Enhanced nuclear magnetic cooling: a new perspective

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Abstract. Conventional wisdom is that thermal transport at milliKelvin temperatures is appreciable only in substances containing conduction electrons. This paper discusses the possibility of attaining temperatures of 0.02–0.2 mK by isentropic demagnetisation of the insulating crystals, semi-dilute $(Y, Ho)VO_4$ and $PrVO_4$, together with, measurement of the final temperature. It is shown that thermal transport to the surface of powders of diameter ~ 0.08 mm takes place in times of order 1–30 min by diffusion through spin–spin interaction between the enhanced nuclear moments. Cross-relaxation between the vanadium nuclear spins (^{51}V, $I = \frac{7}{2}$) and the lanthanide nucleii ^{165}Ho, $I = \frac{7}{2}$ and ^{141}Pr, $I = \frac{5}{2}$, is also considered.

1. Introduction

The method of magnetic cooling to attain temperatures below those reached by pumping liquid helium was suggested by Debye (1926) and Giauque (1927). For an electronic paramagnetic ion with spin $J\hbar$, application of a field of a few tesla at a temperature of 1.5 K splits the electronic levels sufficiently to remove most of the entropy, $S/R = \ln(2J + 1)$. The heat of magnetisation is transferred to the helium bath through the exchange gas in 10–20 min; the sample is then thermally isolated by removal of the exchange gas, and on demagnetisation the temperature falls to 10–50 mK. Insulating paramagnetic compounds such as chromium or ferric alum were used, in which the magnetic ions are well separated, reducing exchange and magnetic dipole interactions. These effects are particularly small in cerium magnesium nitrate, making it possible to reach temperatures of about 2 mK (see Wheatley 1975).

The corresponding experiment utilising nuclear spins was discussed by Simon (1939). Since the nuclear moments are smaller by a factor $\sim 10^{-3}$, correspondingly greater values of magnetic field or lower initial temperatures are required. The former are prohibitively large, the latter can easily be attained only with a modern dilution refrigerator. Thermal contact from the nuclear spins through the lattice to a heat bath is impossibly small except in a metal, where conduction electrons interact with the nuclear moments. The first nuclear cooling experiment was carried out by Kurti et al (1956) on copper metal, where the two copper isotopes each have $I = \frac{3}{2}$. Indium metal (^{115}In, $I = \frac{9}{2}$) has also been used (Symko 1969); the crystal structure is tetragonal, and the sign of the quadrupole splitting has recently been determined $(e^2 qQ/h = -47.8\,MHz)$ in a nuclear cooling experiment (Yi-Hua Tang et al 1985).

The large gap in size between electronic and nuclear moments caused considerable cryogenic problems. An intermediate solution, the use of enhanced nuclear moments,

Table 1. Data for the hexagonal compound $PrNi_5$, and the tetragonal compounds $PrVO_4$ and $HoVO_4$. Values of $\gamma/2\pi$ are in MHz T^{-1}, and of P/h in MHz.

	$PrNi_5$[a]	$PrVO_4$[b]	$HoVO_4$[c]
a_0 (nm)	0.4948	0.7367	0.71214
c_0 (nm)	0.3973	0.6468	0.62926
Molar volume (cm^3)	50.7	52.85	48.1
Ionic states	$4f^2$	$4f^2$	$4f^{10}$
	$^3H_4$	$^3H_4$	$^5I_8$
g_J	0.805	0.805	1.241
$\gamma_1/2\pi$	12.929(2)	12.929(2)	8.99(6)
$\gamma_{\parallel}/2\pi$	82.0(1)	24.5	13(5)
$\gamma_{\perp}/2\pi$	164.2(1)	77.62	1526(3)
P/h	0.6	+3.35(3)	+25.9(3)

[a] Kaplan *et al* 1980.
[b] Bleaney *et al* 1977.
[c] Bleaney *et al* 1978b.

was first suggested by Al'tshuler (1966). This was developed by Andres and Bucher (1968, 1971), who utilised intermetallic compounds of lanthanide elements. The trivalent ions of praseodymium, $4f^2$, $^3H_4$ and thulium, $4f^{12}$, $^3H_6$ appeared most suitable, with values of g_J close to unity, 0.805 and 1.164 respectively, since exchange interaction through the conduction electrons was expected to vary as $(g_J - 1)$. The intermetallic compound $PrNi_5$ has been widely used (see Andres 1978, Andres and Lounasmaa 1982); it becomes ferromagnetic below 0.4 mK, but a temperature of 0.19 mK has been reached by demagnetisation from 6 T and 10 mK (Folle *et al* 1981). To reach μK temperatures, it has been combined with a second stage demagnetisation unit in which metallic copper is the working material (see, for example, Pickett 1988).

Compounds with conduction electrons have two disadvantages: (i) these electrons provide a mechanism for exchange interaction between the magnetic ions so that magnetic ordering limits the temperatures that can be attained; and (ii) precautions must be taken against eddy current heating, both through AC ripple on the magnetising field, and during demagnetisation. Electrically insulating compounds have been avoided because thermal transport problems have been assumed to be insuperable. This question is discussed below in section 3, following estimates of the temperatures that can be reached (section 2) using enhanced nuclear magnetic substances without conduction electrons. The temperature measurement procedure is briefly discussed in section 4.

2. $PrVO_4$ and $HoVO_4$

These two compounds have the tetragonal (zircon) crystal structure, space group D_{4h}^{19} ($I4_1/amd$); the unit cell contains four ions, that are magnetically identical. Their main characteristics are listed in table 1, together with those of $PrNi_5$, which is hexagonal.

For each of these substances the axial crystal field splits the $(2J + 1)$ manifold, leaving a singlet as the ground state. The next levels are a doublet at 20 cm^{-1} and three levels at

Table 2. Values of the quadrupole parameter P/k (all positive), and the quadrupole splittings in zero magnetic field, all in mK, for ^{141}Pr and ^{51}V in PrVO$_4$, and ^{165}Ho and ^{51}V in (Y, Ho)VO$_4$.

	PrVO$_4$		(Y, Ho)VO$_4$	
	^{151}Pr	^{51}V	^{165}Ho	^{51}V
P/k	0.1595	0.009075	1.214	0.007943
States				
$\pm(\frac{7}{2})$	—	0.1089	14.57	0.0953
$\pm(\frac{5}{2})$	0.957	0.05445	7.29	0.0477
$\pm(\frac{3}{2})$	0.319	0.01815	2.43	0.0159
$\pm(\frac{1}{2})$	0	0	0	0

47 cm^{-1} for HoVO$_4$ (Battison *et al* 1975), while in PrVO$_4$ the first excited level is a second singlet at 35 cm^{-1}, with a doublet at 84 cm^{-1} (Bleaney *et al* 1978a). In PrNi$_5$ the excited levels are thought to lie above 30 cm^{-1}. For each substance, in the liquid helium range, the electronic paramagnetism is independent of temperature.

These two lanthanide ions each have only a single stable isotope: ^{165}Ho, $I = \frac{7}{2}$, and ^{141}Pr, $I = \frac{5}{2}$. In the ground singlet state the nuclear spin Hamiltonian for axial symmetry has the form

$$H = \gamma_{11}\hbar B_z I_z + \gamma_\perp \hbar (B_x I_x + B_y I_y) + P[I_z^2 - I(I + 1)/3]. \qquad (1)$$

Values of the parameters are given in table 1. The unenhanced nuclear resonance frequencies in a field of 1 T are followed by the enhanced values, parallel and perpendicular to the axis of symmetry, and the quadrupole splitting P/h (in MHz).

HoVO$_4$ has the higher nuclear entropy, $S/R = \ln(2I + 1) = \ln 8$, but because of its large enhancement it enters a nuclear antiferromagnetic state at about 4.8 mK. The lowest temperature reached by demagnetisation from a field of 1.8 T at 35 mK was estimated (Allsop *et al* 1980) to be about 1 mK, and use of higher fields and lower initial temperatures is unlikely to reduce the final temperature significantly. However, as an alternative the moderately diluted compound (Y, Ho)VO$_4$ may be useful; trivalent yttrium has almost exactly the same ionic size as holmium, and the resonance parameters (Bleaney *et al* 1978b) are very close to those in the undiluted compound. In the latter the ordering (see Bleaney 1980) arises from predominantly dipolar interactions with just four nearest-neighbours, and dilution by a factor 8 (say) may result in no ordered state being reached at any temperature. For example, MnF$_2$ has a Néel temperature at 67 K, but diluted to 25% in ZnF$_2$ it appears not to order down to 4 K (Baker *et al* 1961). For HoVO$_4$ the large value of $(\gamma_\perp/2\pi)$ means that nearly all the nuclear entropy can be removed on magnetisation, even when allowance is made for non-linearity in the nuclear splitting at high fields. Thus, at a field of 7 T and a temperature of 10 mK, the entropy should be reduced to $S/R \sim 5 \times 10^{-6}$, and in a dilute sample the temperature reached after demagnetisation will be determined by the residual interactions between the holmium nuclei. An estimate of the latter suggests that with (Y$_{7/8}$, Ho$_{1/8}$)VO$_4$ a final temperature of order 0.2 mK can be reached; here allowance has been made for the fact that only the $|\pm\frac{1}{2}\rangle$ nuclear states are occupied, because of the quadrupole splitting (see table 2).
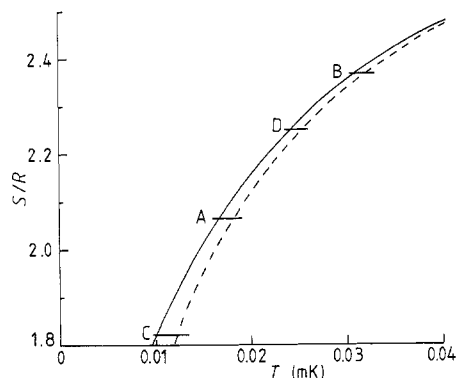
Figure 1. The combined entropy S/R of the praseodymium and vanadium nuclear spins in $PrVO_4$, at temperatures from 0–0.04 mK. The effect of interactions between the praseodymium nuclei is included in the lower curve. The horizontal lines mark the values of S/R resulting from magnetisation in a field of 7 T at an initial temperature of 10 mK (A, B), and at 8 mK (C, D). In A and C it is assumed that the vanadium nuclei are initially magnetised; in B and D that they are not.

Table 3. Estimates of the temperatures T_f reached in $PrVO_4$ after demagnetisation from a field of 7 T at temperature T_1. For (a) it is assumed that the vanadium ions are magnetised in the initial field; for (b), that they are not. In (d), but not in (c), allowance is made for interactions between the praseodymium ions. All temperatures are in mK.

T_1	10		8	
S/R (Pr)	0.2842		0.1694	
S/R (V)	1.7771		1.6510	
S/R (Pr + V)	2.0613		1.8204	
	(c)	(d)	(c)	(d)
T_f (a)	0.0165	0.018	0.010	0.012
T_f (b)	0.031	0.032	0.024	0.0255

Use of a compound diluted by a factor f entails a corresponding reduction in the entropy available per unit volume. An undiluted substance with a lower enhancement is preferable, because the interactions are correspondingly smaller, and lower temperatures should be reached. A suitable compound is $PrVO_4$, for which the enhanced nuclear parameters have been determined by magnetic resonance, and are listed in table 1. An additional feature of this substance is that, if the nuclear entropy can be extracted, the temperature that can be reached on demagnetisation can be calculated from the measured NMR parameters. This is because the final temperature is determined mainly not by magnetic interactions between the Pr nuclear spins (see below), but by the quadrupole interactions and sharing of the entropy with the V nuclei through cross-relaxation (see section 3).

The overall quadrupole splittings are listed in table 2, and the combined entropy of the praseodymium and vanadium nuclei at temperatures from 0.1–0.04 mK is shown in figure 1 (the upper curve). This is based on the assumption of $S/R = \ln 2 = 0.6915$ for the former nuclei, since only the $|\pm\frac{1}{2}\rangle$ states are occupied, together with a curve computed from the quadrupole splittings (see table 2) of the vanadium nuclei. In a field of 7 T at 10 mK, the entropy is reduced from $S/R = \ln 6 = 1.792$ to 0.2858 for Pr and from $\ln 8 = 2.0794$ to 1.7771 for V, total 2.0629. If the initial temperature is somewhat lower at 8 mK, the values of the entropy are significantly smaller: $S/R = 0.1706$ for Pr, and 1.6510 for V, total 1.8216. These values are listed in table 3, together with the

Figure 2. Recorded trace of the differential of the nuclear resonance lines in $PrVO_4$ at 4.2 K and a frequency of 12.916 MHz. The external field is applied along the [001] axis. The broad lines are from ^{141}Pr ($I = \frac{5}{2}$), the narrow lines from ^{51}V ($I = \frac{7}{2}$). The latter are saturated except where they are sufficiently close to a praseodymium line for cross-relaxation to occur.

temperatures that should be reached after demagnetisation. Two alternative conditions are considered: (i) the vanadium nuclei are initially magnetised, so that their entropy is reduced; and (ii) that they are not magnetised, because of the long spin–lattice relaxation time, and their entropy remains at $S/R = \ln 8$.

Obviously, estimates of the final temperatures attained after demagnetisation can be improved by including the entropy arising from interactions between the praseodymium nuclei. The heat capacity can be correlated with the linewidth observed in the enhanced nuclear resonance by combining equations (9.57) and (A.46) of Abragam and Bleaney (1970 and 1986). This yields the relation

$$CT^2/R = [2I(I + 1)/9] (h/k)^2 \langle \Delta \nu^2 \rangle \tag{2}$$

where the measured value of the mean square width $\langle \Delta \nu^2 \rangle$ is about 0.022 $(MHz)^2$, the linewidth being some ten times larger than expected for purely dipolar interactions. Hence the entropy of the Pr nuclei in the lowest doublet becomes $S/R = \ln(2) - 13.8 \times 10^{-6}\, T^{-2}$, where T is in mK. This gives the lower curve for S/R in figure 1, from which are obtained the final temperatures in table 3(d). Clearly, the changes from (c), where interactions are neglected, are not very large.

The fact that the linewidth is appreciably greater than in the dipolar case may be due to anisotropic exchange interaction or to Jahn–Teller interactions. The latter are probably dynamic, and may account for the exceptionally fast relaxation rate; figure 2 shows that the ^{51}V nuclei cross-relax rapidly to the Pr when the NMR frequencies coincide, whilst otherwise the vanadium resonances are strongly saturated.

The final temperatures in table 3 are higher than the probable nuclear ordering temperature for the Pr ions in $PrVO_4$. At the lowest temperatures only the $|\pm\frac{1}{2}\rangle$ doublet

is occupied, for which the effective gamma perpendicular is $3 \times 77.6 = 233$ MHz per tesla, and this substance should order like $HoVO_4$ (Bleaney 1980). Exchange interactions from the four nearest-neighbours should cancel, since two are parallel, and two anti-parallel. Thus, scaling down the dipolar interactions leads to the conclusion that in $PrVO_4$ antiferromagnetic order should set in only at $T_N \sim 0.006$ mK. This estimate could be checked if the initial magnetisation were made in a field of 7 T at the lower temperature of 5 mK, for which S/R is reduced to 0.0340 for ^{141}Pr, and 1.2912 for ^{51}V. The total of 1.3252 suggests that the temperature reached after demagnetisation would be <0.002 mK if interactions are not included. In fact, the final temperature must be close to the estimated ordering temperature (0.006 mK). If the vanadium nuclei are not initially magnetised, the end temperature would be ~ 0.018 mK.

3. Thermal transport

It has generally been assumed that thermal transport in an enhanced nuclear magnet at temperatures below 1 K is negligible except when conduction electrons are present, and on this basis, metals (Cu, In) or intermetallic compounds such as $PrNi_5$ have been used for nuclear magnetic cooling. The latter may form the first stage of a double demagnetisation experiment. For example, Ishimoto et al (1984) used 11 mol of $PrNi_5$ in a field of 6 T at a temperature of 28.5 mK as the initial condition, and in the next stage 7.67 mol of copper metal were magnetised at 5 mK in a field of 6.7 T. On demagnetisation, a temperature of 0.027 mK was attained, measured by platinum (^{195}Pt) NMR thermometry.

The lanthanide vanadates are electrical insulators, and thermal transport through the usual mechanism of lattice vibrations at temperatures below 1 K is quite negligible. There is, however, another mechanism not previously considered: thermal transport by diffusion through the spin system. Obviously this is much larger for an enhanced nuclear moment system, and particularly so in $HoVO_4$, where the nuclear frequency is increased by a factor of 150. The basic process is the interchange of magnetic quanta between adjacent nuclei, of which there are four within 0.4 nm, and a further twelve within 0.6 nm.

Diffusion rates may be estimated from the linewidth observed in a nuclear magnetic resonance experiment. For $HoVO_4$, the measurements of Bleaney et al (1978b) showed that the interactions between the enhanced holmium nuclear moments are mainly dipolar. Their results give a spin–spin relaxation rate $1/T_2'$ of order 5×10^7 s^{-1}. This rate and the diffusion parameter, D, are closely related; $D = d^2/T_2'$, where d is the distance between neighbours. The volume occupied by one molecule of $HoVO_4$ is 79.8×10^{-30} m^3, giving an average value of $d = 0.43$ nm, not much different from the distance $d = 0.389$ nm between an ion and each of its four nearest-neighbours. Hence, a value for D of order 10^{-11} m^2 s^{-1} is obtained.

We first calculate the diffusion time through the enhanced nuclear spin system for $HoVO_4$. For a sphere of radius r, $\frac{7}{8}$ of the volume is within a distance $r/2$ of the surface, and $r/2$ is a good approximation to the distance through which diffusion must take place. For a sphere of diameter 8 mm, $r/2 = 2 \times 10^{-3}$ m, and the diffusion time is roughly $(r/2)^2/D = (2 \times 10^{-3})^2/D = 0.4 \times 10^6$ s, or about five days. However, for a sphere with a diameter of 80 micron, $r/2 = 2 \times 10^{-5}$ m, and the time is reduced to ~ 40 s. Clearly the diffusion mechanism is very effective for such small particles. The vanadates are hard

substances, and there should be no problem in preparing particles of the size assumed in this calculation.

For $(Y, Ho)VO_4$, the diffusion mechanism is obviously slower. For dilution by a factor f, the spin–flop rate is decreased by f, but the mean value of d, the distance to nearest neighbours is increased by $f^{-1/3}$. With $f = \frac{1}{8}$, as in $(Y_{7/8}, Ho_{1/8})VO_4$, the diffusion times are increased by a factor $f^{-2/3} = 4$ over those estimated above, a difference that is not critical.

After demagnetisation this diluted compound should attain a temperature of ~ 2 mK, at which only the lowest doublet $|\pm\frac{1}{2}\rangle$ is occupied because of the quadrupole splitting (see table 2). Below 0.1 mK this is true also for $PrVO_4$, but the effect on estimates of diffusion times in zero-field is minor. For this substance the rates are of course considerably slower, since the resonant frequencies are smaller. If only dipolar interactions are present, a value of $D = 2 \times 10^{-14}$ m^2 s^{-1} is obtained, giving a time of ~ 200 s for particles of diameter 8×10^{-6} m. However, resonance experiments (Bleaney *et al* 1978a) show that the linewidth is about ten times the dipolar value; this suggests that the diffusion time may be shorter by a factor ~ 0.1; i.e., ~ 20 s. If so, for particles ten times larger in diameter (8×10^{-5} m) the time should only be about 2×10^3 s, or roughly half an hour.

In the previous section the question of whether the vanadium nuclei would become magnetised at high fields was left open. Diffusion by spin–spin interaction through the vanadium nuclear spin system itself is slow, with $D = 5 \times 10^{-16}$ m^2 s^{-1}. For a sphere of 8×10^{-6} m diameter, this leads to a time of about one hour, and for a sphere 10 times larger the time is approximately one hundred hours. However, there are two enhanced praseodymium nuclear spins at a distance of only 0.30 nm from each vanadium nucleus, and cross-relaxation between them is likely to be a much faster process, even though the resonance frequency of Pr in a field of 7 T is 540 MHz against 78 MHz for the vanadium nuclei. A rough estimate of the time required for mutual spin-flips between the two systems is 15 min, and the vanadium nuclei should therefore become magnetised at the same rate as the praseodymium nuclei. This is true also for $(Y, Ho)VO_4$, but in this case the additional entropy removed does not greatly effect the temperature attained on demagnetisation. For both substances, equilibrium between the vanadium and lanthanide systems should be established very quickly in zero magnetic field by cross-relaxation.

4. Thermometry

In experiments at mK temperatures and below, the usual method of determining the temperature has been to use nuclear magnetic resonance of ^{195}Pt ($I = \frac{1}{2}$) in the metal. The measured quantity is the intensity of the resonance, with allowance made for deviations from Curie's law. A similar system can be used with $PrVO_4$, for which, at temperatures below 0.05 mK, only the ground $|\pm\frac{1}{2}\rangle$ doublet is occupied, with an effective resonant frequency normal to the c axis three times the value of $(\gamma_\perp/2\pi)$ in table 1, or ~ 233 MHz T^{-1}. Thus a field of only 0.01 T is sufficient to give a resonance frequency of 2.33 MHz; at the same field, the frequency is only 0.0915 MHz for ^{195}Pt, and the intensity is further diminished by the low abundance (33.8%) of this isotope. Thus the praseodymium resonance should be considerably stronger in spite of greater linewidth. The applied field should be kept to the minimum value compatible with observing the resonance, in order to avoid raising the temperature. The advantage of using this

resonance from $PrVO_4$ itself is that temperature differences between the magnetic refrigerant and a separate thermometer are absent.

Two alternative methods avoid the need for a magnetic field, and can therefore be used with a randomly oriented powder: (i) measurement of the intensity of the praseodymium nuclear quadrupole transition from the $|\pm\frac{1}{2}\rangle$ doublet to the $|\pm\frac{3}{2}\rangle$ doublet, at a frequency of $2P/h = 6.7$ MHz; or (ii) at temperatures approaching 0.1 mK, comparison of the intensity of this transition with that from $|\pm\frac{3}{2}\rangle$ to $|\pm\frac{5}{2}\rangle$, which occurs at 13.4 MHz. Obviously, very low RF fields must be used to avoid appreciable heating.

The vanadium resonance lines are considerably narrower than those of the praseodymium nuclei (see figure 2), and at lower temperatures an alternative is to utilise the quadrupole transitions for ^{51}V, that occur at $2P/h$, $4P/h$ and $6P/h$, with $P/h = 189.1(6)$ kHz. Since the overall splitting for this nucleus is about 0.109 mK, the exponential variation of the populations between 0.01 and 0.1 mK gives a sensitive method of measuring the temperature. This would be a novel form of NQR thermometry.

5. Discussion

Thermal transport between liquid ^3He and a powder of the electronic paramagnet cerium magnesium nitrate was found (see Wheatley 1975) to be much faster than expected, and this was ascribed by Leggett and Vuorio (1970) to magnetic dipolar interaction between the two sets of spins. Furthermore, an experiment at Kazan (Egorov *et al* 1984) on a single crystal of thulium ethylsulphate immersed in ^3He showed that the spin–lattice time decreased noticeably when the angle of the magnetic field was adjusted to make the resonance frequency of the ^{169}Tm nuclei equal to that of the ^3He nuclei (32.433 MHz per tesla). This is again attributed to spin–spin interaction by-passing the Kapitza resistance at the crystal/liquid interface. In principle, a similar experiment should be possible using a single crystal of $PrVO_4$, since the resonant frequency of ^3He lies between the parallel and perpendicular values for ^{141}Pr. The nuclear electric quadrupole splitting in this substance means that frequency crossings with ^3He should occur at a number of field strengths.

The vanadates are better than thulium ethylsulphate; they have a much higher density of lanthanide nuclei, and the nuclear spins, $\frac{3}{2}$ and $\frac{7}{2}$, give a larger nuclear entropy than ^{169}Tm ($I = \frac{1}{2}$). They are hard substances that can be ground down to small particles, for which thermal transport of energy to and from the surface should take place in reasonably finite times (see section 3). It would be worthwhile to attempt to cool ^3He by immersing a fine powder of $PrVO_4$ in the liquid. In zero-field the ^3He frequency should overlap with both ^{141}Pr and ^{51}V nuclei, because of the finite linewidth.

At room temperature the electronic magnetic susceptibility is appreciably anisotropic, and in an applied field the particles should line up with directions in the perpendicular plane along the field; if they can then be fixed in a matrix that allows penetration of the liquid ^3He to the surface of the particles, the temperature after demagnetisation should be close to that derived in section 2. However a random orientation of the particles is still quite effective; calculation shows that after demagnetising from a field of 7 T at 5 mK, over 90% should cool to temperatures below 0.018 mK, and over 50% to below 0.01 mK.

Acknowledgments

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