Novel Pr-Cu Magnetic Phase at Low Temperature in $PrBa_2Cu_3O_{6+x}$ Observed by Neutron Diffraction

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We have studied by neutron diffraction the magnetic ordering in Al-free crystals of $PrBa_2Cu_3O_{6+x}$ ($x = 0.35$ and 0.92) that do not display the AFII Cu magnetic phase. We find that the Pr ordering below 20 K is accompanied by a counterrotation of the Cu antiferromagnetism on each plane of the bilayer. The maximum turn angle between the two planes is 60° ± 9° for the $x = 0.92$ crystal, and 40° ± 11° for the $x = 0.35$ crystal. This is the first observation of a noncollinear ordering of Cu moments in the bilayer, and is evidence for significant magnetic coupling between the Cu and Pr sublattices. [S0031-9007(96)01945-X]

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The absence of superconductivity in $PrBa_2Cu_3O_7$ has proven difficult to explain, especially in view of evidence that the Pr ions are essentially trivalent [1], and that the density of holes on the copper-oxygen planes and chains is virtually the same as in the isostructural parent $YBa_2Cu_3O_7$ [2]. These observations exclude the possibility of significant charge transfer off the Pr ions onto the planes. It is widely believed, nonetheless, that a degree of hybridization of the Pr $4f$ and nearest neighbor O $2p$ orbitals takes place and plays a central role in preventing superconductivity. The model of Fehrenbacher and Rice [3], for example, explains the phenomenon through the localization of holes in hybridized Pr $4f$–O $2p_\pi$ orbitals.

As well as modifying the transport properties of $PrBa_2Cu_3O_{6+x}$, Pr $4f$–O $2p$ hybridization could also be expected to enhance the magnetic coupling between the Pr ions and the CuO_2 planes. This may account for the following anomalous magnetic behavior. First, antiferromagnetic order on the CuO_2 planes and semiconducting resistivity, both characteristic of reduced, nonsuperconducting $YBa_2Cu_3O_{6+x}$, persists over the entire range of oxygen content in $PrBa_2Cu_3O_{6+x}$[4,5]. Second, the Pr sublattice is reported to order magnetically at temperatures between 10 and 20 K (depending on x) [6–8], an order of magnitude higher than is typical for lanthanides (L) in $LBa_2Cu_3O_{6+x}$. The likelihood that the transport and magnetic anomalies of $PrBa_2Cu_3O_{6+x}$ are linked through a common dependence on hybridization means that further studies of the magnetic ordering, particularly that of the Pr sublattice, can contribute towards an understanding of the superconductivity suppression phenomenon.

The need for more information about the Pr ordering was recently emphasized by a ^{141}Pr NMR study of a $PrBa_2Cu_3O_7$ single crystal [9]. The authors questioned the conventional interpretation of the Pr ordering phase, concluding that the size of the ordered Pr moment at 1.3 K was only $0.017\mu_B$, some 40 times smaller than had been obtained in neutron diffraction studies [7,10]. They also disagree on the direction of the Pr moment, which they found to lie in the *a*-*b* plane. Mössbauer [11] and neutron studies [10] had earlier determined the moment to be at an angle of ~30° to the *a*-*b* plane.

In this Letter we describe new properties of the magnetic ordering of $PrBa_2Cu_3O_{6+x}$ revealed by neutron diffraction. Of crucial importance to this work was the use of crystals which contained no Al impurity since partial substitution of Al on the Cu site, a feature of crystals grown in Al_2O_3 crucibles [12], causes the well-known AFI-AFII spin reorientation transition in the Cu sublattice [13–15]. By using Al-free crystals we not only achieve results more characteristic of the pure compound, but we can also probe the Pr ordering in much greater detail than before because the absence of the AFI-AFII transition simplifies the interpretation of the data. Our results support the established view of a large ($\sim 0.5\mu_B$) ordered Pr moment, but reveal a new, noncollinear ordering of the bilayer Cu moments which accompanies the Pr ordering.

Crystals of $PrBa_2Cu_3O_{6+x}$ were grown in MgO crucibles by the method described in Ref. [16]. Their chemical composition was analyzed by inductively coupled plasma mass spectrometry, and the most significant impurities were found to be Sr (0.7 at. %) and Mg (0.1 at. %). Crystals of masses 27 and 12 mg were prepared with oxygen concentrations $x = 0.92$ and 0.35, respectively, as determined from crystal structure refinements of data from the four-circle neutron diffractometer TAS 2 at Risø.

The magnetic ordering was studied over the temperature range 2 to 350 K with the TAS 1 triple-axis neutron spectrometer at Risø. The experimental arrangement was the same as described in Ref. [10]. Integrated intensities were determined in the (h, h, l) scattering plane either via linear scans in reciprocal space or crystal rotations (ω scans). We index the magnetic reflections with reference to the chemical unit cell, but in our calculation of the magnetic structure factors we summed over a cell equivalent to $2 \times 2 \times 2$ chemical unit cells [10]. Structural parameters used in the calculation were taken from the four-circle refinements. For the Cu magnetic form factor we assumed that the moment arises from an unpaired hole in a square planar $3d_x2_{-y}2$ orbital [15]. For the Pr ions we used the dipole form factor for the $4f^2$ configuration [17], neglecting crystal field and hybridization effects.

We observed two ordered magnetic phases in our crystals. The high temperature phase is the well-known AFI ordering, first determined [18] in reduced samples of $\mathrm{YBa_2Cu_3O_{6+x}}$. In this structure the Cu spin directions in the $\mathrm{CuO_2}$ planes alternate antiferromagnetically along all three axes, with no ordered moment on the Cu chain sites. The magnetic Bragg peaks are resolution limited and of the form $(h + \frac{1}{2}, k + \frac{1}{2}, l)$ with h, k, l integers, $l \neq 0$. The onset temperatures of this phase in our $\mathrm{PrBa_2Cu_3O_{6+x}}$ crystals were 266 K ($x = 0.92$) and 347 K ($x = 0.35$), in reasonable agreement with literature results for polycrystalline samples [4,5], but lower than for impure single crystals [10,19]. The AFI model describes the observed intensities very well, as demonstrated in Table I for the $x = 0.92$ crystal, and the ordered moments are $\mu_{\mathrm{Cu}} = 0.58\mu_B$ ($x = 0.92$) and $0.57\mu_B$ ($x = 0.35$), respectively, for the two crystals.

TABLE I. Observed and calculated integrated intensities of the magnetic reflections measured at 30 K (AFI phase) and 4.2 K (AFIII phase) for the crystal of $\mathrm{PrBa_2Cu_3O_{6.92}}$. The observed intensities have been corrected for the Lorentz factor. The errors indicated are the statistical uncertainties, but there is also a systematic error in the absolute intensity of approximately 10%.

	$T = 30$ K (AFI)		$T = 4.2$ K (AFIII)	
(h,k,l)	$I_{\mathrm{obs}}(\mu_B^2)$	$I_{\mathrm{calc}}(\mu_B^2)$	$I_{\mathrm{obs}}(\mu_B^2)$	$I_{\mathrm{calc}}(\mu_B^2)$
$(\frac{1}{2},\frac{1}{2},0)$	0.0 ± 0.5	0.0	36.0 ± 1.5	36.9
$(\frac{1}{2},\frac{1}{2},1)$	30.1 ± 1.7	28.8	48.5 ± 2.5	44.9
$(\frac{1}{2},\frac{1}{2},2)$	46.0 ± 1.7	48.1	46.3 ± 2.5	46.7
$(\frac{1}{2},\frac{1}{2},3)$	5.2 ± 0.3	5.3	24.0 ± 2.5	22.9
$(\frac{1}{2},\frac{1}{2},4)$	21.7 ± 1.1	20.8	29.0 ± 1.5	30.7
$(\frac{1}{2},\frac{1}{2},5)$	59.0 ± 2.0	56.6	45.0 ± 2.0	48.5
$(\frac{1}{2},\frac{1}{2},6)$	17.6 ± 1.3	17.7	30.0 ± 2.0	28.1
$(\frac{1}{2},\frac{1}{2},7)$	4.5 ± 0.7	5.2	24.0 ± 2.0	19.9
$(\frac{3}{2},\frac{3}{2},0)$	0.0 ± 0.5	0.0	17.8 ± 1.0	20.4
$(\frac{3}{2},\frac{3}{2},1)$	9.3 ± 0.6	10.0	26.0 ± 1.0	22.6
$(\frac{3}{2},\frac{3}{2},2)$	16.0 ± 2.0	14.3	20.5 ± 2.0	19.3
$(\frac{3}{2},\frac{3}{2},3)$	1.2 ± 0.7	1.5	5.0 ± 2.0	9.7
		$\chi^2 = 0.7$		$\chi^2 = 4.5$

The second magnetic phase we observed corresponds to the low temperature phase usually known as "Pr ordering," hereafter referred to as AFIII. In our crystals this phase was signaled by the appearance of peaks at $l = 0$ in addition to those present in the AFI phase [20]. Figure 1(a) displays the integrated intensities of the $(\frac{1}{2}, \frac{1}{2}, 0)$ reflections for the $x = 0.92$ and 0.35 crystals. The onset temperatures are $T_{\mathrm{III}} = 19 \pm 0.5$ K and 11 ± 0.5 K, respectively.

As found previously [10], the AFIII magnetic peaks are resolution limited in the *a-b* plane, but in l scans (except $l = 0$) they exhibit a two-component profile, with Lorentzian-like scattering at the base of the resolution-limited Gaussian peaks characteristic of the AFI phase. The width of the Lorentzian component depends strongly on oxygen content, but compared with the Al-doped crystals of our earlier study we find much narrower widths with the present crystals. At 4.2 K the intrinsic widths (HWHM) of the $(\frac{1}{2}, \frac{1}{2}, 0)$ reflections fitted to a Lorentzian in the c direction are $\Gamma_c = 0.06\ \mathrm{nm^{-1}}$ ($x = 0.92$) and $0.90\ \mathrm{nm^{-1}}$ ($x = 0.35$). These correspond to c axis correlation lengths of 16 and 1.1 nm, respectively, the latter of which agrees with an earlier estimate from neutron powder diffraction [21]. More surprisingly, the widths were found to vary with temperature, as shown in Fig. 1(b) for the oxygenated crystal. Γ_c increases below T_{III}, and the rise follows the integrated intensity [cf. Fig. 1(a)].

We turn now to the magnetic structure of the AFIII phase, and concentrate first on the oxygenated crystal. In this crystal the magnetic diffuse scattering was too narrow to be separated from the sharp peaks, and Table I lists the integrated intensities (sum of both components) measured

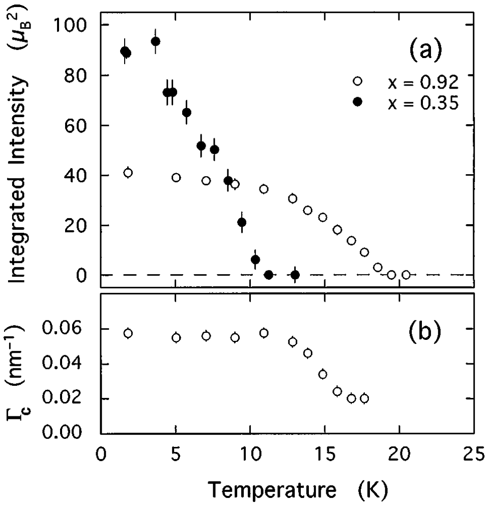

FIG. 1. (a) Integrated intensity of the $(\frac{1}{2}, \frac{1}{2}, 0)$ magnetic reflection as a function of temperature for crystals of $\mathrm{PrBa_2Cu_3O_{6+x}}$ with $x = 0.92$ 0.35; (b) temperature dependence of the c axis intrinsic width (HWHM) of the $x = 0.92$ crystal.

at 4.2 K in *l* scans. We neglect the Cu chain spins for the time being since NMR measurements [5] have ruled out any significant static moment on the chains. We first considered the model given in Ref. [10], in which the Cu moments remain in the AFI structure and the Pr moments form a collinear arrangement, antiferromagnetic in the *a* and *b* directions and ferromagnetic in the *c* direction. The adjustable parameters are the sizes of the moments (μ_{Cu} and μ_{Pr}), and the angle of the Pr moment to the *a*-*b* plane (θ_{Pr}). This model gave a reasonable description ($\chi^2 = 11.5$) of the present data at 4.2 K, but showed systematic discrepancies which modulated with *l*. In addition, the fitted value of μ_{Cu} decreased considerably below T_{III}.

We discovered a much better fit ($\chi^2 = 4.5$) when, in addition to the other degrees of freedom, we allowed the antiferromagnetic arrangement on the bilayer CuO_2 planes to counterrotate about the *c* axis. This model is illustrated in Fig. 2, and the calculated integrated intensities are given in Table I. The Cu moments are collinear within the planes as before, but not collinear within the bilayer as a whole. The turn angle between the Cu moment axes is $2\phi_{\mathrm{Cu}} = 60 \pm 9°$. The other parameters are $\theta_{\mathrm{Pr}} = 55 \pm 20°$, $\mu_{\mathrm{Pr}} = (0.56 \pm 0.07)\mu_B$, and $\mu_{\mathrm{Cu}} = (0.58 \pm 0.05)\mu_B$. The fit also gave a slight preference for the in-plane component of the Pr moment to lie along the former direction of the Cu moments, $\phi_{\mathrm{Cu}} = 0$ on Fig. 2, but the twinning makes this difficult to establish with certainty. We also examined various structures in which the Cu spins tilt out of the *a*-*b* plane instead of rotating about the *c* axis. None of these models gave fits with χ^2 values of less than 12.

We adopted a similar procedure for the reduced crystal except that ω scans were used to measure most of the intensities because the mosaic of this crystal exceeded the resolution. With ω scans the broad and sharp components of the peaks have different Lorentz factors, and so had to be corrected separately, then added to give the total integrated intensity. The separation of the two components was not difficult for most reflections because of their very different *c* axis widths. Applying the same AFIII model to the data at 2 K we obtained a good fit ($\chi^2 = 3.2$) with $2\phi_{\mathrm{Cu}} = 40 \pm 11°$, $\theta_{\mathrm{Pr}} = 38 \pm 6°$, $\mu_{\mathrm{Pr}} = (1.15 \pm 0.11)\mu_B$, and $\mu_{\mathrm{Cu}} = (0.64 \pm 0.09)\mu_B$. Compared with the oxygenated crystal the Pr moment of the reduced crystal is larger and ϕ_{Cu} is smaller.

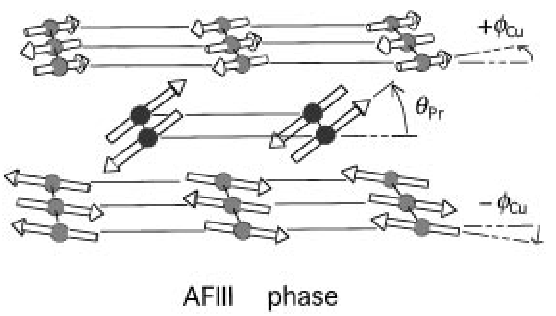

FIG. 2. Proposed magnetic structure of the AFIII phase. The diagram represents part of one magnetic unit cell, showing the two CuO_2 planes either side of the Pr layer. The antiferromagnetic arrangement on each CuO_2 plane has rotated by $\pm\phi_{\mathrm{Cu}}$ from the AFI collinear structure. θ_{Pr} is the angle of the Pr moments away from the CuO_2 plane, with the direction of the in-plane component as indicated.

The key new feature of the model proposed here is the noncollinear arrangement of Cu spins in the bilayer. We continue by justifying this idea on energy grounds. The energy required for two antiparallel Cu spins to counterrotate through angles $\pm\phi_{\mathrm{Cu}}$ is given in the Heisenberg model by $J_{\perp 1} S_{\mathrm{Cu}}^2 [1 - \cos(2\phi_{\mathrm{Cu}})]$, where $J_{\perp 1}$ is the interlayer exchange energy and $S_{\mathrm{Cu}} = \frac{1}{2}$ is the Cu spin. For $2\phi_{\mathrm{Cu}} = 60°$ and $J_{\perp 1} \approx 100$ K [15] this energy is ~13 K. Since this is comparable with T_{III} we conclude that the reorientation of the antiferromagnetism on the CuO_2 bilayers is driven by the ordering of the Pr sublattice, and we infer from this that a sizable Pr-Cu magnetic coupling must exist to bring about this change. Out of plane Cu rotations are also possible, since the anisotropy is small (~0.5 K [15]), but our fits did not reveal any evidence for a nonzero θ_{Cu} as mentioned earlier.

We further argue that the coexistence of magnetic order on the Pr and Cu sublattices linked together by a Pr-Cu magnetic interaction is not only consistent with, but *requires* a reorientation of the Cu magnetic structure. This follows because in the AFI phase the Pr site is at a center of symmetry with respect to the arrangement of Cu moments, and so the total effect of any Pr-Cu coupling would cancel. A nonvanishing coupling between the two sublattices can be allowed only after removal of the center of symmetry. In the AFIII arrangement isotropic exchange fields from the Cu spins still cancel at the Pr site by symmetry, but an anisotropic interaction, e.g., the dipole field, can be nonzero.

It is of interest next to correlate the two-component line shapes observed in *l* scans with the underlying magnetic structure. The $(\frac{1}{2}, \frac{1}{2}, 0)$ is particularly informative in this respect as the line shape of this peak was observed to consist only of the broad constituent. According to our model, the scattering at $(\frac{1}{2}, \frac{1}{2}, 0)$, and hence the broad component of all the peaks, arises from two sources: (1) the ordered Pr moments, and (2) the component of the Cu spins stacked ferromagnetically along the *c* axis. The sharp component, therefore, corresponds to the projection of the Cu spins along the $\phi_{\mathrm{Cu}} = 0$ direction, i.e., the AFI structure but with an effective moment $\mu_{\mathrm{Cu}} \cos(\phi_{\mathrm{Cu}})$.

The correlation between the *c* axis broadening and the $(\frac{1}{2}, \frac{1}{2}, 0)$ intensity, Fig. 1(b), suggests there is frustration in the AFIII magnetic structure. A possible source of this frustration is the coupling between adjacent Cu moments in neighboring bilayers separated by a chain layer. In ideal crystals this coupling is expected to be antiferromagnetic, as in the AFI phase. To achieve this with the AFIII model of Fig. 2 would require the sense of ϕ_{Cu} to vary in the sequence $(-,+)\,(+,-)\,(-,+)$ etc., i.e., doubling the magnetic unit cell in the c direction. Such a doubling has indeed been observed in polycrystalline samples of $\mathrm{PrBa_2Cu_3O_{6+x}}$ [20]. In our crystals, however, the observed sequence is $(-,+)\,(-,+)\,(-,+)$ etc., and so the Cu-Cu coupling through the chains is the same as in the AFII phase, with both ferromagnetic and antiferromagnetic components. The competition between two different spin rotation mechanisms may cause frustration and interrupt the ϕ_{Cu} sequence at antiphase boundaries, resulting in the observed short range order. Small amounts of impurities in the crystals, or Pr ions on the Ba site, may be responsible for the difference in coupling compared with polycrystalline material [22].

Finally, we comment on the recent NMR report [9] of a vanishingly small ordered Pr moment below T_{III}. It is difficult to reconcile such a result with our diffraction data. The extra scattering we observe below T_{III} can only be explained by a relatively large ordered moment in the unit cell *in addition to* that present in the AFI phase. If $\mu_{\mathrm{Pr}} \approx 0$ then four sources for this scattering might be considered.

(1) The Cu plane moments could increase in size and acquire a ferromagnetically coupled component parallel to the c axis, as proposed in Ref. [9]. We have allowed both in-plane and out-of-plane rotations, but we find the quality of the best fit is poor ($\chi^2 = 24$). Furthermore, an enhancement in μ_{Cu} below T_{III} by a factor 1.5–2 would be required to match the observed intensities, and this seems unphysically large.

(2) Ordered moments could develop on free holes on the $\mathrm{CuO_2}$ planes. For $x \approx 1$ Fehrenbacher and Rice have estimated [3] approximately 0.35 holes per unit cell, localized in hybridized Pr $4f$–O $2p_\pi$ orbitals. If the magnetic moments on these holes combined ferromagnetically they could contribute up to $0.35\mu_B$ to the magnetic structure. This is still insufficient, however, to explain the diffraction intensities since an additional $\sim 0.6\mu_B$ would be required to compensate for $\mu_{\mathrm{Pr}} = 0$ in the $x = 0.92$ crystal.

(3) An ordered moment could develop on the Cu chain site. Allowing for this possibility we found that the best model for the $x = 0.92$ crystal ($\chi^2 = 6.7$) also had the noncollinear bilayer structure (Fig. 2), with $\mu_{\mathrm{Cu}} = 0.60\mu_B$, $\mu_{\mathrm{Cu(chain)}} = 0.65\mu_B$, and $\phi_{\mathrm{Cu}} = 33°$. As already mentioned, however, NMR data [5] seem to preclude this possibility.

(4) The excess scattering at $(\frac{1}{2}, \frac{1}{2}, l)$ could be structural in origin, either from an antiferrodistortion accompanying the Pr ordering or from charge localization. X-ray synchrotron measurements on the $x = 0.92$ crystal [23], however, showed no such scattering, and so structural effects seem unlikely.

We conclude therefore that the AFIII phase has a significant ordered moment ($>0.5\mu_B$) on the Pr sites, and a noncollinear Cu spin arrangement in the bilayer. Strong magnetic coupling, perhaps due to the hole localization in the Pr-O bonds, links the Pr and Cu sublattices. This could explain the elevated Pr magnetic ordering temperature, and is consistent with the notion that hybridization of the Pr and O states underpins both the anomalous transport and magnetic behavior of $\mathrm{PrBa_2Cu_3O_{6+x}}$.

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[1] Experiments prior to 1992 are reviewed by H. B. Radousky, J. Mater. Res. **7**, 1917 (1992).

[2] J. Fink *et al.*, Phys. Rev. B **42**, 4823 (1990).

[3] R. Fehrenbacher and T. M. Rice, Phys. Rev. Lett. **70**, 3471 (1993).

[4] I. Felner *et al.*, Phys. Rev. B **40**, 6739 (1989); D. W. Cooke *et al.*, J. Appl. Phys. **67**, 5061 (1990).

[5] A. P. Reyes *et al.*, Phys. Rev. B **42**, 2688 (1990).

[6] A. Kebede *et al.*, Phys. Rev. B **40**, 4453 (1989).

[7] W.-H. Li *et al.*, Phys. Rev. B **40**, 5300 (1989).

[8] G. Wortmann and I. Felner, Solid State Commun. **75**, 981 (1990); A. Kebede *et al.*, J. Appl. Phys. **69**, 5376 (1991).

[9] K. Nehrke and M. W. Pieper, Phys. Rev. Lett. **76**, 1936 (1996).

[10] A. Longmore *et al.*, Phys. Rev. B **53**, 9382 (1996).

[11] J. A. Hodges *et al.*, Physica (Amsterdam) **218C**, 283 (1993).

[12] J. M. Tarascon *et al.*, Phys. Rev. B **37**, 7458 (1988).

[13] H. Kadowaki *et al.*, Phys. Rev. B **37**, 7932 (1988).

[14] H. Casalta *et al.*, Phys. Rev. B **50**, 9688 (1994); E. Brecht *et al.*, Phys. Rev. B **52**, 9601 (1995).

[15] S. Shamoto *et al.*, Phys. Rev. B **48**, 13 817 (1993); J. M. Tranquada *et al.*, Phys. Rev. B **40**, 4503 (1989).

[16] Th. Wolf *et al.*, J. Crystal Growth **96**, 1010 (1989).

[17] A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

[18] J. M. Tranquada *et al.*, Phys. Rev. Lett. **60**, 156 (1988).

[19] N. Rosov *et al.*, Physica (Amsterdam) **204C**, 171 (1992).

[20] In neutron powder diffraction studies, Refs. [7,21], the Pr ordering phase is signified by reflections of the form $(h + \frac{1}{2}, k + \frac{1}{2}, l + \frac{1}{2})$. Impurities in the chains in single crystals may alter the c axis coupling, and thereby cause the different stacking sequence of Pr moments.

[21] M. Guillaume *et al.*, J. Appl. Phys. **75**, 6331 (1994).

[22] Recent neutron diffraction studies on reduced $\mathrm{YBa_2Cu_3O_{6+\chi}}$ doped with La on the Ba site have revealed AFII ordering [N. H. Andersen *et al.* (unpublished).

[23] N. H. Andersen *et al.* (unpublished).