetic behaviour below $T_N = 5.8$ K. On the basis of powder neutron diffraction data the magnetic structure of the compound has been redefined and found to be more complex than reported earlier. In the temperature region from 20 K to 5 K a short-range magnetic order develops. Between 1.5 K and 5 K a long-range magnetic ordering, that could be described in an enlarged magnetic unit cell ($a_m = 7a$, $b_m = a$ and $c_m = 6c$), is observed. A complex magnetic structure of sine-wave modulated type with two propagation vectors and Ho magnetic moments parallel to the b-axis is proposed. Moreover, a new attempt to understand the transition from long- to short-range magnetic ordering observed in some rare earth compounds with Pd is made.

1. Introduction

$HoPd_2Si_2$ belongs to the large family of ternary rare earth compounds that crystallize in the body-centred tetragonal $ThCr_2Si_2$-type crystal structure (space group $I4/mmm$) [1, 2]. At low temperatures RPd_2Si_2 compounds develop complex magnetic ordering schemes [2–6].

In the course of our study of magnetic properties of pseudo-ternary $HoRh_{2-x}T_xSi_2$ (T = Ru, Pd) systems we have found the ordering temperature of RPd_2Si_2 to be about 5.8 K [7], that is much lower than the value reported earlier ($T_N = 21$ K) [2]. Moreover, the evolution of the magnetic structure found in the $HoRh_{2-x}Pd_xSi_2$ series of solid solutions [8] has been not consistent with the magnetic ordering reported for the limiting $HoPd_2Si_2$ [2]. To clear up these

problems a new sample has been prepared and investigated as now we have an opportunity to carry out neutron diffraction measurements using the E6 diffractometer installed at the BERII reactor at the Hahn–Meitner Institute, Berlin. This instrument offers excellent resolution and it is possible to obtain full diffraction patterns at selected temperatures so temperature variation of intensities and positions of magnetic peaks could be traced.

2. Experimental details and results

2.1. Sample preparation and powder x-ray diffraction

The sample was prepared by standard arc melting of stoichiometric amounts of high purity elements in the argon atmosphere. Then the sample was annealed at 800 °C for one week.

The x-ray powder diffraction pattern (Siemens, Co Kα) was consistent with the one calculated for the $ThCr_2Si_2$-type crystal structure (space group $I4/mmm$) with Ho at 2(a): (0 0 0), Pd at 4(d): (0 1/2 1/4) and Si at 4(e): (0 0 z) positions with $z = 0.385(1)$.

2.2. Magnetometric measurements

Magnetometric data were collected using a vibrating sample magnetometer and a SQUID magnetometer. The temperature dependence of the magnetic susceptibility was measured at $H = 10$ kOe over the temperature range 1.8–300 K. The temperature dependence of the magnetization over the temperature range 1.8–8.5 K was collected at 50 Oe and 75 Oe. Magnetization versus external magnetic field up to 50 kOe was measured at 1.9 K.

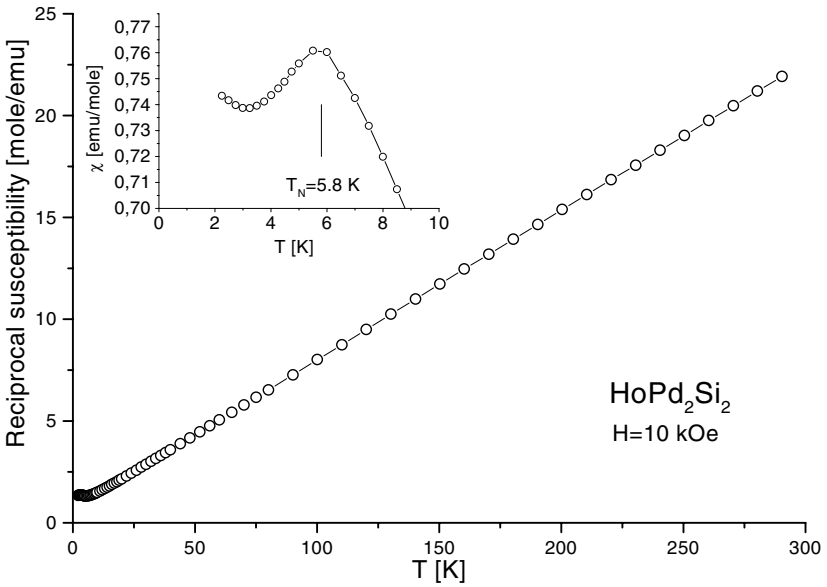

Figure 1. Reciprocal magnetic susceptibility of $HoPd_2Si_2$ as a function of temperature. The inset shows the temperature dependence of the susceptibility for temperatures up to 9 K.

Magnetic susceptibility (figure 1) and magnetization data (figure 2(a)) indicate antiferromagnetic behaviour below the Néel temperature $T_N = 5.8$ K. Below 3 K a sharp increase in the magnetization value is observed (figure 2(a)). Above the Néel temperature the

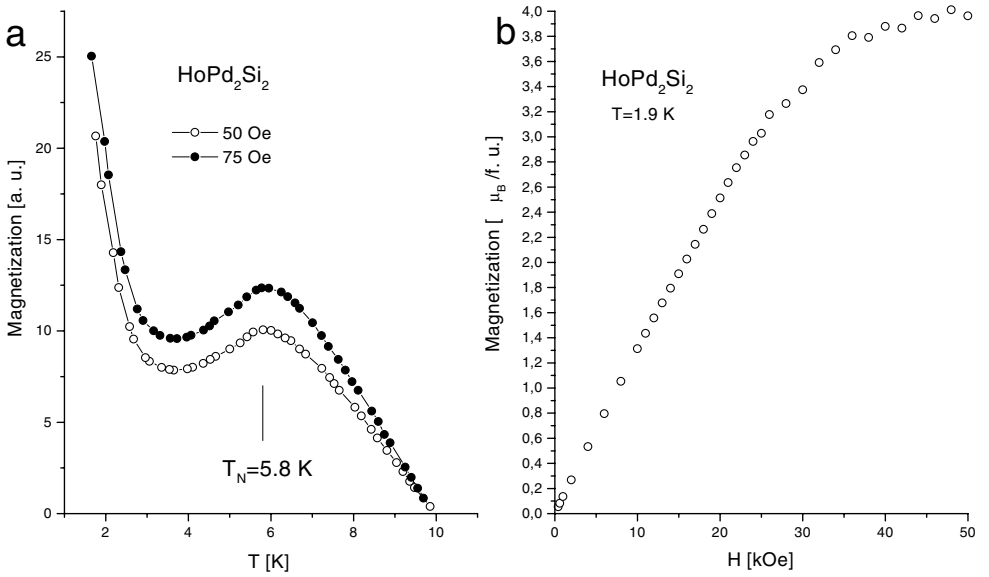

Figure 2. Magnetization of $HoPd_2Si_2$ as a function of (a) temperature and (b) external magnetic field.

reciprocal susceptibility obeys the Curie–Weiss law with negative value of the paramagnetic Curie temperature equal to -6.5 K and effective magnetic moment of 10.54 μ_B that is close to the free Ho^{3+} value (10.61 μ_B). Up to 25 kOe the magnetization curve measured at 1.9 K (figure 2(b)) is a linear function of the external field and then it saturates. The value of Ho magnetic moment determined at 1.9 K at the external magnetic field of 50 kOe is equal to 4.0 μ_B, that is much smaller than the free Ho^{3+} value. That confirms the above stated antiferromagnetic coupling of holmium magnetic moments.

2.3. Powder neutron diffraction

Neutron diffraction patterns were collected over the temperature range 1.5–20 K using the E6 diffractometer ($\lambda = 2.4383$ Å) at the BERII reactor, Berlin Neutron Scattering Centre, Hahn–Meitner Institute, Germany. The type of magnetic ordering and values of the coordinates of the propagation vector of the magnetic structure were initially determined by means of the program UNDMA [9]. Then the magnetic and structural parameters were simultaneously refined by means of the Rietveld-type profile refinement program FULLPROF [10]. The coherent neutron scattering lengths of [11] and the magnetic form factor of Ho^{3+} of [12] were used.

Neutron diffraction pattern recorded at 20 K (figure 3) could be indexed on the basis of the space group $I4/mmm$. The crystal structure parameters refined on the basis of these data are as follows: $a = 4.0989(8)$ Å, $c = 9.8727(60)$ Å, $z_{Si} = 0.385(1)$ (reliability factors of the refinement: $R_{Bragg} = 6\%$, $R_f = 4\%$).

In the neutron diffraction patterns recorded at 6, 8, 12 and 20 K a broad diffuse maximum about $2\theta = 20^\circ$ is present (the inset in figure 3). In this region three principal lines of magnetic origin develop at low temperatures so the diffuse peak may represent a short-range magnetic order existing above 5 K.

The best refinement of the intensities of magnetic contributions was obtained for a complex sine-wave modulated structure described by two propagation vectors: $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$. The magnetic

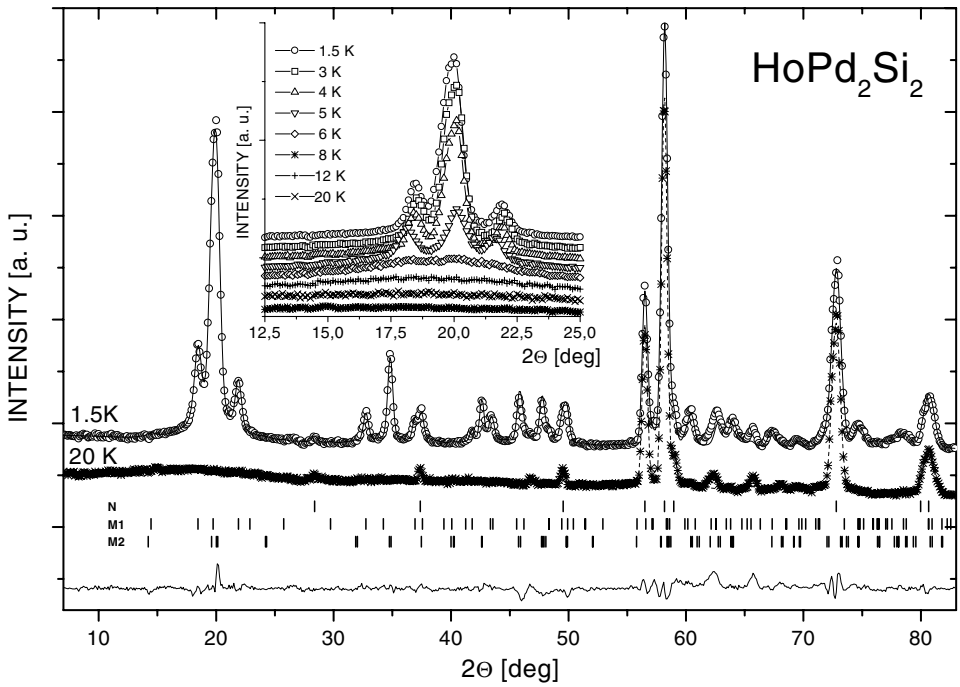

Figure 3. Neutron diffraction patterns of $HoPd_2Si_2$ collected at 20 K (paramagnetic region) and at 1.5 K (solid lines show results of the refinements). The inset shows the temperature variation of the diffraction pattern about $2\theta = 20^\circ$. The vertical bars mark the positions of nuclear (N) and magnetic (M1 and M2) peaks as refined for $T = 1.5$ K. The curve at the bottom is the difference between the experimentally observed and the refined pattern at 1.5 K.

satellites corresponding to the propagation vector $\boldsymbol{k}_1$ (denoted as M1 in figure 3) are observed only if the sum of the Miller indices is even ($h+k+l = 2n$). If the sum of the Miller indices is odd ($h+k+l = 2n+1$) only the magnetic satellites corresponding to the propagation vector $\boldsymbol{k}_2$ (denoted as M2 in figure 3) are observed. The intensities of the magnetic peaks decrease with increasing temperature. At the lowest available temperature in the reported study ($T = 1.5$ K) the best refinement was obtained for the propagation vectors $\boldsymbol{k}_1 = (0.5775(6), 0, 0.1717(7))$ and $\boldsymbol{k}_2 = (0.5783(2), 0, 1.0054(13))$ and Ho magnetic moments parallel to the b-axis and equal to $\mu_1 = 4.94(7)\ \mu_B$ and $\mu_2 = 6.54(6)\ \mu_B$ for the magnetic phase described by the propagation vectors $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$, respectively. It is worth noting that the x-components of these vectors are equal while significant difference is observed for their z-components. The analysis of the intensities of magnetic contribution leads to similar models of the magnetic structure at 3, 4 and 5 K, as described above for $T = 1.5$ K: the direction of the magnetic moments as well as the x- and z-components of the wavevectors do not change with increasing temperature while the values of the magnetic moments μ_1 and μ_2 both decrease (figure 4).

Neutron diffraction patterns confirm that in the studied temperature range (1.5–20 K) $HoPd_2Si_2$ crystallizes in the body-centred $ThCr_2Si_2$-type structure. However, the temperature dependence of the lattice parameters (a and c) and the unit cell volume V has anomalous character: with the temperature increasing up to about 4 K these parameters increase (as could be expected) but with further increase in the temperature they start to decrease (figure 4).

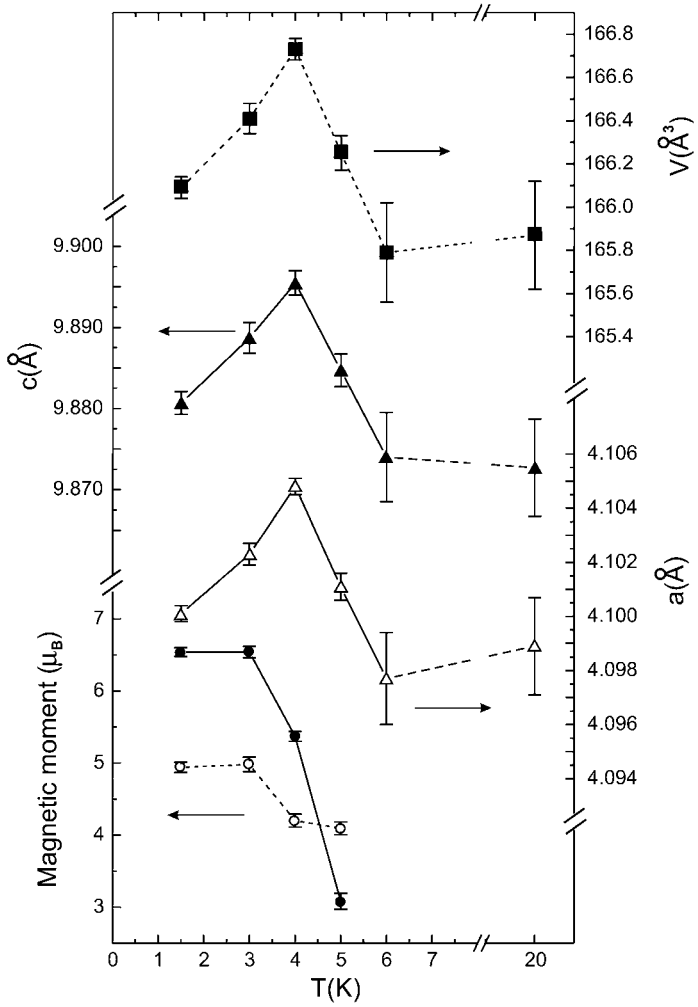

Figure 4. Temperature dependence of the lattice parameters a (△) and c (▲), the chemical unit cell volume V (■) and the magnetic moments μ_1 (○) and μ_2 (●) of the magnetic structures of $HoPd_2Si_2$ described by the propagation vectors $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$, respectively. (The lines are only a guide to eye.)

3. Discussion

The magnetic measurements show that $HoPd_2Si_2$ is an antiferromagnetic compound with the Néel temperature $T_N = 5.8$ K. The reported neutron diffraction data lead to a new description of the magnetic structure of $HoPd_2Si_2$. Between 1.5 K and 5 K a long-range magnetic order is evidenced and a complex magnetic structure of sine-wave modulated type described by two propagation vectors fits well to the obtained neutron diffraction patterns. In the temperature region from 6 K up to about 20 K a short-range magnetic order gives a broad diffuse maximum about $2\theta = 20^\circ$ and no reflections of any long-range magnetic structure are present.

The modulated magnetic structure of $HoPd_2Si_2$ could be satisfactorily described within a model that is similar to the one reported for isostructural $ErPd_2Si_2$ where a sine-wave modulated

magnetic structure, described by two propagation vectors and Er magnetic moments parallel to the c-axis, was reported [5]. In the model proposed for $HoPd_2Si_2$ the x-components of both propagation vectors are equal to each other and close to 4/7 (0.5714) while the z-component is close to 1/6 (0.1667) for the first propagation vector and to 6/6 for the second one. So the magnetic ordering of $HoPd_2Si_2$ could be discussed in the enlarged unit cell: $a_m = 7a$, $b_m = a$ and $c_m = 6c$. Ho atoms located at the (0, 0, 0) Wyckoff position of the crystal unit cell carry the magnetic moment defined as: $\mu_S = \mu_{Ho}\{P_1 \cos(A_{xz}) + (1 - P_1)\cos(B_{xz})\}$ and those located at the (1/2, 1/2, 1/2) Wyckoff position carry the magnetic moment $\mu_C = \mu_{Ho}\{P_1 \cos(A_{xz}) - (1 - P_1)\cos(B_{xz})\}$. Here μ_{Ho} is the maximum value of the Ho magnetic moment component along the (010) direction and P_1 is the contribution to the total magnetic moment connected with the $\boldsymbol{k}_1$ propagation vector. The modulation angles (A_{xz} and B_{xz}) related to the propagation vectors $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$ are defined as: $A_{xz} = 2\pi(4x + z)$ and $B_{xz} = 2\pi(4x + 6z)$, where x and z are the coordinates of the given Ho atom in the magnetic supercell. The maximum value of μ_{Ho} (equal to the sum of $\mu_1(\boldsymbol{k}_1)$ and $\mu_2(\boldsymbol{k}_2)$) is 11.5(1) μ_B at $T = 1.5$ K. The projection of the magnetic structure onto the a–c plane is shown in figure 5.

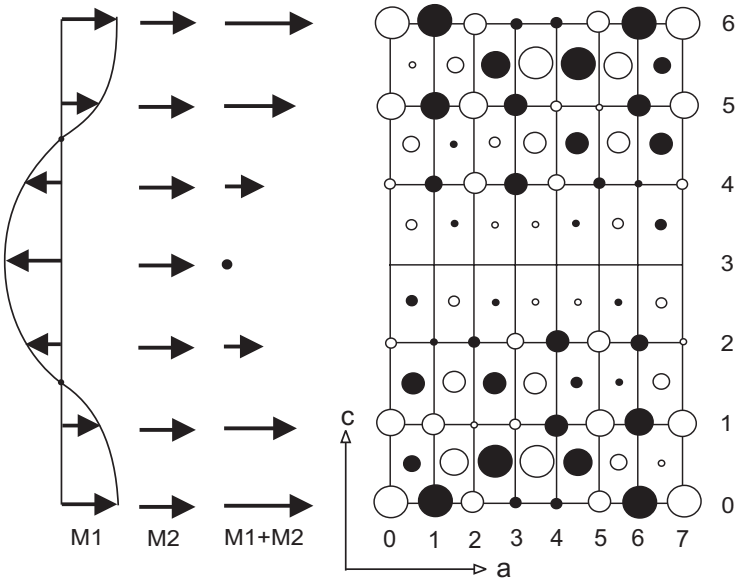

Figure 5. The projection of the magnetic structure of $HoPd_2Si_2$ onto the a–c plane for a temperature of about 4.5 K, at which the values of magnetic moment components M1 and M2 are equal each other. Magnetic moments are perpendicular to the plane of the picture; full and open circles mark their direction while the diameter of the circle reflects the magnitude of the magnetic moment.

The scheme of the magnetic structure of $HoPd_2Si_2$ shown in figure 5 is drawn for a temperature of about 4.5 K, at which the magnetic moment components originating from the sine-wave modulated structure M1 and M2 are equal to each other. That leads to extinction of the magnetic moment in the plane denoted as 7 in figure 5. At lower temperatures, down to $T = 1.5$ K, the magnetic moment component M2 is bigger than M1 and no extinction of magnetic moments in the planes perpendicular to the c-axis take place. At temperatures higher than 4.5 K the situation is just the opposite, i.e. $\mu_1 > \mu_2$, and, as a result, increases the number of the planes with zero or very low Ho magnetic moments. In the absence of any magnetic moments in some planes (or significant lowering of their values) the between-planes interactions are weakened. As a consequence, the long-range magnetic ordering vanishes

and only short-range ordering is observed at higher temperatures. This explains how, under some circumstances, in such complex systems a transition from long- to short-range magnetic ordering (in which some planes do not take part in magnetic interactions) takes place. The change in the magnetic ordering scheme of $HoPd_2Si_2$ is reflected in the temperature dependence of the lattice parameters (figure 4) and in the increase of the magnetization at low temperatures (figure 2(a)).

The short-range magnetic order visible as a broad diffuse scattering maximum below the appropriate Néel point has been reported also for the isostructural $ErPd_2Si_2$ [5], $TbPd_2Si_2$ and $TbPd_2Ge_2$ [6]. Moreover, in the case of $TbPd_2Ge_2$ the long-range magnetic order at $T = 1.5$ K was reported as not extending over the whole crystal but confined to clusters [6].

Such large magnetic unit cells as the one of $HoPd_2Si_2$ were found for some isostructural RT_2Si_2 and RT_2Ge_2 compounds, namely for $ErPd_2Si_2$ [5], $TbPd_2Si_2$ and $TbPd_2Ge_2$ [6], $DyNi_2Ge_2$ [13] and $TbNi_2Ge_2$ [14]. The common feature of the RPd_2Si_2 family of compounds is that the component of the propagation vector along the c-axis is about $1/6$ for all of them while the one in the basal plane depends on the rare earth element and changes monotonically with their atomic number: $2/5$ for Tb [6], $4/7$ for Ho [this work] and $4/9$ for Er [5].

For compounds crystallizing in the tetragonal $ThCr_2Si_2$-type crystal structure the direction of the magnetic moment in the magnetic unit cell depends on the sign of the B_2^0 parameter of the crystal electric field. In the case of $ErPd_2Si_2$ $B_2^0 = -0.20(5)$ K, which is in agreement with the direction of the magnetic moment found in this compound [5]. In $HoPd_2Si_2$ (similarly to $TbPd_2Si_2$ [6]) the magnetic moment lies in the basal plane, which suggests a positive value of the B_2^0 parameter. Such a change of the sign of the B_2^0 parameter, from positive for the Ho to negative for the Er compound, have been also observed in the isostructural RCu_2Si_2 series of compounds [15].

The CEF effects are rather small in the RPd_2Si_2 series of compounds as is evidenced by the values of the B_2^0 parameter [16–18] so the ordering of the magnetic moments in this compounds is mainly due to exchange interactions, very probably of the RKKY type.

The data presented in this work show that $HoPd_2Si_2$ belongs to the materials with mixed magnetic phases where the same element (here Ho) localized at a unique crystallographic site has two distinct magnetic states: the nonmagnetic one and the other with a well defined magnetic moment. Mixed magnetic phases were observed in CeSb [19], $PrCo_2Si_2$ [20] and $TbRu_2Si_2$ [21, 22] where magnetically non-ordered rare earth planes coexist with magnetically ordered ones. That was observed in several high-temperature phases of compounds with complex H–T phase diagrams and numerical simulations performed in the frame of the self-consistent periodic field model gave satisfactory agreement with the experimental data [23].

Acknowledgments

AS, SB and JL gratefully acknowledge kind hospitality and financial support of the Hahn–Meitner Institute.

This work was supported by the European Commission under the Access to Research Infrastructures of the Human Potential Programme (contact number HPRI-CT-1999-00020).

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