PHYSICAL REVIEW B VOLUME 35, NUMBER 4 1 FEBRUARY 1987

Calculations of the local orbital moment in Y_2Co_{17} using the recursion method

Barbara Szpunar and W. E. Wallace
Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

(Received 20 June 1986)

The local orbital moments on different sites in Y_2Co_{17} have been calculated. The recently proposed continued-fraction technique has been used in these calculations. The calculated local orbital moments are in quantitative agreement with NMR experiments.

I. INTRODUCTION

R_2Co_{17} and $R_2(Co_{1-x}T_x)_{17}$ intermetallic compounds have been studied recently using NMR technique.[1-3] The different sign of the stabilization energy on different sites suggests that competitive basal and axial magnetocrystalline anisotropy are present in these compounds.

The measurements of the magnetocrystalline anisotropy[3-8] of ternary intermetallic compounds $R_2(Co_{1-x}T_x)_{17}$ support such conclusions. Because of the complexity of the crystal structure (Th_2Zn_{17} or Th_2Ni_{17}) *ab initio* band-structure calculations of the local orbital moment in these compounds would be very difficult. We will use a method based on a continued-fraction technique in the local orbital moment calculations. It has already been pointed out by Streever[1] that a local magnetocrystalline anisotropy is proportional to a difference between the local expectation values of the orbital moments which are correspondingly parallel and perpendicular to the c axis. A high component of the orbital moment parallel to the c axis suggests preference of the uniaxial anisotropy on this site.

In this paper we estimate a component of the orbital moment parallel to the c axis. The complexity of Y_2Co_{17} structure forces us to assume simplifications. A model structure consists of a narrow band formed essentially with $4d$ and $3d$ states from yttrium and cobalt metals. It has been demonstrated already that the tight-binding Hamiltonian describes well the magnetic properties of the rare-earth—transition-metal intermetallic compounds.[9-11]

II. THE CONTINUED-FRACTION METHOD

The continued-fraction method has been used recently in calculating the local density of states.[12] This technique provides a convenient method for calculating the density of states in any system described by a tight-binding Hamiltonian. For such Hamiltonians the most convenient basic functions are those which form a set of the localized atomic states for which the electron states of a type m, n are such that $\langle m,R_i | H | n,R_j\rangle \neq 0$ if R_i and R_j are near-neighbor atomic sites.

Haydock *et al.*[12] proposed an alternative set of orthonormal functions using the recurrence formula:

$$b_{n+1}|\mu_{n+1}\rangle = H|\mu_n\rangle - a_n|\mu_n\rangle - b_n|\mu_{n-1}\rangle \; , \tag{1}$$

where $|\mu_0\rangle$ is a function describing the electron state on site O. The Hamiltonian in this representation is a tridiagonal matrix, and this leads to an expression for the local electronic density of states which is in the form of the continued fraction. If we set $|\mu_0\rangle$ equal to $|m,R_0\rangle$ we may calculate the density of states projected onto orbital m. In practice the only limitation which exists is imposed by a computer memory which limits the number of orbitals and atoms considered in each single cluster. At first sight this seems to be a serious limitation, especially as particles are usually much larger in size than a model cluster which might be used in the computer experiments. Fortunately, however, Beer and Pettifor have shown[13] that it is not necessary to consider a very large cluster. They have proposed and demonstrated a technique for terminating the continued fraction, yielding results that are very close to the exact band calculations. In the Beer-Pettifor approximation the Green's function, whose imaginary part describes the density of states, is a continued fraction of the form

$$G_{00}(\epsilon) = \cfrac{b_0^2}{\epsilon - a_0 - \cfrac{b_1^2}{\cdots\, t(\epsilon)}} \tag{2}$$

and a tail of the fraction $t(\epsilon)$ is given by

$$t(\epsilon) = \tfrac{1}{2}\{\epsilon - a - [(\epsilon-a)^2 - 4b^2]^{1/2}\} \; , \tag{3}$$

where a and b are calculated assuming that the δ functions must be situated at the band edges. In the presence of gaps in the density of states, this terminator yields spiky features; however, it does not influence the integrated values.[14] The Beer-Pettifor terminator protects weights in the band, and this is most essential for estimation of the integrated quantities. We apply the continued-fraction method in our calculation in order to determine the local partial density of states on various sites.

Our calculations are limited to a cluster of 4167 atoms and we use 16 levels of the continued fraction expansion.

III. CALCULATION OF THE SPIN AND THE ORBITAL MOMENT CONTRIBUTION

In our spin-polarized calculations we take into account two effects: magnetic splitting and spin-orbit interaction. First, using the Stoner model we assume a splitting of spin-up and spin-down electrons which is proportional to the magnetization

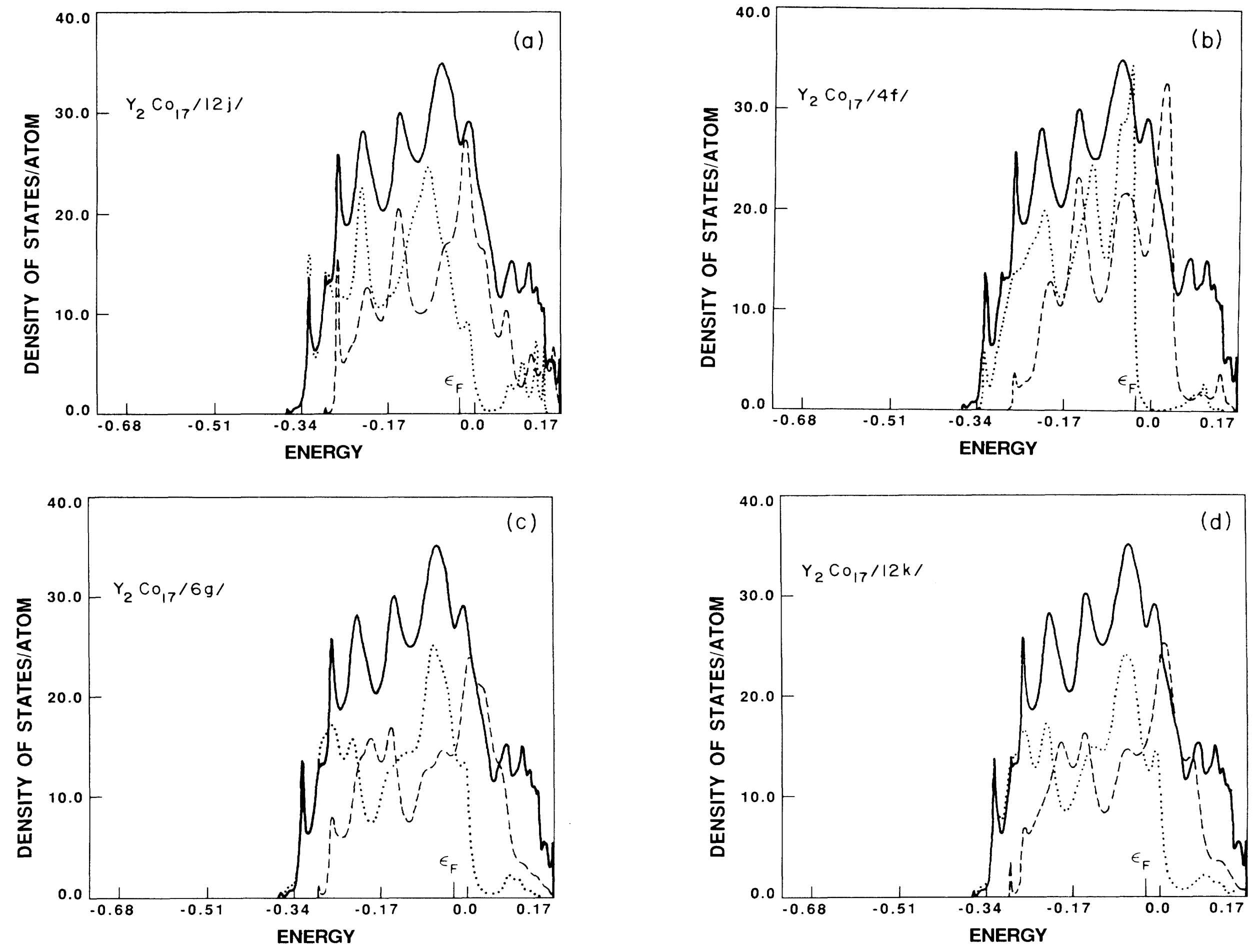

FIG. 1. (a)—(d) The local density of states on the Co(II), Co(IV), Co(I), and Co(III) sites in Y_2Co_{17}. Solid line, total density of states; dotted line, majority-spin-up local density of states; dashed line, minority-spin-down local density of states.

$$\Delta E = \tilde{U} m \ , \tag{4}$$

where $\tilde{U}$ is an effective intra-atomic Coulomb energy and

$$m_s = \tfrac{1}{2} g_s \mu_B \sum_{\nu=1}^{5} (\langle n_{i\uparrow}^{\nu} \rangle - \langle n_{i\downarrow}^{\nu} \rangle) \tag{5}$$

where

$$\langle n_{is}^{\nu} \rangle = \int_{\infty}^{\epsilon_F} \rho_{is}^{\nu}(\omega) d\omega \ . \tag{6}$$

At room temperature the spin-flip scattering can be neglected, and this provides us with a method for calculating the density of states of spin-up and spin-down electrons separately. According to our previous calculations for YCo_5,[15] we assume that the energy level for cobalt spin-up electrons is equal to −0.14 Ry and for spin-down electrons is −0.08 Ry. For yttrium, both energy levels are equal to 0.0 Ry. This gives us an effective intra-atomic Coulomb energy equal to 0.05 or 0.04 Ry for the magnetic moment equal to $1.2\mu_B$ or $1.5\mu_B$ and is comparable with the value proposed by Ishida ($\tilde{U}$=0.053 Ry).[16] The same band splitting gives for Y_2Co_{17} a higher moment than for YCo_5, and this is due to a modification of the shape of the density of states, see Fig. 1. The most interesting result is obtained when there is antiferromagnetic ordering between the spins of 3*d* and 4*d* electrons.[11] We believe this is due to a higher hybridization between spin-down than between spin-up electrons on both atoms of cobalt and yttrium.

The second and a much smaller effect is a splitting of the density of states on cobalt originating from the spin-orbit interaction which is equal to

$$\Delta(\mathrm{so}) = \xi \hat{\mathrm{l}} \cdot \hat{\mathrm{s}} \ , \tag{7}$$

where $\hat{\mathrm{l}}$ and $\hat{\mathrm{s}}$ are the orbital- and spin-angular-momentum operators, respectively. The spin-orbit energy can be expressed for two possible values of the total angular momentum (j) using the following expressions:

$$\Delta(\mathrm{so})^{(j=l+1/2)} = l(\xi/2) = lE(\mathrm{so}) \ , \tag{8}$$

$$\Delta(\mathrm{so})^{(j=l-1/2)} = -(l+1)(\xi/2) = -(l+1)E(\mathrm{so}) \ . \tag{9}$$

Notation by Herman and Skillman[17] is used. Using the continued fraction method we can calculate a partial den-

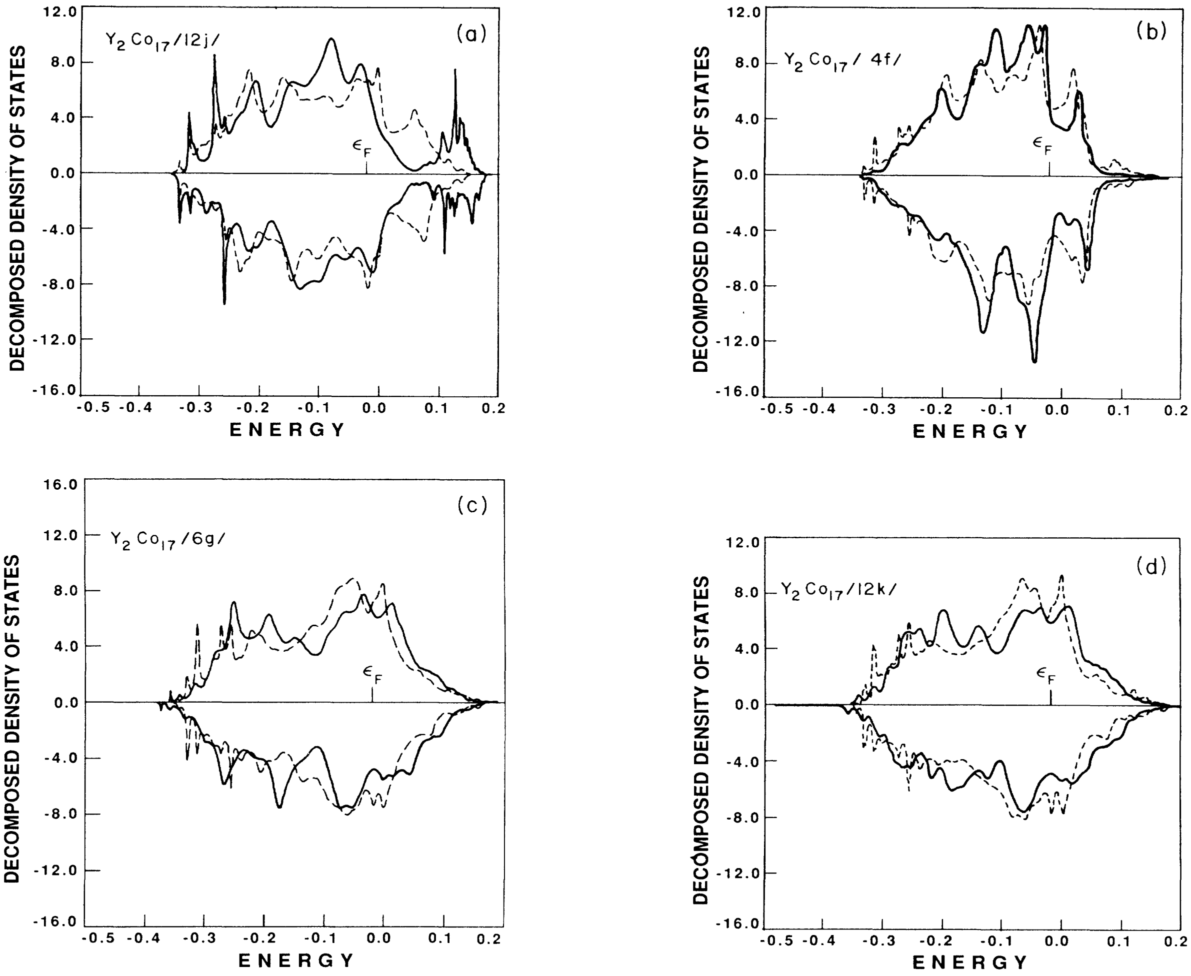

FIG. 2. (a)–(d) The decomposed local density of states on the Co(II), Co(IV), Co(I), and Co(III) sites in Y_2Co_{17}. The solid line corresponds to the density of states with $m_l = \pm 2$; dashed line corresponds to the density of states with $m_l = \pm 1$.

sity of states for a real angular wave function (Table I). To take into account spin-orbit effect, it is sufficient to calculate the density of states with different j equal to $l \pm \frac{1}{2}$.[18] The proportion of electrons having specified j and m values is calculated assuming the well-known relation,[19] for $j = l + \frac{1}{2}$,

$$m_j = m + \tfrac{1}{2}, \quad -(l+1) \le m \le l , \tag{10}$$

TABLE I. Real angular momentum wave functions for d electrons ($l = 2$).

$\mid m \mid$	$\psi_{l\mid m\mid}$
2	$\sqrt{15/2}\frac{x^2-y^2}{r^2}$, $\sqrt{15}\frac{xy}{r^2}$
1	$\sqrt{15}\frac{xz}{r^2}$, $\sqrt{15}\frac{y^2}{r^2}$
0	$\sqrt{5/2}\frac{3z^2-r^2}{r^2}$

$$\psi_{jm_jl} = \frac{1}{(2l+1)^{1/2}}\left(\sqrt{l+m+1}\,\psi_{lm}^{\uparrow} + \sqrt{l-m}\,\psi_{lm+1}^{\downarrow}\right) , \tag{11}$$

for $j = l - \frac{1}{2}$,

$$m_j = m + \tfrac{1}{2}, -l \le m \le l - 1 , \tag{12}$$

TABLE II. A proportion of d electrons correspondingly for spin up and down for different m values ($j = l \pm 1/2$) (Ref. 18).

	Spin up			Spin down	
m	$j = 2.5$	$j = 1.5$	m	$j = 2.5$	$j = 1.5$
-2	$\frac{1}{10}$	$\frac{4}{10}$	-2	$\frac{1}{2}$	0
2	$\frac{1}{2}$	0	2	$\frac{1}{10}$	$\frac{4}{10}$
-1	$\frac{2}{10}$	$\frac{3}{10}$	-1	$\frac{4}{10}$	$\frac{1}{10}$
1	$\frac{4}{10}$	$\frac{1}{10}$	1	$\frac{2}{10}$	$\frac{3}{10}$
0	$\frac{3}{5}$	$\frac{2}{5}$	0	$\frac{2}{5}$	$\frac{3}{5}$

TABLE III. The calculated spin contribution and the orbital moment on Y_2Co_{17}, the measured $\Delta m_l = m_{l\parallel} - m_{l\perp}$ value (Ref. 2) and the stabilization energy, E_s (Ref. 1). For comparison, anisotropy field calculated by use of screened charge point model (Ref. 3) is presented.

Presented value	12*j* 12Co(II) (18*f*)	4*f* 4Co(IV) (6*c*)	6*g* 6Co(I) (9*d*)	12*k* 12Co(III) (18*h*)	E(so) (Ry)
Concentration	0.315 78	0.105 26	0.157 89	0.315 18	
m_s^{th}(units of μ_B)	1.41	1.67	1.55	1.51	
m_l^{th}(units of μ_B)	0.17	0.08	0.01	0.02	0.0034
m_l^{th}(units of μ_B)	0.23	0.12	0.03	0.04	0.005
$m_{\text{th}}^{\text{tot}}$(units of μ_B)	1.58	1.76	1.56	1.53	0.0034
$m_{\text{th}}^{\text{tot}}$(units of μ_B)	1.64	1.79	1.58	1.55	0.005
m(units of μ_B)[a]	1.89	2.12	1.87	1.87	
$\overline{m}$(units of μ_B)[b]	1.65	1.65	1.65	1.65	
E_s(units of cm^{-1})[c]	12	-18	-3.5	-5.2	
E_A(units of K)[d]	35.49	-2.27	-64.59	-4.16	
Δm_l(units of μ_B)[e]	0.06	0.0	-0.09	0.0	

[a] Reference 20.
[b] Reference 7.
[c] Reference 1.
[d] Reference 3.
[e] Reference 2.

$$\psi_{jm_j l} = \frac{1}{(2l+1)^{1/2}} \left(\sqrt{l-m}\,\psi^{\uparrow}_{lm} - \sqrt{l+m+1}\,\psi^{\downarrow}_{lm+1} \right) . \tag{13}$$

The results for spin up and spin down are presented in Table II.

The orbital moment can then be calculated using the formula

$$m_l = g\mu_B \sum_{m=-2}^{2} m \int_{-\infty}^{\epsilon_F} \rho_l^m(\omega) d\omega$$

where $\rho_l^m(\omega)$ is a partial density of states of d electrons with an azimuthal quantum number m, see Fig. 2. There is some uncertainty about what value should be taken as E(so) for cobalt atoms in the compound. E(so) constants are calculated by Herman and Skillman[17] for Fe: $E(\text{so}) = 0.002\,65$ Ry and for Ni: 0.004 07 Ry. This gives as the value $E(\text{so}) = 0.0034$ Ry for pure cobalt. Following suggestions from our preceding paper we performed as well calculations for a higher value of $E(\text{so}) = 0.005$ Ry, and the results are presented in Table III.

IV. RESULTS AND DISCUSSION

The calculated spin contribution and the orbital moments for different sites of cobalt are shown in Table III. The magnetic moment on yttrium is on the $2d$ site equal to $-0.42\mu_B$ and $-0.40\mu_B$ on the $2b$ site, and the absolute value of the moment is very much dependent on the chosen value of the atomic level for yttrium and cobalt atoms.

The stability energies obtained by NMR by Streever[1] are in disagreement with Figiel[2] NMR measurements. It has been shown experimentally[1-8] that in ternary alloys the substitution of 4Co(IV) ($4f$,$6c$) sites by a nonmagnetic metal causes an increase in the anisotropy. Streever[1] concluded that the 4Co(IV) atoms contribute mainly to the basal anisotropy. However, more precise analysis of ternary alloys $Y_2(Co_{1-x}Mn_x)_{17}$ by Figiel *et al.*[2,3] has shown that while Co(IV) has some influence, the Co(I) ($6g$,$9d$) sites give the main contribution to the basal plane magnetocrystalline anisotropy. This conclusion agrees with our calculation. The component of the orbital moment which is parallel to the c axis is the smallest on Co(I) sites.

The highest orbital moment is on Co(II) ($12j$,$18f$) sites. These sites contribute to uniaxial anisotropy. Such anisotropy competes with the basal plane anisotropy of Co(I) sites. This may explain the change in the total magnetocrystalline anisotropy from the basal to the uniaxial anisotropy in the studies of ternary substitutional alloys.

The correlation between calculated local magnetocrystalline anisotropy by the screened charge point model[3] and the calculated local-orbital moment is quite interesting (Table III), especially in the light of recent calculations by Horiuchi *et al.*[21] The anisotropy constants obtained by them using a tight binding approximation in band-structure calculations are unreliable, as they depend strongly on the number of d electrons. In their calculations, they do not distinguish between different cobalt sites and this is the reason why they had to vary artificially the number of d electrons to get quantitative agreement with experiment. For example, a change of the number of d electrons on Co_5 cluster by 0.01% changes the anisotropy constant from -6.7×10^4 to 465×10^4 and 7.7×10^7 erg/cm^3.

The presented method of the calculation requires a knowledge of spin-orbit interaction constant [E(so)]. Although the absolute values of the results depend on values of the parameters, the presented method gives important information about the various contributions at the orbital moment from different sites.

In Table II we have calculated as well the total magnetic moment for different sites. The theoretical results are in good agreement with experimental measurements of the magnetic moment; however, the values given by Schweizer and Tasset[20] are much higher than the results of Perkins *et al.*[7]

ACKNOWLEDGMENT

This work was supported by the National Science Foundation through Grant No. CHE-8208048.

---

[1] R. L. Streever, Phys. Rev. B **19**, 2704 (1979).

[2] H. Figiel, J. Magn. Magn. Mat. **27**, 303 (1982).

[3] H. Figiel and Z. Kakol, Proceedings of the Sixth International Workshop on Rare-Earth—Cobalt Permanent Magnets and Their Applications, Vienna, 1982, edited by Josef Fidler (unpublished), p. 757.

[4] K. S. V. L. Narasimhan, W. E. Wallace, and R. D. Hutchens, IEEE Trans. Magn. **MAG-10**, 729 (1974).

[5] H. Fujii, M. V. Satyanarayana, and W. E. Wallace, Solid State Commun. **41**, 445 (1982).

[6] M. V. Satyanarayana, M. Fujii, and W. E. Wallace, J. Appl. Phys. **53**, 2374 (1982).

[7] R. S. Perkins and S. Strässler, Phys. Rev. B **15**, 477, 490 (1977).

[8] H. J. Schaller, R. S. Craig, and W. E. Wallace, J. Appl. Phys. **43**, 3161 (1972).

[9] B. Szpunar and B. Kozarzewski, Phys. Status Solidi B **82**, 205 (1977).

[10] B. Szpunar, J. Phys. F **12**, 759 (1982).

[11] B. Szpunar, Physica **130B**, 29 (1985).

[12] V. Heine, D. W. Bullett, R. Haydock, and M. J. Kelly, Solid State Phys. **35** (1980).

[13] W. Beer and D. G. Pettifor, in *The Electronic Structure of Complex Systems,* NATO ASI Series, Physics, Ser. B, edited by P. Phariseau and W. M. Tennerman (Plenum, New York, 1984), p. 769.

[14] P. Turchi, F. Ducastelle, and G. Treglia, J. Phys. C **15**, 2891 (1982).

[15] B. Szpunar and W. E. Wallace (unpublished).

[16] S. Ishida, J. Phys. Soc. Jpn. **33**, 369 (1972).

[17] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice Hall, New Jersey, 1963).

[18] B. Szpunar, Phys. Lett. A **115**, 157 (1986).

[19] D. S. Saxon, *Elementary Quantum Mechanics,* (Holden-Day, San Francisco, 1968).

[20] J. Schweizer and Tasset, *Proceedings of the International Conference on Magnetism, Moscow, 1973* (Nauka, Moscow, 1973), Vol. 4, p. 257.

[21] F. Horiuchi, N. Hirose, S. Ohtsuka, T. Ukai, and N. Mori (unpublished).