

magnitude, but these are expected to be at least somewhat quenched by the environment.

<sup>11</sup>An antiparallel moment on the 12 Be sites implies a corresponding increase in the moment attributed to the

Cr. Cr dipolar fields could then become quantitatively important (but only to the extent that there exists a moment on the Be). This does not affect our qualitative conclusions.

## RANDOM IMPURITIES AS THE CAUSE OF SMOOTH SPECIFIC HEATS NEAR THE CRITICAL TEMPERATURE

Barry M. McCoy

Institute for Theoretical Physics, State University of New York, Stony Brook, New York 11790

and

Tai Tsun Wu\*

Gordon McKay Laboratory, Harvard University, Cambridge, Massachusetts 02138

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We present a modification of the two-dimensional Ising model which incorporates random impurities. The specific heat of this model is infinitely differentiable even at the critical temperature where it possesses an essential singularity. We find this specific heat to be in perfect quantitative agreement with the smooth peak recently observed by van der Hoeven, Teaney, and Moruzzi for  $T \gtrsim T_c$  in the specific heat of EuS.

Recently very precise measurements of specific heats near the Curie or Néel temperature  $T_c$  have been carried out by several investigators: van der Hoeven, Teaney, and Moruzzi on EuS,<sup>1,2</sup> Handler, Mapother, and Rayl on Ni,<sup>3</sup> Teaney, Moruzzi, and Argyl on RbMnF<sub>3</sub>,<sup>4</sup> Keen, Landau, and Wolf on dysprosium aluminum garnet,<sup>5</sup> and Robinson and Friedberg on MnBr<sub>2</sub>.<sup>6</sup> These experiments share the striking property that the measured specific heats are smooth functions of the temperature even at  $T_c$ . In this paper we explore the possibility of attributing these smooth specific heats to the presence in the sample of random impurities.

These recent experimental results are somewhat puzzling if they are contrasted with the usual theoretical treatments<sup>7</sup> and models of (anti)ferromagnetic phase transitions. These theories predict that at  $T_c$  the specific heat will have some sort of observable singularity that is expressible in the form

$$\text{const} \ln|T - T_c| \text{ or } \text{const} |T - T_c|^\alpha, \quad (1)$$

where  $\alpha$  and the constants may be different for  $T$  above or below  $T_c$ . However, these treatments are all overidealizations of the true physical situation because they deal with completely pure materials. To study the effect of random impurities on the form (1) in a concrete fashion we have constructed a modification of the two-dimensional Ising model which includes random impurities.

We find that the specific heat at  $T_c$  is an infinitely differentiable function for which the form (1) does not provide an adequate description.

The model we consider is the two-dimensional rectangular Ising model in which all horizontal interaction energies  $E_1$  are fixed and all vertical interaction energies  $E_2(j)$  between the  $j$  and  $j+1$  row are the same. However,  $E_2(j)$ ,  $j = 0, 1, 2, \dots$ , are considered to be independent random variables. The calculation of the specific heat which is based on recent work of Furstenberg<sup>8</sup> is rather lengthy and is reported elsewhere.<sup>9</sup> The final result for a particular narrow distribution of bonds  $E_2$  of width  $w$  is that, to leading order in  $w$ , near  $T_c$  the specific heat is given approximately by

$$c_1[R(\delta) + c_2 - \ln w^2], \quad (2)$$

where

$$R(\delta) = \int_0^\infty d\varphi \left[ \frac{\partial^2}{\partial \delta^2} \ln K_\delta(\varphi) - (\varphi + 1)^{-1} \right], \quad (3)$$

$$\delta = -(1 - T/T_c)w^{-2}, \quad (4)$$

$c_1$  and  $c_2$  are known constants, and  $K_\delta(\varphi)$  is the modified Bessel function of the third kind of order  $\delta$ . It can be shown that the integral  $R(\delta)$  of (3) has an essential singularity at  $\delta = 0$ . It has been computed numerically and is plotted in Fig. 1.

When  $\delta$  becomes large, the specific heat (2) re-

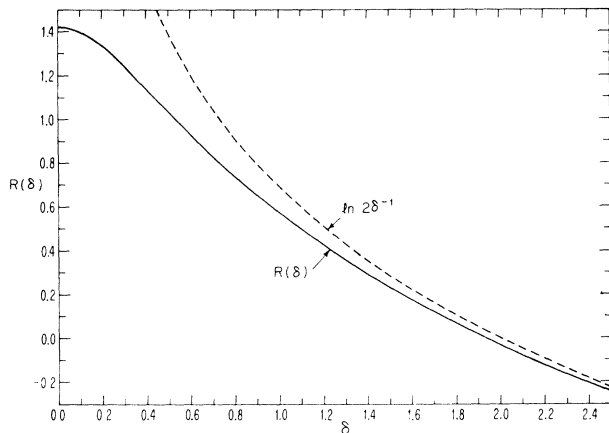


FIG. 1. The function  $R(\delta)$  and its asymptotic behavior  $\ln 2\delta^{-1}$ .

duces to

$$c_1[-\ln(T/T_c - 1) + \ln 2 + c_2]. \quad (5)$$

This specific heat appears to have a logarithmic singularity at  $T_c$ . Such a result is to be expected since when  $\delta$  is large, the effect of the impurities is small and, to leading order in  $w$ , the specific heat should have the logarithmic divergence of Onsager's result.<sup>10</sup>

We may gain further insight into the specific heat (2) if we compare it with the specific heat of EuS. Van der Hoeven, Teaney, and Morruzzi<sup>1</sup> have shown that when  $T$  is sufficiently larger than  $T_c$ , the specific heat is very well described by (5) with  $c_1 = 4.13$  J/mole deg and  $c_2 = -1.30$ . If in addition we choose  $w = 2.68 \times 10^{-2}$ , we see in Fig. 2 that the specific heat (2) is in beautiful quantitative agreement with van der Hoeven's measurements.<sup>11</sup> On the basis of this beautiful agreement, we propose that random impurities are responsible for the observed "roundings" of specific heats in Refs. 1-6.

Since EuS is microscopically very different from a two-dimensional Ising model,<sup>12</sup> the effect of random impurities must be rather insensitive to the details of the interactions. The agreement of Fig. 2 indicates that the important point is the "logarithmic singularity" in the specific heat for both cases, Onsager's solution<sup>10</sup> on the one hand and the experimental measurement for  $T/T_c - 1 > 10^{-3}$  on the other. We also believe that when  $T \lesssim T_c$ , random impurities influence the detailed shape of the specific heat. However, detailed comparison is more difficult.

In order to exclude the possibility that other effects, such as long-range forces,<sup>13</sup> are responsi-

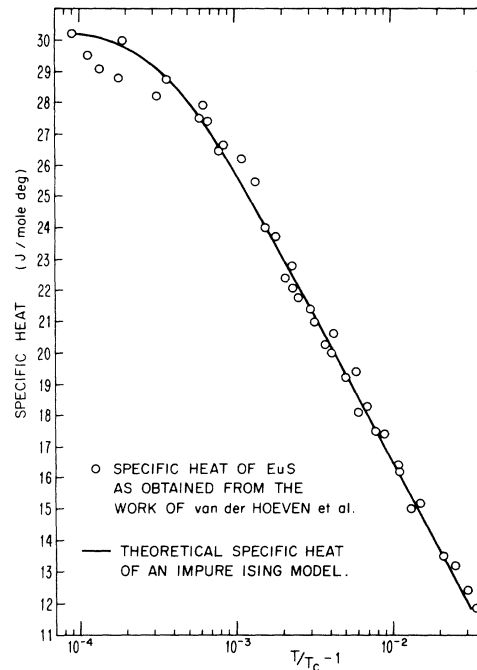


FIG. 2. Comparison of the impure-Ising-model specific heat with the observed specific heat of EuS for  $T > T_c$ .

ble for the observed roundings of specific heats, we propose that specific-heat measurements similar to those of Refs. 1-6 be carried out for several samples of the same material with different concentrations of impurities.

There are several different types of random impurities which broaden specific-heat singularities. We mention three:

(A) Chemical impurities in the usual sense.

Certainly in the rare-earth compounds such as EuS and dysprosium aluminum garnet we expect trace impurities of other rare earths to be present because it is very difficult to purify rare earths.

(B) Vacancies and dislocations in the lattice.

Therefore the stoichiometry of compounds should be rigidly controlled and single crystals should be used if one wants to reduce the amount of observed specific-heat broadening.

(C) Different isotopes of the same element.<sup>14</sup>

For example, the natural abundances of nickel are 68% of Ni<sup>58</sup>, 26% of Ni<sup>60</sup>, 1% of Ni<sup>61</sup>, 4% of Ni<sup>62</sup>, and 1% of Ni<sup>64</sup>.

Besides the qualitative explanation of smooth specific heats which our model provides, the specific heat (2) has several more general quantitative features which may be compared with experiment. From (4) we see that an effect of impuri-

ties is to determine a temperature region in which the specific heats deviate appreciably from that of a pure Ising model. At least when  $w$  is small the only effect of changing  $w$  is to change the scale of this temperature region; once this change of temperature scale is made the shape of the specific-heat curve does not further depend on the impurities. It is very reasonable to suppose that this is also the case in the actual experimental situation. In other words, the specific heat is a function of the single variable  $(T/T_c - 1)\tau(w)$ . One simple form of  $\tau(w)$  is

$$\tau(w) = \text{const} w^{A'}, \quad (6)$$

where  $A'$  is defined to be the broadening index of the transition for  $T_c < T$  ( $A$  may be analogously defined for  $T < T_c$ ). If  $A$  and  $A'$  are both defined, the requirement that the specific heat be continuous at  $T_c$  shows that  $\alpha A = \alpha' A'$ . The broadening index is a quantitative measure of the influence of random impurities on specific heats. If our model is completely relevant to EuS, then  $A' = 2$ . These and other broadening indices which may be defined for the spontaneous magnetization, zero-field susceptibility, etc. are the subject for future study.

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<sup>5</sup>B. Keen, D. Landau, and W. Wolf, J. Appl. Phys. 38, 967 (1967).

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<sup>9</sup>B. McCoy and T. T. Wu, Phys. Rev. (to be published).

<sup>10</sup>L. Onsager, Phys. Rev. 65, 117 (1944).

<sup>11</sup>Numerically, for all real  $\delta$ ,  $R(\delta)$  is well approximated by  $2 \ln 2 - \frac{1}{2} \ln(1 + 4\delta^2)$ . This is precisely the form used arbitrarily by Teaney, van der Hoeven, and Moruzzi (Ref. 2) to fit their data. However, we wish to emphasize that, contrary to the suggestion of Teaney, van der Hoeven, and Moruzzi, this is merely a numerical approximation and the critical temperature occurs at a real value of  $T$  corresponding to  $\delta = 0$ .

<sup>12</sup>EuS is generally believed to be described by a cubic Heisenberg Hamiltonian. See Ref. 1.

<sup>13</sup>A. Arrott, Phys. Rev. Letters 20, 1029 (1968).

<sup>14</sup>For example, different isotopes have different sizes. This finite size effect slightly modifies the electronic structure of the atom and hence must slightly change the magnetic interactions. This and other higher order effects will influence the effective (e.g., Heisenberg or Ising) Hamiltonian that describes the magnetic interaction. This isotope effect should not be confused with the situation considered by D. C. Mattis and W. P. Wolf, Phys. Rev. Letters 16, 899 (1966), who show that the direct  $I_2\sigma_z$  interaction between random nuclear spins and Ising-model spins does not alter the analytic nature of the critical point.