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Moolenaar, A.A.; Gubbens, P.C.M.; van Loef, J.J.; Menken, M.J.V.; Menovsky, A.A.

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$\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ investigated by ^{141}Pr Mössbauer spectroscopy

A.A. Moolenaar, P.C.M. Gubbens, J.J. van Loef

Interfacultair Reactor Instituut, TU Delft, 2629 JB Delft, The Netherlands

M.J.V. Menken and A.A. Menovsky

Van der Waals–Zeeman Laboratorium, 1018 XE Amsterdam, The Netherlands

The ^{141}Pr Mössbauer isomer shift and hyperfine field spectrum of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ were measured at 25 and 4.2 K, respectively. The isomer shift corresponds to an intermediate valency of 3.4(1) and the hyperfine field spectrum at 4.2 K seems to indicate a hyperfine field of 29(3) T.

The compound $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ (with y between 0 and 0.4) has a rather special place in the yttrium and rare-earth substituted $\text{REBa}_2\text{Cu}_3\text{O}_{7-y}$ compounds: (a) this compound is not a superconductor [1]; (b) it is not a metal but a semiconductor; (c) the Cu–O planes order antiferromagnetically near 280 K, in contrast to all other compounds of this stoichiometry, for which no such ordering is observed, and (d) it has by far the highest transition temperature for the antiferromagnetic ordering of the rare-earth sublattice (17 K), much larger than the corresponding Gd compound. Because the first three properties resemble that of the oxygen depleted phase $\text{REBa}_2\text{Cu}_3\text{O}_6$, the suppression of the superconducting state in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ was originally attributed to the filling of the superconducting holes due to a tetravalent or mixed valency of Pr [2]. However, later studies excluded the presence of any Pr^{4+} in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ [3]. In these studies, the hybridization of the Pr-4f levels with the Cu–O plane bands was instead postulated as a cause for the suppression of the superconducting state, but questions remained because some of these studies did show some features that could not be explained on the basis of solely trivalent Pr [3]. Furthermore, other studies, such as neutron diffraction, did indicate an intermediate valent Pr [4].

Apart from this valency, however, also the magnetic properties of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ are not very clear. The neutron scattering experiments of Li et al. [5] indicated fully three-dimensional antiferromagnetic ordering of Pr in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$, but another neutron scattering measurement failed to reproduce magnetic ordering down to 10 K [6].

Fig. 1. ^{141}Pr Mössbauer spectra of PrO_2 , Pr_2O_3 and Pr_6O_{11} at 25 K, and $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ at 4.2 and 25 K with $^{141}\text{CeF}_3$ as a source.

Because the isomer shift and the hyperfine field in Mössbauer spectroscopy are both one of the most direct ways of measuring the valency and the ground-state magnetic moment of Pr in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$, we measured ^{141}Pr Mössbauer spectra of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ at 4.2 and 25 K. In addition, we measured the formally tetravalent PrO_2 , the intermediate valent Pr_6O_{11} and the trivalent Pr_2O_3 compounds at 25 K. Due to the high energy of the Mössbauer transition in ^{141}Pr (145.5 keV) and hence the very low recoilless fraction, these spectra were measured with a special counting technique, the current integrating technique, described elsewhere [7]. The Pr_2O_3 , PrO_2 , and Pr_6O_{11} compounds were purchased from Johnson Matthey Alfa products. The $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ sample was prepared in the usual way, ending by annealing into

Table 1

Mössbauer isomer shifts *IS* with respect to the source, Γ , the FWHM of the lines, the hyperfine fields in PrO₂ and PrBa₂Cu₃O_{7-y} at 4.2 K, and the absorption areas for the listed components. To obtain the spectra, we used a source made of CeF₃.

Compound	<i>T</i> (K)	<i>IS</i> (mm/s)	Γ (mm/s)	<i>HF</i> (T)	Area $\times 10^{-3}$ (mm/s)
Pr ₂ O ₃	25	0.05(5)	1.93(5)	–	2.08(1)
Pr ₆ O ₁₁	25	0.64(5)	2.21(5)	–	3.00(1)
PrO ₂	25	0.83(5)	2.20(5)	–	3.72(1)
	4.2	0.79(5)	2.37(5)	76.1(10)	10.7(3)
PrBa ₂ Cu ₃ O _{7-y}	25	0.40(5)	2.62(5)	–	0.58(1)
	4.2	0.63(20)	– ^{a)}	29(3)	0.40(1)

^{a)} See text.

flowing oxygen for 80 hours. An X-ray analysis showed no impurity phase and a clear orthorhombic distortion. The lattice parameters that were deduced were: $a = 0.386(1)$ nm, $b = 0.393(1)$ nm and $c/3 = 0.390(1)$ nm, in excellent agreement with those of López-Morales [4].

In order to compare the isomer shift of PrBa₂Cu₃O_{7-y} samples with that of PrO₂, Pr₆O₁₁ and Pr₂O₃, we have put the measured spectra together in fig. 1. The spectra were fitted with Lorentzians. The line through the points corresponds to the fit. The parameters from these fits are assembled in table 1. One can see that the isomer shift of PrBa₂Cu₃O_{7-y} lies in between that of Pr₂O₃, Pr₆O₁₁, and PrO₂. However, because of reasons of entropy and because of the fact that at ambient oxygen pressure only Pr₆O₁₁ is stable, it is almost inevitable that PrO₂ is to some extent oxygen deficient. From the ¹⁴¹Pr Mössbauer spectrum of this sample at 4.2 K (not shown), we indeed found that about 6% was nonmagnetic. Because, due to this oxygen deficiency, the isomer shift is presumably too low, we therefore compare the isomer shift of PrBa₂Cu₃O_{7-y} at 25 K with that of Pr₂O₃ and Pr₆O₁₁. Assuming a linear relationship between the valency and the isomer shift, for PrBa₂Cu₃O_{7-y} we then find a valency of 3.4 ± 0.1 . However, the Mössbauer peak of PrBa₂Cu₃O_{7-y} is much broadened with respect to that of Pr₂O₃. Such a broadening can probably not be attributed to an electric field gradient, for its influence is negligible in ¹⁴¹Pr. The broadening of the peak must then be ascribed to a distribution in isomer shifts.

Figure 1 furthermore reveals that the spectrum of PrBa₂Cu₃O_{7-y} at 4.2 K is magnetically split. When we analyze the spectra of PrBa₂Cu₃O_{7-y} measured at 4.2 K with a hyperfine field while taking the width of the peaks equal to the width found at 25 K, we obtain the fit of fig. 1. This analysis gives a hyperfine field of 29(3) T. This is only 10% of the free ion value of 326 T and less than that of PrO₂, indicating for this sample a small magnetic moment of $0.32(3) \mu_B$ only, which is about half the

value found by Li et al. [5]. However, the resonance absorption effect we observe at 4.2 K is less than that at 25 K, in sharp contrast to PrO₂. The analysis furthermore required a rather large peak width. Therefore, we suggest that in fig. 1 we see essentially the inner part of a relaxation spectrum. This means that the moment of the Pr ion is fluctuating on the characteristic time scale of ¹⁴¹Pr Mössbauer spectroscopy (1.85(3) ns). Another explanation would be that the spectrum is composed of two subspectra, one from a tetravalent and magnetically ordered part, and one from a trivalent part which has only a small induced moment. The tetravalent part must then be hidden in the background, for we can exclude the possibility of a single hyperfine field, i.e. there must be a wide distribution in hyperfine fields. Such a distribution may be possible, for a distribution in the direction of the exchange has been observed in Yb-doped PrBa₂Cu₃O_{7-y} with ¹⁷⁰Yb Mössbauer spectroscopy [8], but it is in contradiction to the results of Li et al. [5].

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