

classic results for He vapor on the He liquid. If this should not be the case, the hydrodynamics will be somewhat more complicated.] In some very thin film geometries the $H\uparrow$ third sound speed may be nearly as large as the compressional speed. In this limit, one must take proper account of the compressibility of the $H\uparrow$ film. This is straightforward¹⁶ and leads to a more complicated version of Eq. (15) whose basic physics is unchanged.

We have benefited from extensive conversations with Professor J. S. Brooks, Dr. F. M. Ellis, and Professor R. B. Hallock. This work is partially supported by the U. S. Army Research Office under Grant No. DAAG29-80-C-0146

¹W. C. Stwalley and L. H. Nosanow, *Phys. Rev. Lett.* **36**, 910 (1976).

²I. F. Silvera and J. T. M. Walraven, *Phys. Rev. Lett.* **44**, 164 (1980).

³J. T. M. Walraven and I. F. Silvera, *Phys. Rev. Lett.* **44**, 168 (1980).

⁴R. W. Cline, T. J. Greytak, D. Kleppner, and D. A. Smith, *J. Phys. (Paris), Colloq.* **41**, C7-141 (1980).

⁵M. Morrow, F. Jochemsen, A. J. Berlinsky, and W. N. Hardy, *Phys. Rev. Lett.* **46**, 195 (1981).

⁶D. O. Edwards and I. B. Mantz, *J. Phys. (Paris), Colloq.* **41**, C7-257 (1980).

⁷D. R. Nelson and J. M. Kosterlitz, *Phys. Rev. Lett.* **39**, 1727 (1977).

⁸K. R. Atkins, *Phys. Rev.* **113**, 962 (1959).

⁹F. M. Ellis, R. B. Hallock, M. D. Miller, and R. A. Guyer, *Phys. Rev. Lett.* **46**, 1491 (1981).

¹⁰The zero-concentration chemical potential for a H atom in ⁴He has been calculated to be ~40 K, M. D. Miller, *Phys. Rev. B* **18**, 4730 (1978).

¹¹J. E. Berthold, D. J. Bishop, and J. D. Reppy, *Phys. Rev. Lett.* **39**, 348 (1977).

¹²J. E. Rutledge, W. L. McMillan, J. M. Mochel, and T. E. Washburn, *Phys. Rev. B* **18**, 2155 (1978).

¹³For a discussion of the effects of compressibility on third sound, see R. D. Puff and J. G. Dash, *Phys. Rev. B* **21**, 2815 (1980). (See also the discussion in the last paragraph of this paper.)

¹⁴See, e.g., J. Wilks, *Liquid Helium* (Oxford Univ. Press, New York, 1967).

¹⁵D. V. Osborne, *Proc. Phys. Soc., London* **80**, 103, 1343 (1962).

¹⁶R. A. Guyer and M. D. Miller, unpublished.

Calorimetric Investigation of Spin-Glass Ordering in CuMn

William E. Fogle, James D. Boyer, Norman E. Phillips, and John Van Curen

Department of Chemistry, University of California, Berkeley, California 94720, and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

(Received 7 April 1981)

New measurements near T_{sg} characterize the heat-capacity anomaly associated with spin-glass ordering. There are no discontinuities in the heat capacity or its temperature or field derivatives but there is a relatively sharp anomaly in the field derivative and a broad anomaly in the temperature derivative. A failure of thermodynamics to predict correctly the relation between heat capacity and magnetic susceptibility may be a manifestation of the "nonergodic" behavior of disordered systems.

PACS numbers: 65.40.-f, 65.50.+m, 75.30.Hx

The nature of the transition to the ordered state in metallic spin-glasses continues to be an interesting and challenging aspect of the more general problem of disordered systems. The discovery¹ of a sharp cusp in the low-field ac susceptibility, χ_{ac} , at a characteristic temperature, T_{sg} , led to a renewal of both experimental and theoretical investigations of spin-glasses, and, together with Mössbauer² and magnetic remanence³ data, prompted consideration of the possibility of a thermodynamic phase transition at T_{sg} . Edwards and Anderson (EA) proposed a model in which the

long-range Ruderman-Kittel-Kasuya-Yosida interaction between randomly distributed spins was replaced by a Gaussian distribution of bond strengths coupling spins on a regular lattice.⁴ Mean-field solutions of this model and extensions of it do produce a cusp in χ but they also predict a cusp in the magnetic specific heat, C . Although a broad anomaly that extends from the lowest temperatures at which C has been measured to well above T_{sg} is well known, no feature of the type predicted had been reported. More recent theoretical work has addressed both the essential

randomness of spin-glass systems⁵ and the role of critical fluctuations⁶ but has not yet yielded detailed predictions of physical properties.

The EA theory stimulated a search for a *sharp* anomaly in C at T_{sg} . Wenger and Keesom⁷ and Zweers *et al.*⁸ measured both χ_{ac} and C (on $CuMn$ and $PdMn$, respectively) but reported no evidence for any discontinuous behavior at T_{sg} . Martin^{9,10} has reported measurements on a series of $CuMn$ samples and on a 1.0-at.% $AuFe$ sample. The maximum scatter of the data depends on the temperature, but near T_{sg} is typically $\pm 0.5\%$ to $\pm 1.0\%$ in C . For a 0.083-at.% $CuMn$ sample and for the $AuFe$ sample, he noted a "knee" in a plot of C/T vs T near the expected value of T_{sg} . For more concentrated $CuMn$ samples the feature is less pronounced but a "similar correlation" was observed.

In this Letter we report the results of an investigation of the specific heat of a $CuMn$ spin-glass in the vicinity of T_{sg} that shed new light on the nature of spin-glass ordering. Near and above T_{sg} essentially all of the data points for C fall within $\pm 0.02\%$ of smooth curves. This corresponds to a precision of $\pm 0.01\%$ in total heat capacity—considerably better than that achieved in earlier work, but essential for observation of the effects that we report. The measurements were made on a 39.8-g, 0.279 ± 0.002 -at.%, polycrystalline sample of irregular shape. χ_{ac} was

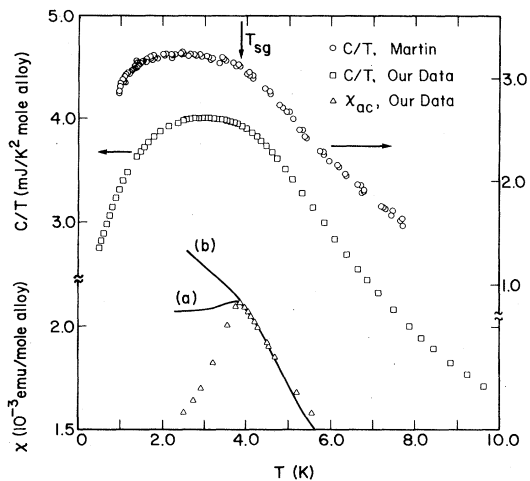


FIG. 1. χ_{ac} (lower part of figure) and C/T (upper part of figure) vs T . Values of both C and T for Martin's data have been scaled by a factor of 2.59 to place the "knee" at T_{sg} for our sample. Note the shift in scales for the two sets of C/T data. Curve *a* represents typical χ_{fc} data and curve *b* is derived from C/T vs T data (see text for explanation).

measured at 5 Hz with an rms field amplitude of 2 Oe after an initial anneal for 8 d at 800°C in an argon atmosphere, and again after a second anneal for 2 d at 1020°C in vacuum. The second set of χ_{ac} data, shown in Fig. 1, was indistinguishable from the first. With respect to sharpness the cusp is very similar to those found by Cannella¹¹ for annealed $CuMn$ samples with similar compositions. All heat-capacity data were taken after the second anneal.

Figure 1 also shows our heat-capacity data and Martin's data for a 0.083-at.% sample (scaled to facilitate comparison—see figure caption) as C/T vs T . The knee in Martin's data (see also Fig. 5 and the accompanying discussion in Ref. 8) appears as a change in slope at T_{sg} . Our data do not show a similar feature. Martin has suggested⁹ that the knee may become less pronounced at higher concentrations, in which case the difference between his data (for 0.083 at.%) and ours (for 0.279 at.%) could be simply a concentration effect, but we can find no evidence in our data for more dilute samples to support that suggestion.

To examine the smoothness of the temperature derivative of C more carefully, we have calculated $\Delta(C/T)/\Delta T$ by taking point-to-point differences between the raw heat-capacity data. $\Delta(C/T)/\Delta T$ varies smoothly and regularly from 0.3 to 25 K, the temperature range in which this sample was studied, *except* in a 4-K interval in the vicinity of T_{sg} . [For pure Cu , measurements with the same apparatus and to the same precision show a linear dependence of $\Delta(C/T)/\Delta T$ on T and therefore that the anomaly exhibited in Fig. 2 is not associated with temperature scale irregularities or other systematic errors.] As shown in Fig. 2 the approximate width of the region of anomalous behavior is clear, but neither the position nor the shape of the anomaly is precisely defined. The solid curve in Fig. 2 is an interpolation from data below 2 K to data above 7 K, and

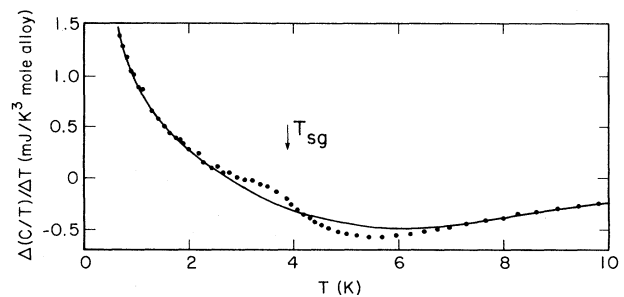


FIG. 2. Derivative of C/T with respect to T .

represents a *possible* smooth "background" curve. Figure 2 shows that the zero-field spin ordering in the vicinity of T_{sg} is energetically different from that over the broader range of temperature. However, the anomaly is spread out over a temperature interval of the order of T_{sg} itself, in contrast with the predictions of EA-type theories and with qualitative, but unfounded, conjecture based on the sharpness of the susceptibility cusp.

Thermodynamics requires only that an anomaly in χ be reflected in the *field dependence* of C . The thermodynamic relation can be expressed in the form

$$(\partial^2 M / \partial T^2)_H = T^{-1} (\partial C / \partial H)_T, \quad (1)$$

where M is the magnetization, $M = \chi H$. This relation, which prompted the in-field measurements, shows that the strong curvature of χ as a function of temperature that occurs near T_{sg} should be reflected in a strong field dependence of C . Measurements of C in each of six magnetic fields from 0 to 1000 Oe were made at nineteen temperatures between 2.5 and 6.5 K. (The thermometer was shielded from the applied field and in separate tests there was no observable effect on its calibration in fields to 75 kOe at the sample.) The field was always changed at $T \approx 10$ K and held constant until a complete set of data in that field was taken. Repeat runs in several fields, in some cases following runs in other fields, showed no evidence of irreproducibility. Two typical sets of C/T vs H data, one for $T \approx T_{sg}$ and one at $T \approx T_{sg} + 1.6$ K, are shown in the inset of Fig. 3. Since M must be an odd function of H , Eq. (1) re-

quires C to be an even function of H . Only the first two terms of a series expansion,

$$C/T = A + BH^2, \quad (2)$$

were useful in fitting the data. These fits are represented by the solid curves in the inset of Fig. 3, and the coefficient $B(T)$ is shown in the main part of Fig. 3. The minimum value of B occurs at a temperature that is equal to T_{sg} to within experimental error.

A fairly complete picture of the magnetic behavior of spin-glasses below T_{sg} can be obtained as a composite of results on different materials and from different laboratories. Briefly, low-frequency measurements at field amplitudes of a few oersteds give χ_{ac} as shown in Fig. 1, but dc field-cooled (fc) measurements of M ,^{12,13} made by cooling from above T_{sg} in fixed fields of a few hundred oersteds or less, give values of χ_{fc} corresponding to curve *a* of Fig. 1. Static fields of a few hundred oersteds broaden the cusp in both χ_{ac} and χ_{fc} conspicuously but do not affect values of χ at temperatures a degree or so above or below T_{sg} (for $T_{sg} \approx 4$ K).¹ When M is measured by changing the applied field at temperatures below T_{sg} , time effects can be observed and the apparent values of χ are intermediate between χ_{ac} and χ_{fc} depending on the time and sample.^{13,14} No time dependence of M has been reported in fc measurements, and there is *no* evidence that χ can exceed χ_{fc} . This picture suggests that the fc data, which are obtained in the *same* way as the C data, are the ones that should be expected to correspond to thermodynamic equilibrium and that should be used in Eq. (1).

As illustrated in the inset in Fig. 3, the field dependence of C , below 1000 Oe, is well represented by a parabolic relation. In this region of field Eq. (1) would then give a field-independent value of $\partial^2 \chi / \partial T^2$. This is clearly at variance with direct measurements of χ which give, in the same range of field and in the immediate vicinity of T_{sg} , a strong dependence of $\partial^2 \chi / \partial T^2$ on field. Furthermore, the values of $\partial^2 \chi / \partial T^2$ deduced from the calorimetric data by Eq. (1) are quantitatively inconsistent with direct measurements of χ_{fc} for all fields in this range. This is demonstrated by curve *b* of Fig. 1, which represents the result of a double integration of the right-hand side of Eq. (1) with the constants of integration evaluated from the experimental values of χ_{ac} and $d\chi_{ac}/dT$ for this sample at 4.25 K. Below T_{sg} curves *a* and *b* are conspicuously different. Since curve *a* represents typical χ_{fc} data these curves might

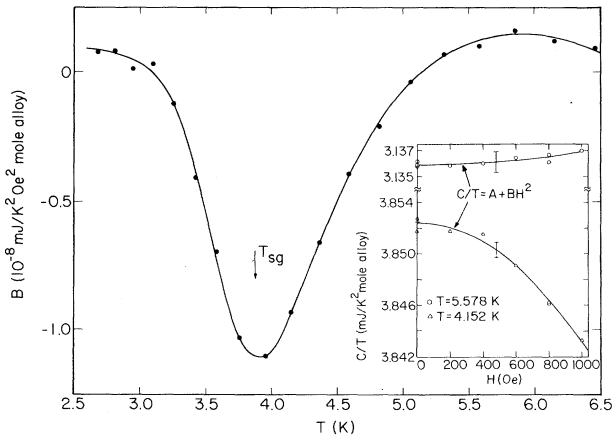


FIG. 3. Temperature dependence of B in $C/T = A + BH^2$. The inset shows typical C/T vs H data. The error bars represent $\pm 0.01\%$ of the total heat capacity. The curves represent best fits of the form $C/T = A + BH^2$.

have been expected to be the same, and the discrepancy reflects a failure of Eq. (1). The source of the disagreement is that the field dependence of C is not large enough in comparison with the observed change in slope of χ_{fc} vs T in the vicinity of T_{sg} —the integral over temperature of $\partial(C/T)/\partial H$ is only one-half of that required by Eq. (1). Since that integral is essentially the difference between two measured energies, and is measured with an accuracy of a few percent, the discrepancy is well outside experimental error.

Even if the field-cooled samples are in (time-independent) metastable states, one would expect Eq. (1) to apply if these states correspond to a single region of phase space within which all microscopic states of the same energy are accessible. Recent suggestions¹⁵ that certain disordered systems including spin-glasses are inherently “nonergodic” in nature offer a possible explanation of the failure of the thermodynamic relation Eq. (1). According to this suggestion the configuration space of a spin-glass contains many potential valleys separated by barriers, with distributions of minimum energies of the valleys and of barrier heights. When a spin-glass is cooled sufficiently far below T_{sg} it is frozen into a particular potential valley and does not sample microscopic states that are energetically allowed but rendered inaccessible by the intervening barriers. (The degeneracies of these valleys are evidently not as high as they are in the somewhat analogous case of a glass because there is no easily measurable¹⁶ residual entropy at $T = 0$, but computer simulations suggest that their numbers are substantial.¹⁷) It is reasonable to assume further that cooling in different fixed fields leaves a sample trapped in different regions of configuration space. If the number of potential valleys is sufficiently high, the properties of the microscopic states associated with them could still vary essentially continuously as a function of the external field that selects them, but not in the way determined by the local properties of the phase space at the bottoms of the valleys. Under these conditions thermodynamic equalities such as Eq. (1) could break down even though both M and C are measured under identical conditions and are “equilibrium” values in the sense of being independent of time. The failure

of thermodynamic relations would then arise as a fundamental consequence of the disorder of the system.

We thank D. Bazell for his assistance with susceptibility measurements, D. L. Martin for sending us his numerical data, and K. Matho for interesting discussions. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under Contract No. W-7405-ENG-48.

¹V. Cannella and J. A. Mydosh, Phys. Rev. B **6**, 4220 (1972); V. Cannella, in *Amorphous Magnetism*, edited by H. O. Hooper and A. M. de Graaf (Plenum, New York, 1973), p. 195.

²R. J. Borg, Rex Booth, and C. E. Violet, Phys. Rev. Lett. **11**, 464 (1963); C. E. Violet and R. J. Borg, Phys. Rev. **149**, 540 (1966).

³J. S. Kouvel, J. Phys. Chem. Solids **21**, 57 (1961); R. W. Schmitt and I. S. Jacobs, J. Phys. Chem. Solids **3**, 324 (1957).

⁴S. F. Edwards and P. W. Anderson, J. Phys. F **5**, 965 (1975).

⁵G. Toulouse, Commun. Phys. **2**, 115 (1977); J. Vanimemus and G. Toulouse, J. Phys. C **10**, L537 (1977); J. A. Hertz, J. Appl. Phys. **50**, 7315 (1979).

⁶A. B. Harris, T. C. Lubensky, and J.-H. Chen, Phys. Rev. Lett. **36**, 415 (1976); J. Chalupa, Solid State Commun. **24**, 429 (1977).

⁷L. E. Wenger and P. H. Keesom, Phys. Rev. B **13**, 4053 (1976).

⁸H. A. Zweers, W. Pelt, G. J. Nieuwenhuys, and J. A. Mydosh, Physica (Utrecht) **86-88B**, 837 (1977).

⁹D. L. Martin, Phys. Rev. B **20**, 368 (1979).

¹⁰D. L. Martin, Phys. Rev. B **21**, 1902, 1906 (1980).

¹¹We thank Dr. Cannella for providing us with his susceptibility data on $CuMn$.

¹²J. L. Tholence and R. Tournier, J. Phys. (Paris), Colloq. **35**, C4-229 (1974); S. Nagata, P. H. Keesom, and H. R. Harrison, Phys. Rev. B **19**, 1633 (1979).

¹³R. V. Chamberlin, M. Hardiman, and R. Orbach, to be published.

¹⁴C. N. Guy, J. Phys. F **5**, L242 (1975).

¹⁵P. W. Anderson, in *III-Condensed Matter*, edited by R. Balian, R. Maynard, and G. Toulouse (North-Holland, New York, 1979), p. 162; A. Blandin, J. Phys. (Paris), Colloq. **39**, C6-1499 (1978).

¹⁶W. E. Fogle, J. C. Ho, and N. E. Phillips, to be published.

¹⁷L. R. Walker and R. E. Walstedt, Phys. Rev. B **22**, 3816 (1980).