represent the higher resistance path for the current at low voltage.

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MAGNETIC EQUATION OF STATE FOR CrO_2 AND NICKEL NEAR THEIR CURIE POINTS*

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The magnetization-field–temperature characteristics of CrO_2 and nickel just above their ferromagnetic Curie points, though quantitatively very different, are found to obey the same special type of equation of state, which is isomorphic with that recently proposed for the critical-point behavior of a fluid.

We have discovered and will demonstrate below that the compound CrO_2 and nickel metal, in the detailed dependence of their magnetization σ on field H and temperature T just above the Curie (or critical) point T_c, both obey the same special type of equation of state. This is particularly remarkable since the critical-point properties of these two ferromagnetic materials are quantitatively very different. The equation of state conformed to by these materials is the exact magnetic isomorph of an equation recently proposed by Widom[1] for a fluid near its critical point and leads to an analogous sum rule (or scaling law) for the indices describing the variation with H or T of the principal thermodynamic properties near T_c. The present work constitutes the first experimental confirmation of such an equation of state with all its simplifying consequences regarding the critical-point indices. While the evidence presented here is specifically magnetic, it suggests that an equivalent situation may obtain in any cooperative system that undergoes a continuous phase transition.

A large body of recent theoretical and experimental research on the critical-point behavior of ferromagnets has been concerned with the values for the aforementioned indices. The index γ in

$$\chi_0 \propto (T-T_c)^{-\gamma} \text{ for } T \to T_c^+ \qquad (1)$$

defines the divergence of the initial paramagnetic susceptibility χ_0. Exact calculations for the three-dimensional Ising[2] and Heisenberg[3] ferromagnets have yielded values for γ close to 5/4 and $\frac{4}{3}$, respectively, in contrast to the molecular-field model prediction of $\gamma = 1$. Experiments have shown that nickel,[4,5] iron,[6] and various other ferromagnetic materials[7,8] obey Eq. (1) with $\gamma = \frac{4}{3}$.

The relationship for the critical isotherm,

$$\sigma \propto H^{1/\delta} \text{ at } T = T_c, \qquad (2)$$

defines the index δ, for which the molecular-field and three-dimensional Ising[9] models predict the values of 3 and 5.2, respectively. Measurements on nickel[4] gave $\delta \approx 4.2$, which is essentially what was later found for gadolinium.[8]

As described in detail elsewhere,[10] we have very recently determined for the ferromagnetic compound CrO_2 that $\gamma \approx 1.6$ and $\delta \approx 5.8$, which differ markedly from the index values cited above, including those for nickel. We will now show that despite this quantitative difference the $\sigma(H, T)$ data for CrO_2 and nickel just above T_c conform to the same simple qualitative scheme. The possible existence of such a scheme was originally suggested[11] to us on the basis of certain systematic variations in the data when plotted as isotherms of σ^2 vs H/σ. This type of plot had been previously used in determining χ_0 vs T for nickel,[4] and we later applied the same technique to our CrO_2 data,[10] for which some of the curves are shown in Fig. 1. Two features of the curves for $T > T_c$ (where $T_c = 386.5$°K from our analysis[10]) should be noted. First, the intercepts with the H/σ axis obey

$$\chi_0^{-1}(T) \equiv [H/\sigma]_{\sigma=0} \propto (T - T_c)^{\gamma}, \qquad (3)$$

which is equivalent to Eq. (1) and for which our analysis[10] gave $\gamma = 1.63 \pm 0.02$. Secondly, the monotonic variation of the initial slopes with temperature suggests that

$$D(T) \equiv [d(H/\sigma)/d\sigma^2]_{\sigma=0} \propto (T - T_c)^{\kappa}, \qquad (4)$$

with $\kappa > 0$; indeed, a closer examination reveals that $\kappa \approx 0.95$. It follows that each isotherm of σ^2 vs H/σ can be represented for small σ as

$$H/\sigma = \chi_0^{-1}(T) + D(T)\sigma^2, \qquad (5)$$

which, by defining $\chi_0^{-1}(T) \equiv H'/\sigma'$ and $\chi_0^{-1}(T)/D(T) \equiv (\sigma')^2$, can be converted to

$$(H/H')/(\sigma/\sigma') = 1 + (\sigma/\sigma')^2. \qquad (6)$$

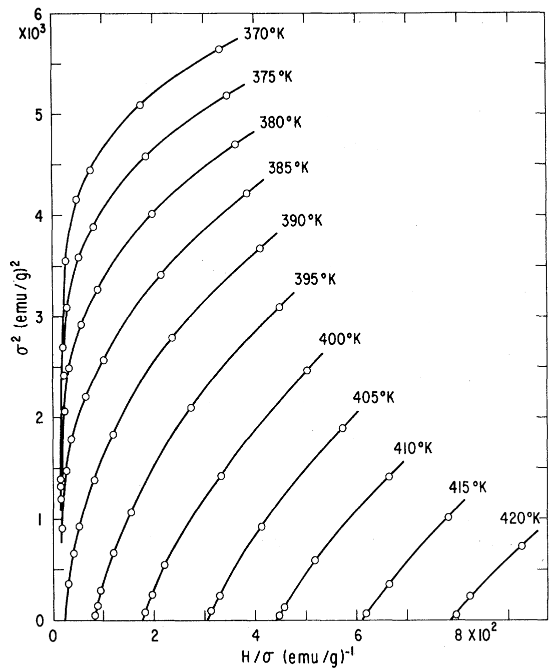

FIG. 1. Isotherms of σ^2 vs H/σ for CrO_2.

Thus, each isotherm above T_c, when plotted as $(\sigma/\sigma')^2$ vs $(H/H')/(\sigma/\sigma')$, will start with a value on the abscissa and an initial slope that are both unity. The crucial question is: will the various isotherms continue to superimpose for all values of these normalized variables?

To test this question against our CrO_2 data, we apply the above normalization to the isotherms of σ^2 vs H/σ just above T_c, using the quantities defined in Eqs. (3) and (4) with $\gamma = 1.63$ and $\kappa = 0.95$. The results are shown in Fig. 2, and it is quite evident that all the normalized ex-

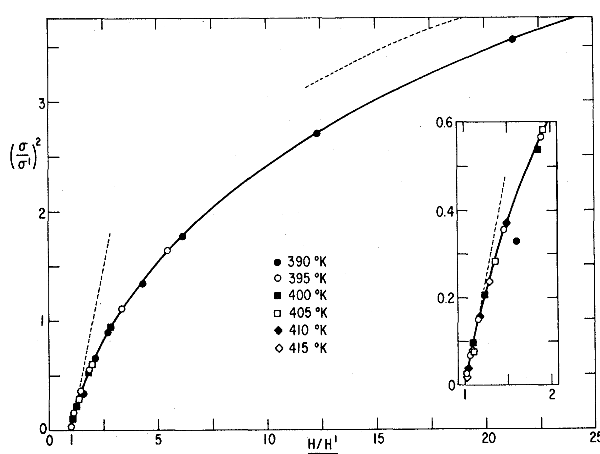

FIG. 2. Normalized isotherms for CrO_2. Dashed curves at low and high σ/σ' derived from Eqs. (6) and (10), respectively.

perimental points describe a single smooth curve; the only exception is the lowest field point for 390°K (see detailed insert in figure), whose departure from the curve is attributable to the magnetocrystalline anisotropy of our CrO_2 powder specimen that persists up to and slightly above T_C.[12] Since this type of plot overemphasizes the region of high σ/σ' (which is dominated by the points for T very near T_C), we show the same normalized data in a log-log plot in Fig. 3(a). An excellent agreement with a single smooth curve clearly holds at all values of these normalized variables.

We now turn to the isotherms of σ^2 vs H/σ for nickel, previously derived[4] from the data of Weiss and Forrer,[13] and follow the same normalization procedure. In this case we take $\gamma = 1.30$ and $\kappa = 0.48$ as the average values pertinent to the temperature region just above $T_C(=627.2°K)$. The log-log plot of these results

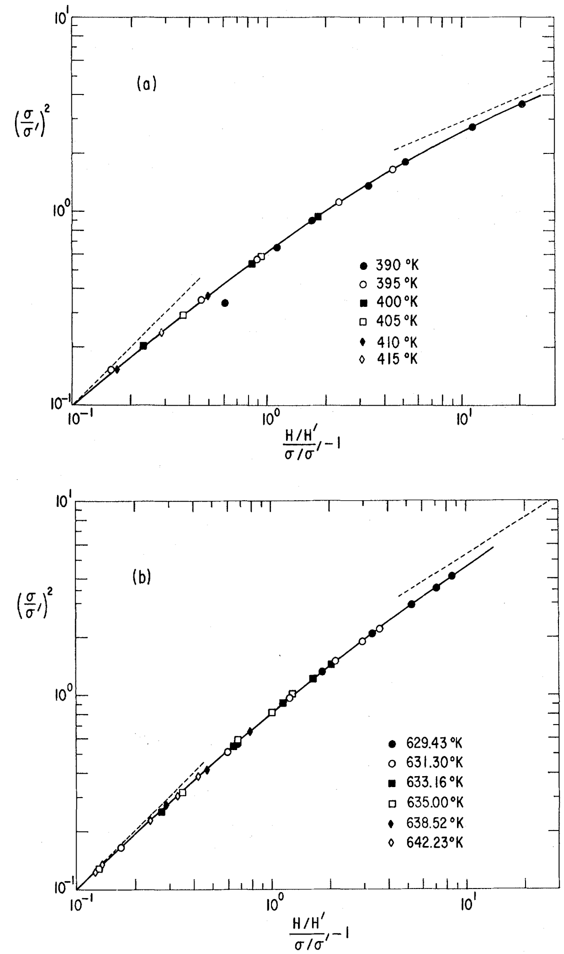

FIG. 3. Log-log plot of normalized isotherms for (a) CrO_2 and (b) nickel. Dashed curves derived as in Fig. 2.

is given in Fig. 3(b); once again there is an excellent fit to a universal curve.

Thus, we have demonstrated that both CrO_2 and nickel obey a general relationship of the form,

$$(H/H')/(\sigma/\sigma') = K(\sigma/\sigma'), \tag{7}$$

where in both cases the function $K(\sigma/\sigma')$ reduces for small σ/σ' to the right-hand side of Eq. (6), as indicated by dashed curves in Figs. 2 and 3. In this relationship, <u>all</u> the variation with temperature is captured in the normalization parameters, σ' and H', for which the above discussion gives

$$\sigma' \propto (T-T_C)^{\lambda}, \quad \lambda = \tfrac{1}{2}(\gamma-\kappa), \tag{8}$$

and

$$H' \propto (T-T_C)^{\mu}, \quad \mu = \lambda + \gamma. \tag{9}$$

In Table I the values used for γ and κ are listed; outside the limits shown, the fit to a universal curve becomes distinctly poor. Also listed are the corresponding values (and limits) for λ and μ.

We will now show that λ and μ must also be related through the index δ if Eq. (7) is to merge properly with Eq. (2) as $T \to T_C$ (which for positive λ is equivalent to $\sigma/\sigma' \to \infty$). In this limit, Eq. (7) must conform to

$$(H/H')/(\sigma/\sigma') \propto (\sigma/\sigma')^{\delta-1}, \tag{10}$$

which, when written as $H \propto \{H'/(\sigma')^{\delta}\}\sigma^{\delta}$ and compared to Eq. (2), requires that $H'/(\sigma')^{\delta}$ be a constant. Consequently, from Eqs. (8) and (9),

$$\delta = \mu/\lambda = 1 + \gamma/\lambda. \tag{11}$$

The values for δ derived from this relationship are compared in Table I with the δ values de-

Table I. Summary of the magnetic critical-point indices for CrO_2 and nickel, as discussed in the text.

	CrO_2	Nickel
γ	1.63 ± 0.02	1.30 ± 0.05
κ	0.95 ± 0.04	0.48 ± 0.03
λ	0.34 ± 0.03	0.41 ± 0.04
μ	1.97 ± 0.05	1.71 ± 0.09
$\delta = \mu/\lambda$	5.79 ± 0.65	4.17 ± 0.62
δ (direct)	5.75 ± 0.05	4.22 ± 0.03
α	-0.31 ± 0.08	-0.12 ± 0.13

termined directly[4,10] from the magnetization data. They are in very good agreement, which bears out the validity of Eqs. (10 and (11) for these two materials. That Eq. (7) takes the form of Eq. (10) in the limit of large σ/σ' is also shown experimentally in Figs. 2 and 3, where this limiting case is represented by dashed curves computed from the measured critical isotherms.

Equation (11) is a sum rule that leaves only two of these critical-point indices (e.g., λ and μ) undetermined and has the same form as an analogous relationship previously deduced by Widom from equations of state for a fluid near its critical point.[1,14] This similarity is not surprising since, as was recently pointed out to us,[15] our Eq. (7) is exactly equivalent to one of the Widom equations of state, in which the free energy contains a homogeneous function of its variables.[16] The same homogeneity condition, leading to a sum rule (or scaling law) analogous to Eq. (11), has subsequently been derived by Kadanoff[17] from a cellular analysis of an Ising ferromagnet near T_c. Hence, our discovery that CrO_2 and nickel obey Eq. (7) and its corollary, Eq. (11), gives experimental support to these different theoretical approaches to the problem of continuous phase transitions.

Another condition placed by Eq. (7) on the critical-point indices stems from its prediction that for fixed σ/σ', $\partial^n(\sigma/\sigma')/\partial(H/H')^n$ for any n is a constant, from which it immediately follows that for $T>T_c$ and $\sigma=0$,

$$\partial^n\sigma/\partial H^n \propto \sigma'/(H')^n, \quad \propto (T-T_c)^{\lambda-n\mu}. \tag{12}$$

This constitutes a recurrence relationship, with μ as the "gap parameter," of the type proposed by Essam and Fisher[18] from general model considerations and later borne out by the Ising-model calculations of Domb and Hunter.[19] It is interesting to speculate that Eq. (12) may be valid even for $n=-1$, when $\partial^n\sigma/\partial H^n$ would correspond to the free energy, F. Since the singular part of the temperature dependence of F just above T_c is generally expressed as $(T-T_c)^{2-\alpha}$, which makes the specific heat vary as $(T-T_c)^{-\alpha}$, it would then follow that

$$2-\alpha=\lambda+\mu \quad =2\lambda+\gamma. \tag{13}$$

This equation is exactly analogous to a similar identity for $T<T_c$ which has previously been deduced on various theoretical grounds[1,17,18] and which corresponds to the Rushbrooke inequality[20] holding as an equality. When applied to our index values for CrO_2 and nickel, Eq. (13) gives the values of α listed in Table I. For nickel the possibility is allowed (though barely) that $\alpha=0$ and, therefore, that the specific heat may have a logarithmic singularity at T_c. In the case of CrO_2, however, α is distinctly negative, and if this result is valid the specific heat should go to a finite limit at T_c (but with a vertical tangent, since $|\alpha|<1$). To test these predictions, direct specific-heat measurements on these two materials are presently underway.

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