

Low-temperature resistivity and thermoelectric ratio of copper and gold

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The resistivity ρ and thermoelectric ratio G have been measured between 0.04 and ~ 7 K for "pure" polycrystalline samples of copper and gold, in a dilution refrigerator with a superconducting quantum-interference device null detector system. The measurements confirm that these metals, like silver, show a $\rho - \rho_0 \propto T^4$ temperature dependence over a substantial temperature range. For the best copper sample a $\rho - \rho_0 \propto T^{2.03}$ temperature dependence below 2 K is strong evidence for electron-electron scattering.

I. INTRODUCTION

Recently, Barnard and Caplin¹ have published resistivity data for single-crystal silver samples which demonstrate a T^4 dependence between 1.2 and 4 K. In this paper we give results of resistivity measurements on copper and gold and show that these metals also exhibit a T^4 ($N \sim 4$) dependence over a similar temperature range. We also present data down to 40 mK in our quest for a definitive answer regarding the existence of a T^2 contribution to the resistivity resulting from electron-electron scattering.

Much of the current theoretical work on the resistivity of metals is concerned with the explanation of a T^N ($N \sim 2.8$) term observed by Rumbo² in high-purity single crystals of copper between 1 and 4 K. Thus Brett and Black³ have proposed that this temperature dependence results because of the change in the predominant scattering mechanism from electron-phonon scattering to electron-impurity scattering in this temperature range. On the other hand, Lawrence⁴ ascribes it to the change from electron-phonon scattering to electron-electron scattering. Dosdale and Morgan⁵ have performed a pseudopotential calculation of the resistivity of copper alloys in the "dirty limit," obtaining a $T^{3.8}$ dependence between 10 and 20 K.

As far as electron-electron scattering is concerned, the results for copper should be the most significant, because in this metal the electron-phonon scattering is expected to diminish to negligible proportions at a comparatively high temperature because of its large Debye temperature (320 K), while the electron-electron scattering should be the same order of magnitude as that of other simple metals.⁴

In Table I we show the theoretically estimated contributions to the resistivity for electron-electron scattering⁴ and expected crossover temperatures⁶ where phonon and electron scattering should be equal. From this table we expect copper to be the easiest noble metal in which to see

an electron-electron contribution and gold with its much lower Debye temperature (~ 180 K) to be the most difficult.

Our procedure has been to analyze the lowest-temperature data which are still appreciably above noise level to see if a T^2 dependence is obeyed. In this way we hope to avoid problems of nonadditivity of the components of resistivity arising from competing scattering mechanisms at higher temperatures. An added advantage of ultralow temperature measurements is that the residual resistivity ρ_0 can be measured precisely provided that there are no apparent resistance minima arising from the Kondo effect. Knowing the value of ρ_0 is very important in the search for a T^2 dependence.

We have also measured the thermoelectric ratio

$$G = (J/Q)_{E=0}, \quad (1)$$

where J and Q are electrical and thermal current densities and E is the electric field. In an elastic scattering regime G should be related to the thermopower S by

$$S = GL_0 T, \quad (2)$$

where L_0 is the Sommerfeld value of the Lorenz number. Simple theory says that $S \propto T$ in this region so that G should be a constant. We label $GL_0 T$ obtained from our experimental results by S' . $S' = S$ in the elastic scattering regime.

The measurement of G and S' ($\sim S$) is an important adjunct to measurement of ρ for the following reasons. First, it gives information regarding the nature of any impurities, particularly those which generate Kondo resistance minima. Second, a large magnitude for S can result in a significant reduction in the precision of ρ measurements since fluctuations in the temperature of the refrigerator could induce significant thermoelectric noise voltage across the sample. Third, our measurements of ρ are not strictly isothermal, since the measuring current, which enters and leaves at opposite ends of the sample via superconducting wires,

TABLE I. Theoretical values of B [Eq. (3)] in the regime where $N \sim 2$ for three noble metals. The crossover temperature is the theoretical value of the temperature at which electron-electron and electron-phonon scattering should make equal contributions to the resistivity.

	B ($10^{15} \Omega \text{ cm K}^{-2}$)	Crossover temperature (K)
Ag	140	2.4
Au	140	2.2
Cu	76	3.6

causes Peltier heating and cooling at the ends of the sample. The heat flow thereby established through the sample will induce a thermoelectric voltage. A large value for S' can result in a significant systematic error. The size of this systematic error is $\sim S^2/L_0$. For all the measure-

ments reported here, the size of this error is negligible on the scale of our precision.

II. EXPERIMENTAL

Cu 1 was prepared from ASARCO copper of high but unknown purity purchased several years ago. Cu 5 and 6 were prepared from ASARCO 99.999+ pure hot-rolled copper. They were machined with potential probe arms and annealed for three days at 1220 K in oxygen at a pressure of 5×10^{-4} Torr.⁷ Au 1 and Au 3 were made by melting COMINCO 99.9999% pure gold pellets in a graphite mold. Gold wire (0.025-cm diam.) potential probes were spot welded to the samples which were then annealed in air at 1220 K for two days to minimize the effect of iron impurities. We also attempted to produce Fe-free Au samples using a chlorine annealing technique.⁸ These chlorinated gold samples gave enormous G values and accompanying resistance minima which completely destroyed

TABLE II. Various parameters for copper and gold samples. ρ_0 , B , and N (and their uncertainties) are obtained by least-squares fitting the data to Eq. (3) over the temperature range shown. λ is the free-electron mean free path for a metal with resistivity ρ_0 . d is the smallest dimension of the sample.

Sample	$\frac{R_{300}}{R_{4.2}}$	λ/d	Temperature range (K)	ρ_0 ($10^{-10} \Omega \text{ cm}$)	B ($10^{-15} \Omega \text{ cm K}^{-N}$)	N	$\rho_{4.2} - \rho_0$ ($10^{-12} \Omega \text{ cm}$)
Cu 1	2 600	0.08	3.06-7.00	6.539 02 $\pm 0.000 04$	5.10 ± 0.05	3.93 ± 0.005	1.44
			0.3-2.1	6.536 36 $\pm 0.000 04$	40.3 ± 1.3	2.38 ± 0.04	
			0.6-1.85	6.536 35 $\pm 0.000 04$	41.9 ± 1.3	2.32 ± 0.09	
Cu 5	5 420	~ 0.10	3.47-7.00	3.129 61 $\pm 0.000 08$	2.55 ± 0.07	4.02 ± 0.015	0.83
Cu 6	4 190	0.11	2.57-7.53	4.042 12 $\pm 0.000 05$	3.0 ± 0.05	3.994 ± 0.007	0.89
			0.064-2.15	4.040 46 $\pm 0.000 01$	34.8 ± 1.7	2.03 ± 0.07	
Rumbo							
Cu 1	13 690	1.34	3.3-7.21	1.131 43 ± 0.001	10.6 ± 2.5	3.32 ± 0.1	1.4
Cu 3	8 810	0.96	3.08-7.28	1.761 2 $\pm 0.000 2$	4.56 ± 0.3	3.69 ± 0.03	0.93
Cu 4	7 380	0.92	3.03-7.27	2.099 1 ± 0.002	15.4 ± 8.0	3.00 ± 0.2	1.12
Au 1	5 600	0.13	1.48-6.40	3.898 40 $\pm 0.000 09$	43.3 ± 0.2	3.975 ± 0.002	130.3
			1.48-6.80	3.897 99 $\pm 0.000 09$	44.5 ± 0.5	3.959 ± 0.006	131.1
			0.5-1	3.898 86 $\pm 0.000 04$	65.2 ± 3	3.28 ± 0.41	
Au 3	2 800	0.07	2-7.1	7.752 20 $\pm 0.000 28$	51.0 ± 0.3	3.987 ± 0.003	157.3
			0.5-1.3	7.751 06 $\pm 0.000 02$	63.7 ± 3	3.47 ± 0.15	

their efficacy as far as the resistance of pure gold was concerned. These samples will be the subject of a future paper.

The measurements were performed using a dilution refrigerator with a superconducting quantum-interference device (SQUID) null detector system as described by Imes *et al.*⁹ and Schroeder and Uher.¹⁰ The CuNi-clad NbTi wires which are part of the SQUID circuit were in each case soldered to the potential probes on the samples. Earlier measurements in which the NbTi leads were directly soldered to the sample at a "point" gave rise to many abnormalities in the measured resistance. Resistance measurements were made with a precision ~ 2 parts in 10^5 .

A germanium resistance thermometer (Cryocal CR-100) calibrated between 0.2 and 3 K was the basic temperature standard. Temperatures from 0.04 and 0.3 K were measured with a second Cryocal CR-50 germanium thermometer calibrated against the CR-100 above 0.3 K and against a diluted cerium-magnesium-nitrate (CMN) thermometer between 0.04 and 0.3 K. The measurements above 3 K were made using another calibrated germanium thermometer. The precision

in temperature measurements was ≤ 1 mK throughout.

III. RESULTS

The resistivity was fitted by least squares to

$$\rho = \rho_0 + BT^N \quad (3)$$

in two ranges of temperature. ρ_0 , B , and N are variable parameters. In the upper range we found $N \sim 4$. In the lower range we were searching for a T^2 dependence with as small a contribution from phonons as possible. We therefore used the lowest temperatures consistent with the need for a finite range of points to fit Eq. (3), and with the temperature variation of the resistance being distinguishable from the noise. The results are given in Table II. We also include analyses of Rumbo's data ($\sim 1/10$ our precision) over approximately the same range as ours using the same computer program. In Fig. 1 we illustrate the T^N , ($N \sim 4$) dependence for the Au 3 and Cu 6 sample, and in Fig. 2 we show the variation of $(\rho - \rho_0)/T^N$ with T for all the samples measured. For comparison we also include some results for silver.^{1,11} In

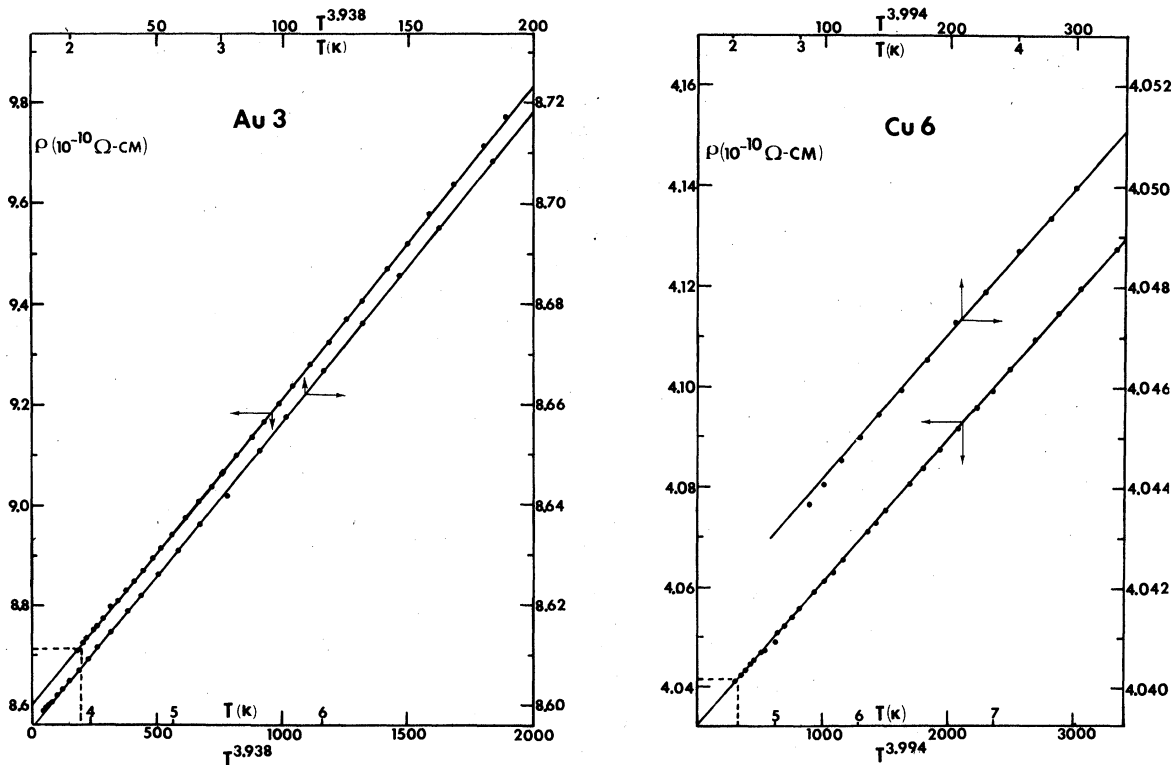


FIG. 1. Resistivity of Au 3 and Cu 6 samples plotted against T^N (N given in Table II). (Note, to be consistent with the parameters correctly given in Table II, the ordinate for Au 3 should be multiplied by 0.9).

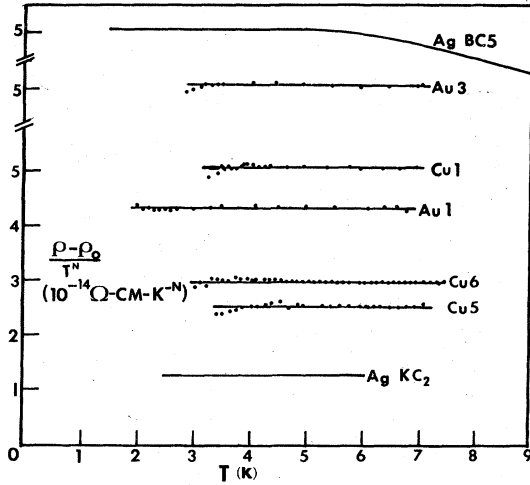


FIG. 2. $(\rho - \rho_0)/T^N$ for Au, Cu, and Ag samples plotted against T . N for Au and Cu is given in Table II. $N = 4$ for Ag BC5 [sample 5, Barnard and Caplin (Ref. 1)] and 3.96 for Ag KC₂ [sample C₂, Khosnevisan *et al.* (Ref. 11)]. For the Cu data, the units of the ordinate are $10^{-15} \Omega\text{-cm-K}^{-N}$.

Fig. 3 we show the results for the low-temperature resistivity with the fits using the parameters in Table II. In Fig. 4 we show the results for G and $S' = GL_0T$. S' will depart from the true thermopower, particularly at the higher temperatures where it is known that $L < L_0$.

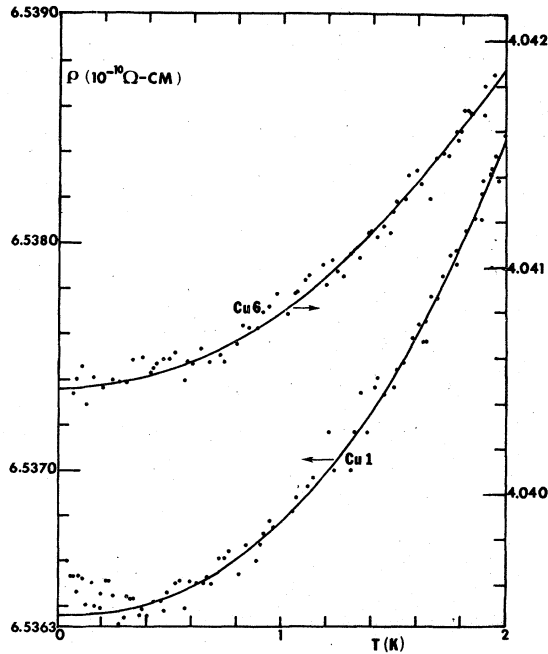


FIG. 3. ρ vs T for the low-temperature measurements on Cu. The curves represent the fits with the parameters given in Table II.

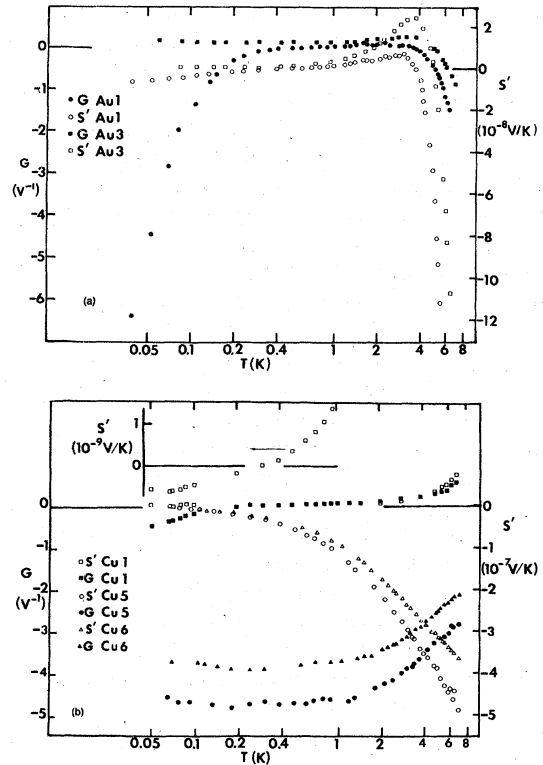


FIG. 4. (a) G and S' plotted against T for Au samples. (b) G and S' plotted against T for Cu samples.

IV. DISCUSSION

First it is clear that the high value N we obtain is close to 4 in both metals, whereas Rumbo's value for copper is generally closer to 3. The other significant difference which may or may not be associated with this is that λ/d (λ is the free-electron mean free path; d is the smallest dimension of the sample) is ~ 1 for Rumbo's samples and ~ 0.1 for ours. Another difference is that Rumbo's samples are single crystal, whereas ours are polycrystalline. More experimental work is required to ascertain the significance of these differences, though both our polycrystalline sample of silver¹¹ and the single crystals of silver of Barnard and Caplin showed a substantial temperature range over which a T^N ($N \sim 4$) dependence held. Another matter that requires a more thorough checking is the variation of B and $\rho_{4.2} - \rho_0$ with resistance ratio, which occurs both in our and Rumbo's data.

The low-temperature values of N for copper, 2.03 and 2.32, are close to 2.00, and give strong evidence for the existence of a T^2 temperature dependence at low T . This is particularly true of the Cu 6 sample in which all experimental diffi-

culties, fatal in some earlier runs, have been successfully avoided. In the near future, we will be making measurements with higher precision using a current comparator, which will enable us to improve the quality of our data at the lowest temperatures and should definitively answer the question of the existence of a T^2 dependence. It should be noted that, as in silver, the presence of a T^N ($N \sim 2$) dependence would not be inferred from high-temperature data. For instance poor fits are obtained if one attempts to fit the data above 1.5 K to an equation of the form

$$\rho = \rho_0 + AT^2 + BT^4, \quad (4)$$

or to various other combinations of power laws. We note that like silver the values of B obtained experimentally for the lowest-temperature data, although not strictly associated with a T^2 dependence, are of the same order of magnitude as those predicted by Lawrence⁴ (Table I) and by Black,¹² whose values are 30%–50% of those of Lawrence.

The low-temperature results for Au are complicated by the fact that the phonon contribution to ρ is higher than for Cu. Presumably, this larger phonon contribution is the reason that N is of the order of 3.3–3.5 for temperatures below approximately 1 K. Also for Au 3 there is a resistivity minimum $\sim 3 \times 10^{-5} \rho_0$ at ~ 0.3 K, but none is detectable within the precision of our experiment (~ 1 in 10^5) for Au 1. Of course, the existence of an appreciable resistivity minimum would severely limit our ability to search for a simple power-law behavior in the resistivity.

For the Kondo effect, thermoelectric powers of rather large magnitude usually occur when a resistivity minimum is observed.¹³ In Fig. 4(a) we exhibit our G measurements for the two gold samples. For Au 1 the fact that G rapidly decreases near the Kondo temperature (~ 0.24 K)¹⁴ for Fe in Au suggests that the decrease is associated with trace amounts of unoxidized Fe. To be consistent with the absence of a resistance minimum we would have to conclude that the sensitivity of G to traces of Fe is extremely high. There is some evidence for this. For example, we have a chlorinated sample with a residual-resistance ratio of 7000, for which G plunges to -1600 V^{-1} at 0.04 K compared with -4.5 V^{-1} observed for Au 1 at approximately the same temperature. We cannot, however, rule out the possibility that these affects are attributable to some other impurity. Unfortunately, there are no measurements of S on Au(Fe) alloys with known fractional ppm Fe levels with which to directly compare our data. The situation is further confused by the fact that Au 3 exhibits a well-behaved G below 1 K and a weak

resistivity minimum. Here we can only argue that the Fe contribution to the thermopower is weighted by a factor ρ_{Fe}/ρ_T , where ρ_{Fe} is the contribution of Fe to the total resistivity ρ_T , and that for Au 3 this factor is very small. The whole matter of preparing Kondo-effect free Au samples will be considered in another paper. Finally, we note that the sign reversals of G for both samples between approximately 4 and 5 K are in rough agreement with the S measurements on oxygen-annealed Au by Guénault and Hawksworth.¹⁵ They interpret the additional negative contribution to S at the higher temperatures as being due to a change in the dominant electron scattering mechanism; electron-impurity at low temperatures to electron-phonon at higher temperatures.

The low-temperature data for Cu 1 again show a minimum at ~ 0.4 K presumably due to the Kondo effect. Its magnitude is such that it is just observable at our level of precision. Cu 6, on the other hand, exhibits no evidence of a resistivity minimum. In Fig. 4(b) we show G and S' for copper. The Kondo temperature for Fe in Cu is much higher (~ 24 K)¹⁴ and typically manifests itself as a minimum in S at ~ 16 K.¹⁶ It would appear likely from our G and S' values for samples 5 and 6 that there is some Kondo effect present, presumably due to unoxidized Fe. In fact, the temperature dependences of S' for these two samples above 1.5 K are very similar to the temperature dependences of S observed by Rumbo² on Cu samples of larger resistance ratio; the magnitudes of our S' measurements are roughly a factor of 3 larger. Our value of $-0.3 \mu\text{V}/\text{K}$ for Cu 6 at 4 K is very small in magnitude compared with a value of $\sim -9 \mu\text{V}/\text{K}$ for a 25-ppm Cu(Fe) sample of Kjekshus and Pearson.¹⁶ We do not believe that a resistivity minimum contribution by unoxidized Fe would appreciably affect the Cu 6 resistivity data below 2 K, for two main reasons: First, the small magnitude for S' implies a relatively small amount of unoxidized Fe. Second, the Fe contribution to the resistivity should be close to the temperature-independent unitarity limit below 2 K.¹³ Our main argument against a significant contribution at higher temperatures is the T^N ($N \sim 4$) dependence which seems to be common to the three noble metals. G and S' for Cu 1 are a different matter. They are an order of magnitude smaller than that for samples 5 and 6; G is positive above 4 K and only below this temperature does it begin to decrease rapidly. This is not typical of Fe in copper and seems more like the results obtained for Au with an impurity of much lower Kondo temperature. A possibility would be manganese, which has a Kondo temperature of $\sim 10^{-1}$ K,¹³ a temperature which seems to correlate with the slight minimum in the very

small thermopower measured on Cu 1. The presence of the resistivity minimum does throw doubt on the significance of the low-temperature data for Cu 1.

In summary we conclude that there is strong evidence of a T^N ($N \sim 4$) region in the electrical resistivity of all the noble metals. More work is required on evaluating what factors influence the temperature range over which this dependence holds and in particular the value of the coefficient B which has considerable significance in "dirty

limit" theories.¹⁷ The evidence for a T^2 electron-electron scattering term is strengthened, but its confirmation will require measurements with one order of magnitude greater precision.

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¹B. Barnard and A. D. Caplin, *Commun. Phys.* **2**, 223 (1977).

²E. R. Rumbo, *J. Phys. F* **6**, 85 (1976).

³M. E. Brett and J. E. Black, *Can. J. Phys.* **55**, 521 (1977).

⁴W. E. Lawrence, *Phys. Rev. B* **13**, 5316 (1976).

⁵T. Dosdale and G. J. Morgan, *J. Phys. F* **4**, 402 (1974); **4**, L32 (1974).

⁶W. E. Lawrence (private communication).

⁷S. S. Rosenblum, W. A. Steyert, and F. R. Fickett, *Cryogenics* **17**, 645 (1977).

⁸C. W. E. Walker, *Can. J. Phys.* **48**, 378 (1970).

⁹J. L. Imes, G. L. Nieheisel, and W. P. Pratt, Jr., *J. Low Temp. Phys.* **21**, 1 (1975).

¹⁰P. A. Schroeder and C. J. Uher, *J. Low Temp. Phys.* **29**, 487 (1977).

¹¹M. Khoshenevisan, W. P. Pratt Jr., P. A. Schroeder, S. Steenwyk, and C. Uher, *J. Phys. F* **9**, L1 (1979).

¹²J. E. Black, *Can. J. Phys.* **56**, 708 (1978).

¹³M. D. Daybell, in *Magnetism*, Vol. 5, edited by H. Suhl (Academic, New York, 1973), p. 138.

¹⁴J. W. Loram, T. E. Whall, and P. J. Ford, *Phys. Rev.* **2**, 857 (1970).

¹⁵A. M. Guénault and D. G. Hawksworth, *J. Phys. F* **7**, L219 (1977).

¹⁶A. Kjekshus and W. B. Pearson, *Can. J. Phys.* **40**, 98 (1962).

¹⁷B. R. Barnard and A. D. Caplin, *J. Phys. (Paris)* (to be published).