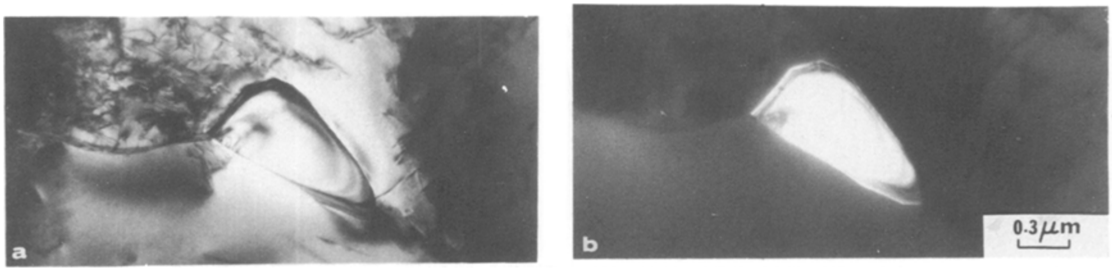

Figure 2 Electron micrographs of the same grain boundary carbide particle as in Fig. 1 (beam parallel to $[1\bar{1}\bar{1}]$). (a) Bright-field image and (b) dark-field image with a (220) particle reflection.

TABLE I Chemical composition in weight per cent

Ni	Mo	Fe	Cr	Co	Si	V	C
70.42	29.92	0.93	0.64	< 0.10	< 0.02	< 0.01	0.002

standard in measuring the camera constant. From the observed *d*-spacings, the lattice constant of the grain boundary phase was calculated to be 10.86 ± 0.01 Å (1.086 nm). This suggests that this phase is an eta-carbide of the form $M_{12}C$ such as that found in the ternary Ni–Mo–C system [3, 4] and in Hastelloy alloy N [5]. The present result and that reported earlier [2] concerning the presence of δ-NiMo in Hastelloy alloy B-2 seem to indicate that $M_{12}C$ and δ-NiMo may co-exist, as has been concluded by Heijwegen and Rieck [4] in the case of the Ni–Mo–C ternary system.

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H. M. TAWANCY
*High Technology Materials Division,
Cabot Corporation,
Kokomo,
Indiana 46901,
USA*

About the origin of magnetoresistance in relatively thin metal films

It has previously been [1] shown that the transport properties of a thin metallic film placed in a transverse magnetic field (perpendicular to its plane) can be, as in the absence of a magnetic field, described in terms of a mean free path model [1, 2] which takes into account the background scattering and the scattering at external surfaces [3, 4], i.e. the scatterings of the Fuchs–Sondheimer conduction model [4]. In this model the film conductivity, σ_F, and the Hall coefficient, R_{HF}, are evaluated by means of the following analytical expressions [1]

$$\sigma_F/\sigma_0 = [A^2 + \alpha^2 B^2]A^{-1} \qquad (1)$$

and

$$R_{HF}/R_{H0} = B[A^2 + \alpha^2 B^2]^{-1}, \qquad (2)$$

where

$$A = \frac{3}{2}\left\{-\tfrac{1}{2}\mu + \mu^2 + \frac{\mu}{2}(1 - \mu^2 + \alpha^2\mu^2) \times \ln\left[\frac{(1+\mu^{-1})^2 + \alpha^2}{1+\alpha^2}\right] - 2\alpha\mu^3 \arctan\left[\frac{\alpha}{\mu}\,\frac{1}{(\alpha^2 + 1 + \mu^{-1})}\right]\right\} \qquad (3)$$

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and

$$B = \frac{3}{2}\left\{-\mu^2+\mu^3 \ln\left[\frac{(1+\mu^{-1})^2+\alpha^2}{1+\alpha^2}\right]\right.$$
$$+\frac{\mu}{\alpha}(1-\mu^2+\alpha^2\mu^2)$$
$$\left.\times \arctan\left[\frac{\alpha}{\mu}\frac{1}{(\alpha^2+1+\mu^{-1})}\right]\right\}, \quad (4)$$

and the subscripts 0 and F refer respectively to the bulk and film parameters.

The size effect parameter μ is related as usual [1, 3] to the film thickness a, the bulk mean free path l_0 and the specularity parameter p [4] by the equation

$$\mu = \frac{a}{l_0}\left(\ln\frac{1}{p}\right)^{-1}. \quad (5)$$

The parameter α is defined by

$$\alpha = l_0 r^{-1}, \quad (6)$$

where r is the radius of an electron in a magnetic field i.e. $r = mv/eH$ [4].

Since small magnetic fields are easily obtainable in practice some authors [4–9] have studied the transport properties of thin metal films in the limit of vanishing magnetic field.

However, a correlated study of conductivity and Hall coefficient of thin films has not been proposed up to now in the limit of strong magnetic fields. Hence this letter is devoted to the study of the influence of strong magnetic fields.

In the limiting case $\alpha \to \infty$ which corresponds to very strong magnetic fields, the following approximate relations are obtained

$$\ln\left[\frac{(1+\mu^{-1})^2+\alpha^2}{1+\alpha^2}\right] \approx \frac{1}{\alpha^2}(2\mu^{-1}+\mu^{-2})$$
$$+\frac{(2\mu^{-1}+\mu^{-2})}{\alpha^4}[-1-\tfrac{1}{2}(2\mu^{-1}+\mu^{-2})]$$
$$+\frac{(2\mu^{-1}+\mu^{-2})}{\alpha^6}\left[(1+\mu^{-1})^2+\frac{(2\mu^{-1}+\mu^{-2})^2}{3}\right] \quad (7)$$

and

$$\arctan\left[\frac{\alpha}{\mu}\frac{1}{(\alpha^2+1+\mu^{-1})}\right] \approx \frac{1}{\mu\alpha}$$
$$-\frac{1}{3\alpha^3}(\mu^{-3}+3\mu^{-2}+3\mu^{-1})$$
$$+\frac{1}{\alpha^5}[\mu^{-1}+2\mu^{-2}+2\mu^{-3}+\mu^{-4}+\tfrac{1}{5}\mu^{-5}]+\ldots \quad (8)$$

which are valid provided that the condition $1 \ll \alpha\mu$ is satisfied.

It can then be easily seen that Equations 3 and 4 reduce, after some simple mathematical manipulations to the limiting forms

$$A \approx \frac{1}{\alpha^2}\left(1+\frac{3}{8\mu}\right)-\left(\frac{1}{8\mu^3}+\frac{3}{5\mu^2}+\frac{9}{8\mu}+1\right)\frac{1}{\alpha^4} \quad (9)$$

and

$$B \approx \frac{1}{\alpha^2}-\left(\frac{1}{5\mu^2}+\frac{3}{4\mu}+1\right)\frac{1}{\alpha^4}. \quad (10)$$

Introducing these approximate forms in Equations 1 and 2 and neglecting any further term α^{-n} containing power n higher than 2 we get

$$\sigma_F/\sigma_0 \approx \left(1+\frac{3}{8\mu}\right)^{-1}+\left(\frac{19}{320\mu^2}+\frac{71}{2560\mu^3}\right)$$
$$\times\left(1+\frac{3}{8\mu}\right)^{-2}\cdot\left(\frac{1}{\alpha^2}\right); \quad \alpha\mu \gg 1 \quad (11)$$

and

$$R_{HF}/R_{H0} \approx 1+\left(\frac{19}{320\mu^2}\cdot\frac{1}{\alpha^2}\right); \quad \mu\alpha \gg 1. \quad (12)$$

Equations 11 and 12 show that the terms containing α^{-2} have slight magnitudes for $\mu \gg 1$ and convenient asymptotic expressions could satisfactorily be

$$\sigma_F/\sigma_0 \approx \left(1+\frac{3}{8\mu}\right)^{-1}$$

or

$$\rho_F/\rho_0 \approx \left(1+\frac{3}{8\mu}\right); \quad \alpha, \mu \gg 1 \quad (13)$$

and

$$R_{HF}/R_{H0} \approx 1; \quad \alpha, \mu \gg 1. \quad (14)$$

In the particular case of nearly specular scattering on external surfaces the μ parameter can be rewritten in the form $\mu \approx a l_0^{-1}(1-p)^{-1}$ and the resistivity ratio (Equation 13) consequently takes the following approximate form

$$\rho_F/\rho_0 \approx 1+\frac{3}{8}\left[\frac{(1-p)l_0}{a}\right] \quad \alpha a l_0^{-1} \gg 1 \quad (15)$$

which is exactly the approximate form of the resistivity of thick films in the Sondheimer model [4].

TABLE I The resistivity ratio ρ_F/ρ_0 (derived from exact Equation 1) for different values of the α and μ parameters. The numerical evaluation has been accomplished with the aid of a pocket calculator and inaccuracies appear for $\alpha\mu \geqslant 160$

μ	$\alpha = 1$	$\alpha = 2$	$\alpha = 4$	$\alpha = 10$	$\alpha = 20$	$\alpha = 40$
0.01	16.94682	18.18758	20.26558	24.27216	28.12963	32.24061
0.04	6.26734	6.74047	7.50758	8.78477	9.63475	10.12228
0.1	3.53138	3.76476	4.10448	4.51761	4.67495	4.72959
0.2	2.43453	2.55690	2.70650	2.83198	2.86309	2.87194
0.4	1.79447	1.84870	1.90009	1.92989	1.93552	1.93697
1	1.34753	1.36106	1.37024	1.37415	1.37481	1.37522
2	1.18026	1.18420	1.18646	1.18734	1.18747	1.18714
4	1.09191	1.09296	1.09351	1.09376	1.09264	–
10	1.03720	1.03738	1.03744	1.03789	1.06402	–

TABLE II Variations of the approximate values of the resistivity ratio ρ_F/ρ_0 (Equation 13)

μ	0.01	0.04	0.1	0.2	0.4	0.8	1	2	4	10	20	40	100
ρ_F/ρ_0	38.5	10.375	4.75	2.875	1.9375	1.46875	1.375	1.1875	1.09375	1.0375	1.01875	1.00938	1.00375

In the absence of a transverse magnetic field and evidently also in the limit of a small magnetic field [6] the expression of the film resistivity in the mean free path model [3] is also given by Equation 13 for $\mu \gg 1$, when nearly specular scattering occurs on external surfaces or when the film exhibits a large thickness.

Numerical results as evaluated from exact Equations 1 and 2, and asymptotic Equations 13 and 14 are reported in Tables I, II and III. It appears that the deviations between asymptotic and exact values of the resistivity ratio ρ_F/ρ_0 and the Hall coefficient ratio R_{HF}/R_{H0} remain less than 0.5 per cent (10%) until the product $\alpha\mu$ satisfies the following condition

$$\alpha\mu \geqslant 4 \quad (\alpha\mu \geqslant 0.8); \qquad (16)$$

this condition is less restricted than the assumption $\alpha\mu \gg 1$ previously used to perform the calculations of asymptotic equations.

Larger deviations are obtained when the asymptotic expression of the conductivity is used, as is usually observed [7].

It then seems that Equation 15 holds for any value of the strength of the transverse magnetic field (i.e. for any value of α) in the case where $\mu \gg 1$. Table IV shows that the resistivity behaviour follows this rule with a good accuracy in a very large μ-range ($\mu > 1$). Hence it is concluded that in the framework of the quasi-free electron model and when both background and external surface scatterings occur simultaneously the film resistivity is not affected by the transverse magnetic field, except in the case of thinner films. The variation in the magnetoresistance effect with the strength of the applied magnetic field must then be interpreted

TABLE III The Hall coefficient ratio R_{HF}/R_{H0} (Equation 2) for different values of the parameters α and μ. The small deviations observed for $\alpha\mu \geqslant 160$ are due to inaccuracies of the numerical work (performed with a pocket calculator)

μ	$\alpha = 1$	$\alpha = 2$	$\alpha = 4$	$\alpha = 10$	$\alpha = 20$	$\alpha = 40$
0.01	3.43719	2.92749	2.33561	1.70016	1.38013	1.17831
0.04	1.8324	1.63508	1.40511	1.16772	1.06632	1.02079
0.1	1.36787	1.26377	1.14746	1.04474	1.01361	1.00363
0.2	1.17848	1.11783	1.05630	1.01325	1.00360	1.00092
0.4	1.07600	1.04467	1.01789	1.00353	1.00092	1.00023
1	1.01946	1.00969	1.00327	1.00058	1.00015	1.00004
2	1.00594	1.00269	1.00085	1.00015	1.00004	1.00001
4	1.00165	1.00071	1.00022	1.00004	1.00002	0.99998
10	1.00028	1.00012	1.00004	0.99994	0.99968	1.00050

TABLE IV The resistivity ratio ρ_F/ρ_0 as evaluated from exact Equation 1. The values for $\mu \geqslant 20$ and $\alpha = 40$ are not reported because of inaccuracies in the numerical work (performed with a pocket calculator)

μ	$\alpha = 0.04$	$\alpha = 0.4$	$\alpha = 4$	$\alpha = 40$
0.8	1.40786	1.41217	1.46091	1.46907
1	1.33337	1.33661	1.37024	1.37522
2	1.17536	1.17655	1.18646	1.18710
4	1.09042	1.09080	1.09351	1.10472
10	1.03693	1.03700	1.03744	1.00074
20	1.01860	1.01862	1.01895	–
40	1.00932	1.00934	1.00800	–
100	1.00347	1.00374	1.01066	–

in terms of complicated models evoking either the anisotropy of the energy surface [10] or two overlapping energy bands of spherical symmetry [11, 12].

Similar behaviour can be predicted when the grain-boundaries act as efficient scatterers, since the Fuchs–Sondheimer (F–S) conduction model can then be replaced by an effective F–S model [13–15] which leads to the same form of equations, as previously shown [14, 15]. However detailed calculations are difficult and are not so easy to interpret as those in the F–S model; this point will be discussed in a future communication.

It can then be theoretically predicted that any experimental observation of the magnetoresistance effect in relatively thick films cannot be attributed to the usual size effect induced by geometrical limitation in the mean free path, but could be due to properties of energy surface [10] or energy bands [12] or to impurities [16].

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C. R. TELLIER*
A. J. TOSSER
C. R. PICHARD
Laboratoire d'Electronique,
Universite de Nancy 1,
CO 140-54037 Nancy, France

*Present address: Laboratoire de Chronométrie et Piézoelectroicité, ENSMM, Route de Gray, 25030 Besançon Cedex, France.

Some comments on ceramic solid-state reaction kinetics using results obtained on the $ZnO–Al_2O_3$ system

Ceramic solid-state reactions are usually carried out by intimately mixing fine powders and then firing them at high temperatures. When the reactions proceed isothermally it has been found [1, 2] that a number of diffusional models, namely those of Jander, Dünwald–Wagner, Valensi, Carter, Zhuravlev–Lesokhin–Tempel'man, Ginstling–Brounshtein and Kröger–Ziegler, hold for many ceramic solid-state reactions. Although these models show differences they all assume particles of uniform radius surrounded by a second reactant and an interface layer of uniform thickness growing with time. The $ZnO–Al_2O_3$ system has appeared to be an interesting system for checking the validity of these models. Indeed, ZnO and Al_2O_3 combine to form a unique stable compound $ZnAl_2O_4$ of normal spinel structure at moderately high temperatures (600 to 1400° C) and it has been demonstrated that the overall reaction process can be seen as a one-way transfer of zinc