

space-group symmetry. The order parameters devised for the spinel space group would then have little significance for the low-temperature phase. More important, though, is the fact that in none

of the published spectra have four *B*-site Mössbauer patterns been resolved below  $T_V$ ; only three patterns for the entire spectrum have been definitely resolved.<sup>8,9</sup>

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<sup>2</sup>E. F. Westrum, Jr. and F. Grønvd, *J. Chem. Thermo.* **1**, 543 (1969). The synthetic  $\text{Fe}_3\text{O}_4$  sample of this study has been further characterized by Mössbauer measurements. The unusually narrow linewidths confirm the stoichiometry and the lack of crystallographic or chemical disorder. [cf. B. J. Evans, in "National Conference on Magnetism and Magnetic Materials," November 1971 (unpublished)]. It is worthy of note that our observed lattice constant on this sample is identical to the value reported by H. E. Swanson, H. F. McMurdie, M. C. Morris, and E. H. Evans, in *Standard X-Ray Diffraction Powder Patterns* (Nat'l. Bur. Std. Monograph No. 25,

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## Comment on the Behavior of the Lorenz Number of Chromium at the Néel Temperature

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The high-precision data of Laubitz and Matsumura showing the behavior of the Lorenz number of chromium in the vicinity of the Néel temperature have been analyzed by a two-electron-group model in which a BCS-like gap is allowed to open in the antiferromagnetic group. The agreement of the data with this model indicates that spin-fluctuation effects in well-annealed pure chromium have a negligible effect on the conductivities.

There has been a recent controversy about the exact behavior of the electrical ( $\sigma$ ) and thermal ( $k$ ) conductivities of chromium at its Néel temperature  $T_N$ .<sup>1-4</sup> These measurements are all claimed to be quite precise; where stated the absolute error is about  $\pm 1\%$  or better and the relative error is as small as  $\pm 0.1\%$ . However, the resulting Lorenz numbers  $L = k/\sigma T$ , which are derived from these data, differ markedly, and the ensuing controversy is essentially whether spin-fluctuation phenomena are seen<sup>1,4</sup> in the vicinity of  $T_N$  or not.<sup>2,3</sup> The purpose of this comment is to point out that the most accurate measurements, which were made by Laubitz and Matsumura (LM),<sup>3</sup> agree well with a model that has been proposed by Goff<sup>5-7</sup> to explain the anomalous values of  $L$  (Cr) that are observed in the temperature range from 100 to 1000 K.<sup>8-10</sup> Since this model explains the anomalous change

of  $L$  below  $T_N$  in terms of the BCS long-range-order parameter  $\Delta(T)$ , it will be seen that spin fluctuation phenomena have a negligible effect on the transport properties of well-annealed pure chromium.

A comparison of these various measurements is best seen in Fig. 2 of LM,<sup>3</sup> where they are expressed as the ratio  $L/L_0$ ;  $L_0 = 2.4453 \times 10^{-8}$  (V/K)<sup>2</sup> is the theoretical value of  $L$ .<sup>11</sup> One should also refer to the subsequent paper of Meaden, Rao, and Tee,<sup>4</sup> which shows the effect of further annealing of their sample. Here the data of LM are shown in Fig. 1 without comparison with the other measurements. LM obtained  $L$  by simultaneously measuring  $k$  and  $\sigma$  with three different temperature gradients. The solid black points, which were taken with a temperature difference of 1 K, were the most precise; they had a relative precision of

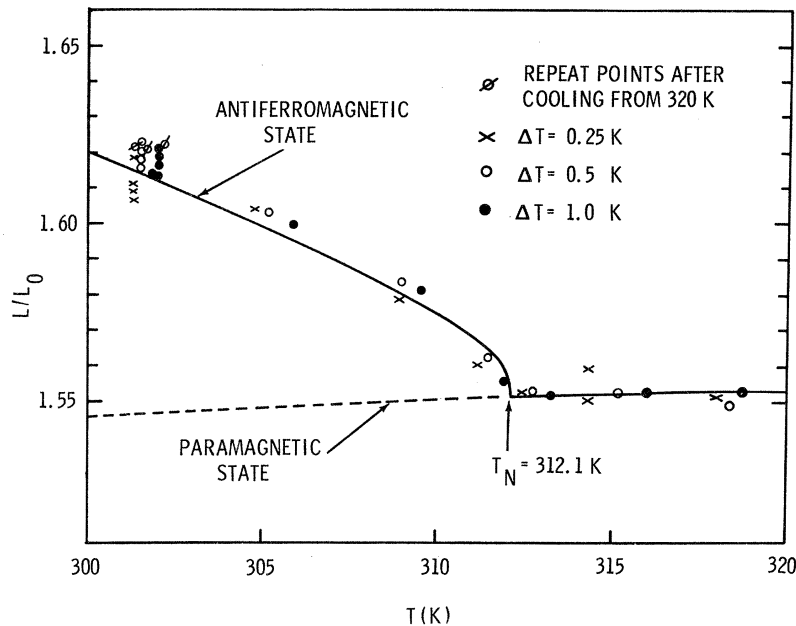


FIG. 1. Fit of the two-electron-group model to the data of Laubitz and Matsumura.

$\pm 0.1\%$ . These data are about 6% greater than the model calculation made previously by Goff.<sup>6</sup> This difference is on the order of the precision of the former data but is consistent with the general observation that  $L$  (Cr) increases upon anneal.<sup>2, 5, 8</sup>

LM determined  $T_N$  from the location of the minimum in the electrical resistivity<sup>12</sup> which was measured separately in an oil bath. The value  $T_N = 311.7$  K was in excellent agreement with the location of the peak in the heat capacity determined by Beaumont, Chihara, and Morrison<sup>13</sup> to be  $38.5^\circ\text{C}$ . However, it can be seen from LM's Fig. 1 that this minimum is shifted to a slightly higher temperature for the resistivity measurement made in the thermal-conductivity apparatus. The location of this shifted minimum as taken from the figure is  $T_N = 312.1$  or  $312.2$  K. This value is indicated here in Fig. 1. Thus, it can be seen that the solid point (precision  $\pm 0.1\%$ ) just to the left of  $T_N$  is significantly above the data just to its right. The appearance of antiferromagnetism causes  $L/L_0$  to abruptly increase.

The solid line in the figure is the fit of the Goff<sup>6</sup> model to the data. The procedure has been described in detail elsewhere.<sup>6</sup> The data were first corrected by the thermoelectric power to eliminate the effect of internal electric fields on the thermal conductivity. After fitting, these calculations were retransformed to the values shown here. For data of this precision, this transformation is significant. The model used is essentially the two-electron-group model of McWhan and Rice<sup>14</sup> in which the electrons are divided dichotomously into a paramagnetic and an antiferromagnetic group. Goff pointed

out that the paramagnetic group had to have a particular energy dependence in order to explain the anomalous values of  $L$  above  $T_N$ ; below  $T_N$  he allowed a gap to open in the antiferromagnetic group with the BCS long-range order parameter given by  $\Delta = \Delta_0 K T_N (1 - T/T_N)^{1/2}$ . Over this short range of temperature the parameters of the model are not uniquely determined. However, to fit the relatively constant but anomalously large values of  $L/L_0$  at temperatures above  $T_N$  it was necessary to decrease the well width  $E_0$  that had been postulated for the paramagnetic group and to increase its depth  $B$ . Below  $T_N$  the value of  $\Delta_0$  was retained because of the agreement with the optical reflectivity measurements of Barker and co-workers.<sup>15</sup> It was necessary to adjust  $R$ , the ratio of the specific conductivities of the antiferromagnetic and paramagnetic electron groups. It turns out that this new value of  $R$  is the same as that found by Heiniger and co-workers<sup>16, 17</sup> in their study of the heat capacity of Cr alloys. This agreement is probably a coincidence since it is known that  $L$  is at least weakly dependent upon scattering processes.<sup>5</sup> These constants are compared with their previous values in Table I. The dashed line shows the extension of

TABLE I. Model parameters for the fit to the Lorenz-number data of Cr.

Reference	$T_N$ (K)	$E_0$ (eV)	$B$		
			(single band)	$\Delta_0$	$R$
Reference 3	312.1	0.185	2.845	2.59	1.1
References 5, 8	312	0.218	2.55	2.59	0.51

the paramagnetic case to lower temperatures according to the model.

Clearly the data shown in the figure are compatible with an abrupt increase of  $L$  at  $T_N = 312.1$  K, caused by the appearance of the BCS-like gap in the antiferromagnetic electron group. In addition, there is no indication of a Lorenz-number catastrophe resulting from spin fluctuations at temperatures just above  $T_N$ .<sup>18</sup> Therefore these data are consistent with the theoretical predictions of Moriya<sup>19</sup> and Moriya and Kato,<sup>20</sup> who argued that there should be no singular behavior in the heat capacity at the antiferromagnetic transition. However, to be certain that there are no effects in

the conductivities one would need a datum near 312.3 K with the precision of the black point. The next three points above  $T_N$  are at 312.6, 312.8, and 313.3, respectively. Thus spin fluctuations, while not evident, cannot be completely dismissed. Since the further work of Meaden, Rao, and Tee,<sup>4</sup> who reannealed their sample, indicated that spin-fluctuation effects were greatly reduced, it seems reasonable to conclude that in well-annealed unalloyed chromium spin fluctuations have a negligible effect on the conductivities except, perhaps, in the immediate vicinity of  $T_N$ .

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## Spin-Correlation Functions for Heisenberg Antiferromagnets in the Callen Decoupling Approximation\*

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The linear-response theory and the Green's-function method in the Callen decoupling approximation are used to study the spin-correlation functions for Heisenberg antiferromagnets with general spin value  $S$ . This work is a generalization of a previous calculation for  $S = \frac{1}{2}$ . As in the case of  $S = \frac{1}{2}$ , the results are consistent with a sum rule for spin operators and the isotropy condition above the Néel temperature.

In a previous study<sup>1</sup> on Heisenberg antiferromagnets, the longitudinal or  $zz$  correlation functions of two spins were calculated only for  $S = \frac{1}{2}$ ,  $z$  being the direction of preferred antiferromagnetic spin alignment. The present work is a generalization to  $S \geq \frac{1}{2}$  of that calculation. Thus, together with the previous work, it completes the task of calculating the

transverse- and longitudinal-correlation functions for Heisenberg antiferromagnets with general spin in the Callen decoupling approximation (CDA),<sup>2</sup> namely,

$$\langle\langle S_{\lambda j}^z S_{\mu j}^+; B \rangle\rangle \approx \langle S_{\lambda i}^z \rangle \langle\langle S_{\mu j}^+; B \rangle\rangle + (2S^2)^{-1} \langle S_{\mu j}^z \rangle \langle S_{\lambda i}^- S_{\mu j}^+ \rangle \langle\langle S_{\lambda i}^+; B \rangle\rangle \quad \text{for } \lambda \neq \mu, \quad (1)$$