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The additivity of partial thermal remanent magnetization in magnetite

Shaul Levi *School of Oceanography, Oregon State University, Corvallis, Oregon 97331, USA*

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Summary. Experiments were done to test the additivity of partial thermal remanent magnetizations (PTRMs) for prepared samples containing magnetite particles whose sizes range from SD (single domain) to MD (multidomain). The experiments compare the sum of two PTRMs with total-TRM, all produced by the same external field of 0.47 oe. The most significant conclusion of this paper is that, to first order, the additivity of PTRMs is obeyed for the magnetites of this study regardless of particle size. However, small, higher order deviations from additivity occur such that $\overline{\Sigma \text{PTRM}} > \overline{\text{TRM}}$ by an average of about 1 per cent. Though small, these departures from additivity are significant at the 99 per cent confidence level, and they can be understood in terms of Néel's theory for SD particles. The small departures from additivity are intrinsic to the experimental procedure in which some particles acquire remanence twice, in each of the two PTRM steps. In the limit of small inducing fields additivity should be obeyed exactly for the magnetites of this study and for samples of interest in palaeomagnetism. The deviations from additivity should have no effect on palaeointensity determinations by the Thelliers' version of the Thellier palaeointensity method. For palaeointensity determinations by Coe's version of the Thellier method the effects of deviations from additivity would be very small, less than 4 per cent on the average for a worst-case experimental configuration, and these effects can be minimized by producing PTRMs parallel to the original NRM and by using weak laboratory fields.

Introduction

The additivity and independence of partial thermal remanent magnetizations (PTRMs) acquired in different temperature intervals were first discovered and enunciated by E. Thellier (1938, 1946). These properties are usually considered to be among the more fundamental properties of thermal remanent magnetization (TRM), and they form the basis for the Thellier method of palaeointensity determinations (Thellier & Thellier 1959; Coe 1967a, b). Thellier's original experiments were done with baked clays and bricks, whose primary magnetic constituent was probably predominantly a dilute mixture of SD (single

domain) hematite (αFe_2O_3) particles. A theoretical foundation for Thellier's observations of the additivity and independence of PTRMs was provided by Néel's (1949) theory for non-interacting SD particles.

In recent years the Thellier palaeointensity method has been applied extensively to volcanic rocks (Thellier & Thellier 1959; Coe 1967a; Kono & Nagata 1968; Kono 1974; Coe & Grommé 1973; Khodair & Coe 1975; Coe, Grommé & Mankinen 1978) whose primary magnetic constituents are usually titanomagnetites. Soffel (1971) observed domain walls in titanomagnetite particles of composition 0.55 Fe_2TiO_4–0.45 Fe_3O_4 whose diameters are as small as 1.3 μm, suggesting that for pure magnetite domain structure might exist in yet smaller particles. Since volcanic rocks usually contain a significant fraction of titanomagnetite particles larger than 1 μm and because magnetite particles larger than SD and in excess of 1 μm have been shown to exhibit stable TRM, comparable to that of many volcanic rocks (Roquet 1954; Rimbert 1959; Parry 1965; Dunlop 1973; Levi & Merrill 1978), it is probable that TRM in many titanomagnetite-bearing volcanic rocks is carried by particles larger than SD; that is, in PSD (pseudosingle domain) and MD (multidomain) particles. (PSD refers to particles whose sizes and magnetic properties are intermediate between 'truly' SD and 'truly' MD particles.) Néel (1955) and Stacey (1963) predicted theoretically that the additivity and independence of PTRMs should also be satisfied by MD particles, but these predictions have not yet been tested experimentally for MD particles.

Ozima & Ozima (1965) argued that the additivity law should be strictly satisfied only where the high temperature IRM (isothermal remanent magnetization) is negligible in comparison with the PTRMs and that in general the sum of the PTRMs should exceed the total-TRM by the sum of the IRMs acquired at the elevated temperatures. In the simplest case, when only one intermediate temperature is used, their prediction leads to:

$$\vec{\mathrm{TRM}}(T_C, T_R, \mathbf{h}) + \vec{\mathrm{IRM}}(T_I, \mathbf{h}) = \vec{\mathrm{PTRM}}(T_C, T_I, \mathbf{h}) + \vec{\mathrm{PTRM}}(T_I, T_R, \mathbf{h}). \quad (1)$$

T_C, T_R, T_I refer, respectively, to the Curie point, room temperature and the intermediate temperature used during the additivity of PTRMs experiment. The notation (T_A, T_B, **h**) denotes the temperature interval T_A, T_B with $T_A > T_B$ during which the external field, **h**, is present. The Ozimas verified their prediction by comparing partial-inverse-TRMs with total-inverse-TRM for an assemblage of magnetite grains approximately 30 μm in size and in an external field of 10 oe. Dunlop & West (1969) verified equation (1) for samples containing single domain grains of γFe_2O_3 and $CoFe_2O_4$ using external fields of 45 and 90 oe, respectively.

Because of the importance of the additivity and independence of PTRMs to theories of TRM and to the Thellier palaeointensity method, this study was undertaken to examine additivity as a function of particle size and domain state for a particular mineral (magnetite). Furthermore, small external fields ($h < 0.5$ oe) were used so that the results may be directly applicable to rocks whose TRM is acquired in the Earth's field.

Magnetite powders, preparation of samples and their TRM properties

Magnetite (Fe_3O_4) was chosen for this study for reasons of experimental convenience and because magnetite is a common constituent of continental igneous rocks. Although the magnetite powders and the samples used in these experiments were described in detail by Levi (1977) and Levi & Merrill (1978), it is important to emphasize that the magnetite powders originate from different sources; while some are synthetic, others were obtained by crushing natural crystals. The samples were prepared by dilutely dispersing a particular magnetite powder (about 1 per cent by weight) in a matrix of high purity alumina and

calcium aluminate cement. The samples were moulded into cylinders about 24 mm in diameter and 22 mm in height, weighing between 15 and 19 gm.

Whereas synthetic samples prepared by precipitation from an aquaeous solution are typically substantially oxidized along the solid solution between magnetite and maghemite (Gallagher, Feitknecht & Mannweiler 1968), natural crystals are usually more nearly stoichiometric. On the other hand, the crushing of the natural crystals introduces internal stresses and strains which affect the particles' magnetic properties. In order to anneal the internal strains and to stabilize the particles' magnetic properties all the samples were heated to 650°C for 6 hr in an atmosphere which reduced maghemite to magnetite. In some cases these heatings caused grain growth due to sintering.

Some of the properties of the magnetite powders and the TRM properties of the samples are given in Table 1. *All* the data of Table 1 were obtained for samples previously heated to

Table 1. Physical characteristics of the magnetites and TRM properties of the samples.

Sample (powder) no.	Particle origin and shape	Particle size (μm)	T_C(° C) ± 10° C	TRM $\times 10^{-3}$ Gauss (h_L = 0.467 oe)	$H_{1/2}$ (oe)	$T_{1/2}$ (° C)	Low temp. cycles, normalized	
2	Natural, Crushed, sieved; Irregular	$\bar{d}$ = 2.7 d < 150	580	0.258	78 ± 4	475 ± 15	0.590 0.465 0.476	
3	Natural, Crushed, sieved; Irregular	$\bar{d}$ = 1.5 d < 50	580	2.32	138 ± 10	493 ± 10	0.593 0.521 0.497	
4	Natural, Ball-milled; Regular Polyg.	$\bar{d}$ = 0.31 d < 2	580	0.964	380 ± 8	444 ± 10	0.936 0.889 0.822	
5	Synthetic, Regular Polyg.; Spheres to cubes	$\bar{d}$ = 0.24 ± 0.1 d < 0.9	565	2.97	347 ± 5	492 ± 10	0.945 0.935 0.929	
6	Synthetic, Regular Polyg.	$\bar{d}$ = 0.21 ± 0.06	570	1.34	334 ± 5	507 ± 10	0.976 0.951	0.965
7	Spheres to cubes	d < 0.5		14.5	360 ± 15	508 ± 10	0.945	0.961 0.955
8	Synthetic, Regular Polyg.;	$\bar{d}$ = 0.12 ± 0.04	575	1.17	292 ± 10	400 ± 15	0.990 0.971	0.986
9	Spheres to cubes	d < 0.3		1.04	295 ± 15	418 ± 10	0.965	0.910 0.907
10	Reduction to Fe_3O_4 of αFe_2O_3 of matrix mix	$\bar{d}$ = ? d < 0.5	–	0.0295	430 ± 20	503 ± 10	0.982 0.974 0.960	
11	Synthetic, Acicular (needle shape)	Mean axial ratio = 8 : 1, 0.35 × 0.04	591	3.36	571 ± 20	519 ± 10	1.003 0.995 0.994	

1 oe = 10^{-4} w m^{-2} = 10^{-4} Tesla
1 gauss = 1 emu cm^{-3} = 10^3 A m^{-1}

650°C for 6 hr in a reducing environment, and the TRM properties were determined after heating the samples several times to above 600°C until the TRM intensity and its stability, as measured by alternating field (AF) demagnetization, were reproducible within about 3 per cent. The TRM of samples 2 and 3 resides primarily in MD particles; this is consistent with optical observations of their particle sizes, their relatively low AF stabilities, characterized by low median demagnetizing fields ($H_{1/2}$), and their relatively low stabilities with respect to low temperature cycles to below magnetite's isotropic temperature near 130° K. At the other end of the particle-size spectrum, stability criteria and direct observations of particle sizes and shapes imply that the TRM of sample 11 is carried by SD particles. Samples 4–10 have stabilities intermediate between samples 3 and 11. Thus the particle sizes of the samples of this study span the gamut from MD to SD, exhibiting a broad range of magnetic properties, which are typically encountered in palaeomagnetism.

PTRM experiments and analysis of the results

Experiments to test the additivity of PTRMs were done as follows:

(a) The samples were heated above T_C and given a total-TRM in the laboratory field, h_L, to obtain TRM(T_C, T_R, h_L).
(b) The samples were reheated above T_C and cooled in *null* field to a temperature T_I where $T_R < T_I < T_C$. The temperature was maintained at T_I to allow the samples to equilibrate thermally. (Depending on the particular T_I, the temperature was maintained at T_I between 60 and 90 min.) The laboratory field, h_L, was turned ON about 5 min before cooling the samples from T_I to T_R to obtain PTRM$_1$(T_C, T_I, NULL; T_I, T_R, h_L).
(c) Step (a) was repeated to obtain TRM(T_C, T_R, h_L). (Step (c) was added during the experiments; therefore, it is absent for slightly more than half the experiments.)
(d) The samples were reheated above T_C and cooled in h_L to T_I. The temperature was maintained at T_I, allowing thermal equilibrium to be established. h_L was turned OFF about 5 min before cooling the samples from T_I to T_R in *null* field to obtain PTRM$_2$(T_C, T_I, h_L; T_I, T_R, NULL).
(e) Step (a) was repeated.

The samples were always heated in a slightly reducing chemical environment to prevent oxidation of the magnetites. The experiments were performed for three and sometimes four different values of T_I for each sample. The data are presented in Table 2. Column 1 identifies the samples from 2 to 11 (as in Table 1) varying gradually from MD to SD. Column 2 lists the total-TRMs of steps (a), (c) and (e) in chronological order, where $h_L = 0.467 \pm 0.002$ oe. Column 3 gives the arithmetic means of the total-TRMs and their standard deviation, s. Column 4 lists the various T_I for each sample. Column 5 lists the values of PTRM$_1$(T_C, T_I, NULL; T_I, T_R, h_L). Column 6 lists PTRM$_2$(T_C, T_I, h_L; T_I, T_R, NULL). Column 7 lists the sums of PTRM$_1$ + PTRM$_2$. The values in the parentheses under each datum in column 3, 5, 6 and 7 are normalized with respect to the mean TRM of each experiment. In column 8 it is noted whether or not the difference between the ΣPTRM and the mean TRM is significant with respect to (1) 1s (68.3 per cent) and (2) 2s (95.4 per cent). Significance is defined as:

Significant: $|\Sigma\text{PTRM} - \overline{\text{TRM}}(T_C, T_R, h_L)| > ns \quad n = 1, 2$

Not significant: $|\Sigma\text{PTRM} - \overline{\text{TRM}}(T_C, T_R, h_L)| \leq ns \quad n = 1, 2$

S (N.S.) in column 8 denotes whether the difference is significant (not significant) according to the above definition.

Table 2. The additivity of PTRM

Sample no.	TRM (T_C, T_R) (emu) h = 0.467 oe	$\overline{TRM} \pm s$	T_I(° C)	$PTRM_1$	$PTRM_2$	ΣPTRM	Significant difference 1s	2s
2	2.175×10^{-3} 2.188 2.200	2.188 ± 0.012 (1.000 ± 0.006)	452	1.234 (0.564)	1.012 (0.463)	2.246 (1.027)	S.	S.
	2.462 —— 2.430	2.446 ± 0.023 (1.000 ± 0.009)	493	1.538 (0.629)	0.935 (0.382)	2.473 (1.011)	S.	N.S.
	2.362 2.360 2.340	2.354 ± 0.012 (1.000 ± 0.005)	511	1.688 (0.717)	0.710 (0.302)	2.398 (1.019)	S.	S.
	2.335 —— 2.325	2.330 ± 0.007 (1.000 ± 0.003)	516	1.681 (0.721)	0.688 (0.295)	2.369 (1.017)	S.	S.
3	2.062×10^{-2} 2.062 2.012	2.045 ± 0.029 (1.000 ± 0.014)	452	0.783 (0.383)	1.281 (0.626)	2.064 (1.009)	N.S.	N.S.
	2.275 —— 2.238	2.256 ± 0.026 (1.000 ± 0.012)	493	1.081 (0.479)	1.181 (0.523)	2.262 (1.003)	N.S.	N.S.
	2.150 2.150 2.150	2.150 ± 0.000 (1.000 ± 0.000)	511	1.265 (0.588)	0.919 (0.427)	2.184 (1.016)	S.	S.
	2.212 —— 2.175	2.194 ± 0.026 (1.000 ± 0.012)	516	1.275 (0.581)	0.888 (0.405)	2.163 (0.986)	S.	N.S.
4	0.894×10^{-2} 0.894 0.881	0.890 ± 0.008 (1.000 ± 0.008)	426	0.322 (0.362)	0.572 (0.643)	0.894 (1.004)	N.S.	N.S.
	0.900 0.900 0.900	0.900 ± 0.000 (1.000 ± 0.000)	485	0.680 (0.756)	0.239 (0.266)	0.919 (1.021)	S.	S.
	0.888 —— 0.875	0.882 ± 0.009 (1.000 ± 0.010)	493	0.770 (0.873)	0.105 (0.119)	0.875 (0.992)	N.S.	N.S.
5	2.475×10^{-2} —— 2.512	2.494 ± 0.026 (1.000 ± 0.010)	468	0.435 (0.174)	2.050 (0.822)	2.485 (0.996)	N.S.	N.S.
	2.512 —— 2.688	2.600 ± 0.124 (1.000 ± 0.048)	490	0.682 (0.262)	1.850 (0.712)	2.532 (0.974)	N.S.	N.S.
	2.700 2.750 2.800	2.750 ± 0.050 (1.000 ± 0.018)	512	1.650 (0.600)	1.094 (0.398)	2.744 (0.998)	N.S.	N.S.

Table 2 *(continued)*

Sample no.	TRM (T_C, T_R) (emu) h = 0.467 oe	$\overline{TRM} \pm s$	T_I(° C)	$PTRM_1$	$PTRM_2$	ΣPTRM	Significant difference 1s	2s
6	1.156×10^{-2}	1.172 ± 0.023	493	0.269	0.944	1.213	S.	N.S.
	——	*(1.000 ± 0.020)*		(0.229)	(0.805)	(1.035)		
	1.188							
	1.250	1.269 ± 0.025	512	0.570	0.740	1.310	S.	N.S.
	1.260	(1.000 ± 0.020)		(0.449)	(0.583)	(1.032)		
	1.298							
	1.150	1.206 ± 0.079	517	0.658	0.582	1.240	N.S.	N.S.
	——	(1.000 ± 0.066)		(0.545)	(0.483)	(1.027)		
	1.262							
7	1.394×10^{-1}	1.384 ± 0.013	493	0.112	1.269	1.381	N.S.	N.S.
	——	(1.000 ± 0.010)		(0.0813)	(0.917)	(0.998)		
	1.375							
	1.310	1.314 ± 0.016	512	0.495	0.775	1.270	S.	S.
	1.300	(1.000 ± 0.012)		(0.377)	(0.590)	(0.967)		
	1.331							
	1.369	1.384 ± 0.022	517	0.541	0.906	1.447	S.	S.
	——	(1.000 ± 0.016)		(0.391)	(0.655)	(1.046)		
	1.400							
8	1.025×10^{-2}	1.029 ± 0.004	426	0.535	0.493	1.028	N.S.	N.S.
	1.031	(1.000 ± 0.003)		(0.520)	(0.479)	(0.999)		
	1.031							
	1.056	1.054 ± 0.003	485	0.838	0.230	1.068	S.	S.
	1.055	(1.000 ± 0.003)		(0.795)	(0.218)	(1.013)		
	1.050							
	1.119	1.104 ± 0.022	493	0.994	0.113	1.107	N.S.	N.S.
	——	(1.000 ± 0.020)		(0.900)	(0.102)	(1.003)		
	1.088							
	1.081	1.075 ± 0.008	517	1.055	0.019	1.074	N.S.	N.S.
	——	(1.000 ± 0.008)		(0.981)	(0.0174)	(0.999)		
	1.069							
9	0.956×10^{-2}	0.950 ± 0.008	468	0.555	0.390	0.945	N.S.	N.S.
	——	(1.000 ± 0.009)		(0.584)	(0.411)	(0.995)		
	0.944							
	0.938	0.934 ± 0.008	485	0.658	0.292	0.950	S.	S.
	0.925	(1.000 ± 0.008)		(0.704)	(0.313)	(1.017)		
	0.938							
	0.938	0.932 ± 0.009	490	0.668	0.280	0.948	S.	N.S.
	——	(1.000 ± 0.010)		(0.716)	(0.300)	(1.017)		
	0.925							

Table 2 *(continued)*

Sample no.	TRM(T_C, T_R) (emu) h = 0.467 oe	$\overline{TRM} \pm s$	T_I(° C)	$PTRM_1$	$PTRM_2$	ΣPTRM	Significant difference 1s	2s
10	2.762×10^{-4} 2.775 2.775	2.771 ± 0.008 (1.000 ± 0.003)	447	0.722 (0.261)	2.100 (0.758)	2.822 (1.018)	S.	S.
	2.762 —— 2.775	2.768 ± 0.009 (1.000 ± 0.003)	501	1.344 (0.486)	1.469 (0.531)	2.813 (1.016)	S.	S.
	2.712 2.710 2.700	2.707 ± 0.006 (1.000 ± 0.002)	520	1.875 (0.693)	0.919 (0.339)	2.794 (1.032)	S.	S.
	2.720 —— 2.712	2.716 ± 0.006 (1.000 ± 0.002)	525	1.869 (0.688)	0.931 (0.343)	2.800 (1.031)	S.	S.
11	2.912×10^{-2} —— 2.925	2.918 ± 0.009 (1.000 ± 0.003)	468	0.349 (0.110)	2.625 (0.900)	2.974 (1.019)	S.	S.
	2.950 —— 3.250	3.100 ± 0.212 (1.000 ± 0.068)	490	0.578 (0.186)	2.325 (0.750)	2.903 (0.936)	N.S.	N.S.
	3.075 2.962 3.062	3.033 ± 0.062 (1.000 ± 0.020)	511	0.950 (0.313)	2.125 (0.701)	3.075 (1.014)	N.S.	N.S.

In addition to samples 2 to 11, additivity experiments were also done for two large crystals of magnetite. Sample 0 is a natural euhedral crystal weighing 6.38 gm and sample 1 is a 3.57 gm chip of a natural crystal. The TRMs of both samples are highly unstable, having median demagnetizing fields of 12 and 17 oe, respectively, and s values of their mean TRMs are of the order of 10 per cent. For sample 1 deviations from additivity are less than one standard deviation of $\overline{TRM}$. However, for sample 0 additivity is not obeyed. Experiments were done at four values of T_I (identical to those of sample 1), and the remanence after each $PTRM_2$ step was opposite to the direction of the laboratory field. Because such large crystals are not usually of interest in palaeomagnetism, further discussion of these data is omitted from this paper. However, due to the importance of these results to the understanding of TRM in large MD particles, a more detailed analysis of these PTRM properties will be given in a future paper. In the following sections only the results of samples 2–11 will be discussed.

For now, we shall disregard differences between samples and consider each of the 34 additivity experiments as independent. For 20 of these 34 experiments there is no significant difference at the 2s level between the mean TRM and the ΣPTRM; that is, $|\overline{TRM} - \Sigma PTRM| < 2s$. For 10 of these 20 experiments $\Sigma PTRM < \overline{TRM}$, and for 10 $\Sigma PTRM > \overline{TRM}$. Furthermore, nine of these 20 experiments have $s \leq 0.01\,\overline{TRM}$. In other words, the deviations from additivity of these 20 experiments are not significant at the 95 per cent confidence level, and additivity is obeyed. In the remaining 14 experiments $|\overline{TRM} - \Sigma PTRM| \geq 2s$. Of these 14 experiments 13 have $\Sigma PTRM > \overline{TRM}$, and only for one is $\Sigma PTRM < \overline{TRM}$.

Among the 14 experiments where $|\overline{TRM} - \Sigma PTRM| \geq 2s$, 12 have $s \leq 0.01\,\overline{TRM}$. Thus there seems to be a positive correlation between small dispersion of the TRM values and deviations from additivity. Relatively smaller dispersions of the TRM determinations suggest less experimental noise and more reliable results. Hence, if we arbitrarily discard experiments for which $s > 0.01\,\overline{TRM}$, we are left with 21 experiments. For 15 of these experiments $\Sigma PTRM > \overline{TRM}$, and for 12 of these $\Sigma PTRM - \overline{TRM} > 2s$. In contrast, all six experiments for which $\Sigma PTRM < \overline{TRM}$, have $\overline{TRM} - \Sigma TRM < 1s$.

Because of the small number of TRMs for each experiment (2 or 3) the estimate of σ for $\overline{TRM}$ is probably quite inaccurate, particularly in the cases where all TRMs are the same for a given experiment. Also, one needs to associate a realistic error with the $\Sigma PTRM$ values. Therefore, we pooled the experiments in several ways to facilitate more reliable statistical analysis of the results. For each grouping we calculated the statistic

$$t = \frac{|\overline{\Sigma PTRM} - \overline{TRM}|}{[(s^2/n) + (s^{*2}/n^*)]^{1/2}}$$

where s^* and n^* are the standard deviation and number of independent determinations, respectively, associated with the total-TRM, and s and n are associated with the $\Sigma PTRM$. Table 3 summarizes the results for five groupings of the experiments. Group I includes all 34 experiments, and $\overline{\Sigma PTRM}$ *exceeds* $\overline{TRM}$ by 0.8 per cent, and there is a greater than 90 per cent confidence that the $\overline{\Sigma PTRM}$ and $\overline{TRM}$ are distinct.

Each additivity experiment requires heating the sample above T_C of magnetite four or five times. Thus the main sources of error in these experiments are (1) chemical and physical changes of the particles at elevated temperatures, near 600°C; (2) uncertainty in reproducing the intermediate temperature, T_I, when producing the PTRMs; (3) uncertainties in reproducing the laboratory field. For each experiment the laboratory field was reproducible to better than 0.5 per cent. Because several samples were in the oven during each heating and because the variations in TRMs and PTRMs of the various samples were not consistent with (2) or (3) above, we strongly suspect that (1) (chemical and physical changes of the magnetite particles at elevated temperature) is the primary source of error in the TRMs and PTRMs. Therefore, the most reliable tests of additivity should be the experiments exhibiting minimum dispersion, s, of their total TRMs. For this reason, in group II we discard experiments for which $s > 0.02\,\overline{TRM}$. Only three experiments are eliminated by this

Table 3. Statistical analysis of PTRM additivity experiments.

Analysis group	Number of experiments	$\overline{TRM} \pm s^*(n^*)$	$\overline{\Sigma PTRM} \pm s(n)$	t	$t^{\star}_{n-1,0.025}$	$t^{\star}_{n-1,0.005}$
I	34	1.000 ± 0.018 (49)	1.008 ± 0.021 (34)	1.90	2.03	
II	31	1.000 ± 0.011 (46)	1.011 ± 0.016 (31)	3.29	2.042	2.750
III	21	1.000 ± 0.006 (31)	1.012 ± 0.012 (21)	4.24	2.086	2.845
IV	19	1.000 ± 0.009 (29)	1.018 ± 0.017 (19)	4.15	2.101	2.878
V	14	1.000 ± 0.006 (23)	1.019 ± 0.017 (14)	3.85	2.160	3.012

★ Crow *et al.* (1960), Table 3, p. 231.

I: All experiments of additivity of PTRM.
II: Experiments for which s of $\overline{TRM} \leq 0.02\,\overline{TRM}$.
III: Experiments for which s of $\overline{TRM} \leq 0.01\,\overline{TRM}$.
IV: Experiments for which $|\overline{\Sigma PTRM} - \overline{TRM}| > 1s$.
V: Experiments for which $|\overline{\Sigma PTRM} - \overline{TRM}| > 2s$.

filter, and the s values of these experiments are 0.048, 0.066 and 0.068 $\overline{\text{TRM}}$. For group II $\overline{\Sigma\text{PTRM}}$ *exceeds* $\overline{\text{TRM}}$ by 1.1 per cent and the difference is significant at the 99 per cent confidence level. Group III excludes experiments with $s > 0.01\ \overline{\text{TRM}}$, leaving 21 experiments under consideration; $\overline{\Sigma\text{PTRM}}$ *exceeds* $\overline{\text{TRM}}$ by 1.2 per cent, and the difference of the two means is also significant at 99 per cent confidence. The key difference between Group I and Groups II and III is not in the difference of the means but in the significantly smaller dispersions of $\overline{\text{TRM}}$ and $\overline{\Sigma\text{PTRM}}$ of groups II and III.

Group IV and V are designed to illustrate the sense of the deviation of $\overline{\Sigma\text{PTRM}}$ from $\overline{\text{TRM}}$. Only experiments having $|\overline{\text{TRM}} - \overline{\Sigma\text{PTRM}}| \geqslant 1s$ ($2s$) are included in Group IV (Group V). $\overline{\Sigma\text{PTRM}}$ *exceeds* $\overline{\text{TRM}}$ by 1.8 per cent and 1.9 per cent for Groups IV and V, respectively, and for both groups the differences of the means are significant with 99 per cent confidence.

The statistic t was also calculated for the individual samples; however, only for sample 2 (MD particles) and for sample 10 (SD particles) were $\overline{\Sigma\text{PTRM}}$ and $\overline{\text{TRM}}$ distinct with 95 per cent confidence. For both samples $\overline{\Sigma\text{PTRM}}$ *exceeds* $\overline{\text{TRM}}$ by 1.8 per cent and 2.5 per cent respectively.

Thus, the results of these experiments show that, to first order, additivity is obeyed for the magnetite samples of this study, whose particles span the gamut from SD to MD. However, there appears to be a significant higher order departure from additivity such that

$$\text{PTRM}_1(T_\text{I}, T_\text{R}, \text{h}) + \text{PTRM}_2(T_\text{C}, T_\text{I}, \text{h}) \geqslant \text{TRM}(T_\text{C}, T_\text{R}, \text{h}). \tag{2}$$

These departures from additivity show no apparent dependence on particle size, inequality 2 being obeyed to the same degree by samples containing either SD or MD particles.

Discussion

1 CAUSE FOR DEVIATIONS FROM ADDITIVITY

Using Néel's (1949) theory for SD particles it will be argued below that the small deviations from additivity are intrinsic to and inseparable from the experimental procedure. Néel's expressions for SD particles will be used despite the fact that the TRM of most of the samples of this study is carried by PSD and MD particles. The relaxation time, τ, of an assemblage of identical, non-interacting, SD particles of aligned uniaxial anisotropy in an external field, h, which is applied along the easy axis of magnetization is:

$$\tau_\pm = f^{-1} \exp\left[\frac{\upsilon J_\text{S}(H_\text{ci} \pm h)^2}{2H_\text{ci}kT}\right] \tag{3}$$

and

$$\tau^{-1} = \tau_+^{-1} + \tau_-^{-1} \tag{4}$$

where υ = particle volume, J_S = particle's spontaneous magnetization, H_ci = particle's microscopic coercivity, k = Boltzmann's constant, T = temperature in K. The plus refers to the relaxation of particles magnetized parallel to h and the minus refers to the relaxation of particles magnetized antiparallel to h. τ is substantially determined by the rapidly varying exponential term, resulting in a very narrow range of parameters over which the magnetization is blocked. f is the frequency parameter, and, since it is a much more slowly varying function of temperature, as compared with the exponential term, it is customarily treated as a constant. To consider the more realistic case where the particles are distributed in both

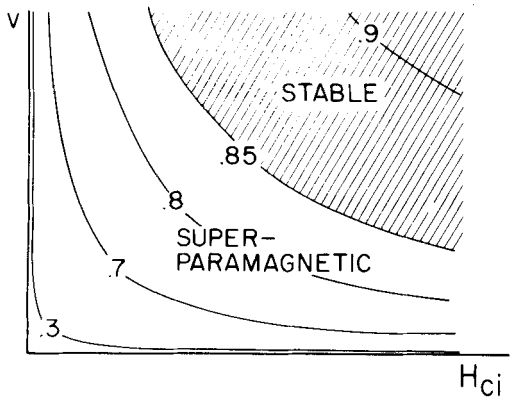

Figure 1. The effect of temperature on blocking and unblocking, illustrated by Néel's blocking curves and the Néel diagram (v versus H_{ci}). Each blocking curve divides the (v, H_{ci}) space into stable and superparamagnetic regions for a given temperature, T/T_C, with τ = constant and $h = 0$. T/T_C is given for each curve, and stable and superparamagnetic regions are shown for $T/T_C = 0.85$.

v and H_{ci} Néel introduced a convenient graphical method (the Néel diagram) which provides insight into many magnetization processes. On the Néel diagram each particle is a point in the v versus H_{ci} space. The blocking curve $\mathscr{H}(T, h, \tau)$, also introduced by Néel, is useful for understanding the effects on blocking of the parameters T, h and τ. Fig. 1 illustrates the effect of temperature on blocking, as the blocking curves are constructed for $h = 0$ and for a single value of τ. Each blocking curve denotes a particular temperature and divides the H_{ci} versus v space into two regions of blocked (stable) and unblocked (superparamagnetic) particles. The region of stable magnetization increases with decreasing temperature from $T/T_C = 1$ to $T/T_C = 0$. Fig. 2 shows that an external field, h, (at constant τ and T) shifts the blocking curve to the right, increasing the region of superparamagnetism.

In this study, during the production of $PTRM_1$, the sample is cooled from T_C to T_I in zero field; at T_I the appropriate blocking curve is $\mathscr{H}(T_I, 0, \tau)$ and the particles of regions a and b of Fig. 2 are blocked but with no net remanence, $J = 0$. As h_L is applied the blocking

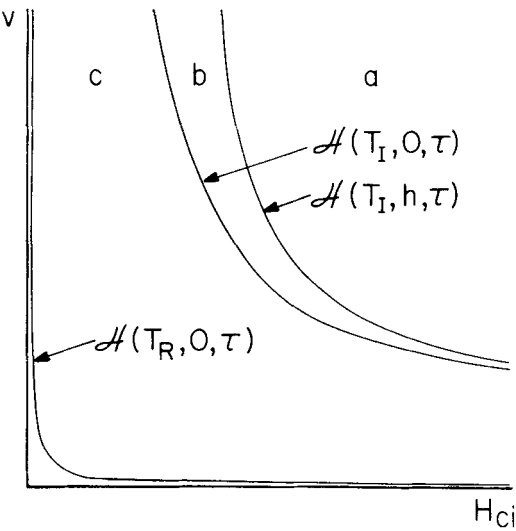

Figure 2. The effect of an external field on the blocking curve at constant T is to decrease the region of stable magnetization. Region b becomes superparamagnetic when h is applied.

curve is shifted to $\mathscr{H}(T_I, h_L, \tau)$ and the particles of region b become superparamagnetic and are statistically aligned parallel to h_L in accordance with the hyperbolic tangent law. As the temperature is decreased from T_I to T_R (with h_L ON) the particles from both regions b and c become stable and contribute to $PTRM_1$ parallel to h_L. In producing $PTRM_2$ the sample is cooled from T_C to T_I in the presence of $\mathbf{h}_L$. At T_I the appropriate blocking curve is $\mathscr{H}(T_I, h_L, \tau)$, and the particles of region a are stable with $\mathbf{J} \| \mathbf{h}_L$. The particles of regions b and c are superparamagnetic but with net alignment parallel to $\mathbf{h}_L$. As $\mathbf{h}_L$ is switched off, the blocking curve is $\mathscr{H}(T_I, 0, \tau)$, and the particles of region b are stabilized parallel to $\mathbf{h}_L$. This constitutes an $IRM(T_I, \mathbf{h}_L)$. Upon cooling to T_R in zero field the particles of region c are blocked with $\mathbf{J} = 0$. Hence, $PTRM_2$, which is parallel to h_L, includes remanence from both regions a and b. Therefore, the particles of region b contribute both to $PTRM_1$ and $PTRM_2$, thus explaining the small deviations from additivity, and satisfying inequality 2. It follows that the deviations from additivity are quantitatively equivalent to the remanence of region b which is also equivalent to $IRM(T_I, \mathbf{h}_L)$, as was pointed out by Ozima & Ozima (1965) and expressed by equation (1).

Of the samples used in this study only sample 11 contains uniaxial and clearly SD particles (Levi & Merrill 1978), and the particles are aligned in none of the samples. However, the discussion above depends primarily on the correctness of the functional form of τ, equations (3) and (4), and only incidentally on the fact that it was derived for particular SD particles. Therefore, it might be that the functional form of equations (3) and (4) is valid for a broader range of particles than those postulated in Néel's derivation; however, in that case the meanings of v, J_S and H_{ci} would be quite different than for ideal SD particles. It must be emphasized that although the deviations from additivity can be satisfactorily explained in terms of Néel's SD theory, samples 2, 3 and 4 exhibit varying degrees of MD behaviour (Table 1). In particular, Levi (1977) used characteristics of MD behaviour to explain the non-linear PNRM–PTRM curves exhibited by samples 2, 3 and 4 during the Thellier experiment. (Samples 5–11, however, behave ideally in the Thellier sense.) Therefore, it might be possible that a different mechanism is responsible for the deviations from additivity of samples 2, 3 and 4.

All the samples of this study with the exception of sample 10 are subject, to some degree, to particle agglomerations (Levi & Merrill 1978) and are undoubtedly subject to magnetic interactions. Although it is difficult to accurately assess this influence, it is unlikely that magnetic interactions are responsible for the deviations from additivity. The main reason for this is that sample 10, which is least subject to magnetic interactions (Levi & Merrill 1976; Table 1, column 5), exhibits the most significant deviations from additivity of all the samples of this study. In addition, we are aware of no interaction scheme (inter or intra-particle) which would explain the experimental results.

2 THE EFFECT OF DEVIATIONS FROM ADDITIVITY ON THE THELLIER PALAEOINTENSITY METHOD

To first order, the additivity of PTRMs is obeyed for the samples of this study. Therefore, to the degree that additivity is obeyed and to the degree that the Thellier palaeointensity method depends on the additivity of PTRM, the Thellier method can be successfully applied to samples whose remanence resides in SD, PSD and MD particles.

It is appropriate to ask how the small, higher order deviations from additivity would affect the Thellier experiment. We assume, in the following, that deviations from additivity result from the mechanism discussed in the previous section, where Néel's SD model was invoked, and, for simplicity, we only consider cases in which the NRM and PTRMs are

produced by identical external fields. In the Thelliers' version of the Thellier experiment (Thellier & Thellier 1959) h_L is *ON* during both heatings, so that a single blocking curve, $\mathscr{H}(T_I, h_L, \tau)$ in Fig. 2, applies to both heatings. Hence, small deviations akin to those observed during the additivity experiments should not occur, owing to the absence of region b of Fig. 2. During the execution of Coe's version of the Thellier experiment (Coe 1967a, b) the first heating is a thermal demagnetization at T_I, for which the blocking curve is $\mathscr{H}(T_I, 0, \tau)$ (Fig. 2), and the particles of region c of Fig. 2 are demagnetized. During the second heating when h_L is *ON* the blocking curve is $\mathscr{H}(T_I, h_L, \tau)$ and the particles in region b of Fig. 2 are superparamagnetic; therefore, in general, the PTRM acquired during the second heating will *exceed* the PNRM lost during the first by an amount of remanence related to that of region b of Fig. 2. The above discrepancy would be completely suppressed whenever the PTRM is applied parallel to the NRM, and maximum deviation, equivalent to *twice* the PTRM associated with region b of Fig. 2, would occur when the PTRM is applied anti-parallel to the NRM. Because the average deviations from additivity, observed in the present experiments, are about 1 per cent, the maximum influence of such deviations on a palaeointensity determination of Coe's version of the Thellier method is about 4 per cent. This estimate is based on a one point palaeointensity determination, the temperature at which 50 per cent of the NRM is thermally demagnetized, and on the supposition that the remanence associated with region b of Fig. 2 comprises 1 per cent of the NRM and that the PTRM is produced antiparallel to the NRM. Clearly, the errors associated with deviations from additivity would be proportionately reduced, if a greater fraction of the NRM is used in a particular palaeointensity determination. Furthermore, as mentioned earlier, errors in palaeointensity determinations associated with departures from additivity would be entirely suppressed if the PTRMs were produced parallel to the NRM. This was demonstrated for sample 10, which is the worst-case example having average deviations from additivity of 2.5 per cent. Using Coe's version of the Thellier method, Levi (1974) showed that sample 10 yielded an accurate palaeointensity value (to 1 per cent) when PTRMs are produced parallel to the NRM, the PTRM-producing, laboratory field being identical to the NRM-producing field. On the other hand, had the PTRMs been produced anti-parallel to the NRM, then the above hypothetical, one point palaeointensity determination would have produced a value which is as much as 10 per cent low.

Evidence that deviations from additivity of the kind observed in our experiments actually do occur during palaeointensity determinations by Coe's version of the Thellier method is provided by Levi (1974, 1977). Two identical samples were subjected to Coe's version of the Thellier experiment; the PTRMs in one sample were produced anti-parallel to the NRM, and the PTRMs in the second sample were produced parallel to the NRM. The normalized anti-parallel PTRMs of the former sample were consistently higher by an average of 1.2 per cent. Although these deviations are small, they are in surprising agreement with the results of the additivity experiments for these samples (samples 8 and 9; Table 2).

Because there are many potential sources for non-ideal behaviour during the Thellier experiment (Thellier & Thellier 1959; Coe 1967b; Levi 1977), the potential errors due to the small deviations from additivity can usually be ignored, especially if care is taken to produce the PTRMs parallel to the NRM and to use weak laboratory fields, comparable to or less than the palaeofield.

Conclusions

The major result of the foregoing experiments is that, to first order, the additivity of PTRMs is obeyed for a broad range of prepared samples containing magnetite whose particle sizes

and stabilities are frequently encountered in palaeomagnetic studies. Additivity seems to be obeyed to the same degree by samples 2–11, whose magnetite particle sizes range from SD to PSD to MD. That additivity is satisfied even for samples whose PTRMs reside substantially in MD particles suggests that the pinning of their domain walls is highly localized within the particle and occurs over a very narrow range of values of the magnetic parameters, as is the case for the blocking of SD particles.

In addition, the above experiments show that higher order deviations from additivity occur such that ΣPTRM > TRM by an average of about 1 per cent. Though small, these deviations from additivity are significant at the 99 per cent confidence level, and they can be understood in terms of Néel's (1949) theory for SD particles. These departures from additivity are intrinsic to the experimental procedure where some particles acquire remanence twice, in each of the two PTRM steps. In the limit of small inducing fields additivity should be obeyed exactly for the magnetites of this study and for samples of interest for palaeomagnetism.

Palaeointensities determined by the Thelliers' version of the Thellier experiment should be unaffected by the deviations from additivity, because identical blocking relationships are associated with the two heatings at each temperature step. For palaeointensity determinations by Coe's version of the Thellier method the effects of departures from additivity are usually very small, less than 4 per cent on average, and these effects can be minimized by producing the PTRMs parallel to the original NRM and by using laboratory fields comparable to or weaker than the palaeofield.

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