RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 35, NUMBER 4 1 FEBRUARY 1987

Random-field effects on Ising Jahn-Teller phase transitions

J. T. Graham, M. Maliepaard,* J. H. Page,† S. R. P. Smith,‡ and D. R. Taylor
Department of Physics, Queen's University, Kingston, Canada K7L 3N6
(Received 26 September 1986)

Metastable ordering due to random fields in the mixed Ising Jahn-Teller system $Dy(As_xV_{1-x})O_4$ has been investigated. The response of the sample capacitance to applied ordering fields shows the existence of a threshold field for initial domain response and an equilibrium field for reversible response. Ultrasonic measurements of the susceptibility critical-exponent indicate random-field Ising behavior.

In their pioneering study of the effects of random fields on phase transitions, Imry and Ma[1] suggested that experimental realizations might be found in situations where lattice distortions are induced by electronic instabilities, and where crystal defects couple linearly to the order parameter. Systems which undergo Jahn-Teller phase transitions would appear to be promising candidates, therefore, and observations of some effects of random fields on transitions in several Jahn-Teller rare-earth compounds have been reported.[2,3] To date, however, for the most interesting properties of random-field Ising systems—the new critical behavior and the slow equilibration near and below the transition temperature—the available experimental information has come almost exclusively from diluted antiferromagnets in a uniform field, following a later suggestion by Fishman and Aharony.[4] While these experiments have led to substantial progress in understanding random-field effects,[5] it would be desirable for several reasons to have results from other systems, for example, to avoid possible problems associated with dilution of the magnetic species.[6] There is some evidence that magnetic dilution introduces strong pinning forces, in addition to the random fields, which, on the one hand, complicate the kinetics of domain-wall motion[7] and, on the other hand, may substantially impede equilibration and thus prevent observation of the equilibrium critical behavior. Furthermore, it would be of interest to study systems which exhibit a crossover in critical behavior to random-field exponents from pure Ising exponents, rather than from random-exchange exponents.[8]

The mixed Jahn-Teller system discussed here, $Dy(As_xV_{1-x})O_4$, has the advantages that the active ions (Dy) are not diluted, and that the transition is ferrodistortive, i.e., the structural counterpart of ferromagnetic ordering. The pure compounds $DyVO_4$ and $DyAsO_4$ undergo tetragonal-to-orthorhombic transitions at 14.6 and 11.4 K, respectively, driven by the coupling of the nearly degenerate Dy electronic levels to lattice distortions.[9,10] For this case the effective ion-ion interaction can be described by a pseudospin Ising Hamiltonian to an excellent approximation.[9] The two pseudospin orientations correspond to the two orientations of the orthorhombic unit-cell axes. The order parameter is proportional to the B_{1g} strain below the transition temperature T_D. Random static fields originate as a result of crystal defects, which generate electric fields, one component of which has the right symmetry to couple to the order parameter. In mixed $Dy(As_xV_{1-x})O_4$ the As-V mismatch generates random fields with a distribution which can be taken as Gaussian, and with a width Δ which depends on x.

The critical properties of these and related Jahn-Teller systems (in the absence of random fields) are known to be classical as a result of the coupling of the ions to uniform strains.[11,12] For the Dy systems of interest here, this coupling has been found to be small compared with the short-range interactions, so that the temperature regime for classical exponents is inaccessible experimentally, and Ising exponents are observed over the usual power-law regime.[13] In the presence of random fields, the critical behavior is expected to remain classical,[14] but in an even smaller range of reduced temperature, and it is expected to cross over first to a regime of random-field Ising exponents, and perhaps ultimately to a regime of pure Ising exponents.

Good-quality single crystals of $Dy(As_xV_{1-x})O_4$ spanning the entire composition range were prepared by flux growth.[15] Compositions were analyzed by proton-induced x-ray emission (PIXE) and by x-ray diffraction. The As-V concentration ratios were found to be much higher in the crystals than in the starting materials, but were uniform ($\Delta x/x < 10^{-3}$ in 2.5 mm according to PIXE measurements) in the samples examined. For intermediate compositions the random fields were large enough to suppress the transition entirely, but well-defined transitions were observed at temperatures T_D/T_D (pure) $=0.94$, 0.91, 0.78, and 0.56 for crystals with $x=0.9985$, 0.9954, 0.9843, and 0.148, respectively. These transitions were, however, less sharp than those of the pure compounds in all cases. The discontinuity present at T_D in pure $DyAsO_4$ [but not in $DyVO_4$ (Ref. 11)] disappears smoothly but rapidly for $x < 1$.

Capacitance measurements, similar to those described for the pure compounds,[10] were carried out to study equilibration in several samples. Measurements parallel to the crystal a axis give the electric susceptibility χ_a, which is sensitive to changes in both sample dimension and permittivity, and from which the order parameter σ can be determined if the sample is a single domain.[10,16] Measurements parallel to the c axis give χ_c, which depends on σ^2 and which, therefore, should be insensitive to domains.[10] As will be discussed, this was found not to be the case, and both χ_a and χ_c data gave qualitatively similar information

on equilibration behavior. Since the random fields are fixed in this system, we studied equilibration by applying ordering fields and observing the sample response. The conjugate field for this ordering is a B_{1g} stress, but in practice a magnetic field parallel to the crystal a axis was used to induce ordering.[17] It can be shown that the effective ordering field H in this case is not the applied field H_{app} but $H_{app}^2/4k_BT$.

In all samples examined, capacitance measurements showed anomalous time- and history-dependent effects below the transition temperature T_D which are attributed to domain motion. Typical time-domain responses (Fig. 1) show several features of interest: There is a threshold field, labeled H_t, below which the system has negligible response on the time scale of the experiment ($\approx 10^2$ s); when a larger field is applied the susceptibility changes significantly and continues to increase slowly until further changes are masked by apparatus instability; after removal of the field the recovery towards the initial susceptibility is slower, and only partial in accessible times. The later portions of the response and recovery data can be well fitted to a logarithmic function of time. To within the resolution and sensitivity of these experiments, the response to and recovery from ordering fields is reversible and instantaneous at all temperatures above T_D. Below T_D the threshold field H_t becomes nonzero and at low temperatures increases rapidly. Likewise, the recovery falls below 100% at temperatures less than T_D, as shown in Fig. 2.

The random fields also have important effects on the "static" response χ_c, as Fig. 2 also indicates. If the sample is cooled through T_D in a small ordering field $H/k_BT_D \approx 0.02$, χ_c is dramatically reduced relative to the $H=0$ response. Such a field is too small to change σ significantly, or to flip an Ising domain at temperatures appreciably below T_D. This effect can be plausibly interpreted only by the assumption of domain-wall motion together with an interaction range comparable to domain size. In the corresponding pure compounds, previous work has shown that Jahn-Teller ordering invariably occurs in a multidomain phase, and that conversion to a single domain shows hysteresis.[18] However, small ordering fields have no such effect on χ_c,[10] showing that domains in the pure crystals differ in important ways: They are presumably larger and are pinned by static defects such as flux inclusions and dislocations. Clearly the mechanism for domain response in the mixed crystals must involve much smaller energy barriers, such as those encountered in the motion of domain walls through local random fields.

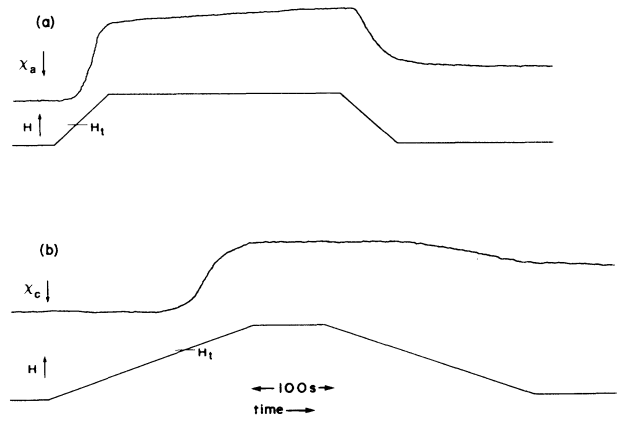

FIG. 1. Response of the electric susceptibilities χ_a and χ_c of $Dy(As_xV_{1-x})O_4$ to magnetic (ordering) fields. H_t indicates the threshold field for significant response. (a) $T=4.3$ K, $x=0.984$, $T_D=8.9$ K, maximum field $=0.10$ T. (b) $T=5.5$ K, $x=0.9985$, $T_D=10.7$ K, maximum field $=0.07$ T.

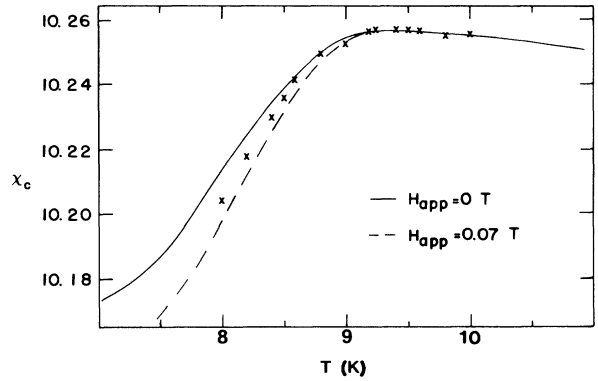

FIG. 2. Electric susceptibility χ_c vs temperature for $Dy(As_{0.984}V_{0.016})O_4$, cooled in zero field (solid line) and in a magnetic field of 0.07 T (dashed line) through the transition temperature $T_D \approx 8.9$ K. Each point x was obtained by cooling in zero field to that temperature, applying, and then removing, a 0.26-T magnetic field.

At any temperature, for large ordering fields, the response to an *incremental* ordering field was found to be fully reversible for fields above some field $H_{eq}(T)$. $H_{eq}(T)$ therefore defines a boundary between metastable and equilibrium phases, in close analogy with the spin-glass–ferromagnet transition line observed in some spin-glass systems.[19] H_{eq} was, in general, larger than H_t, and appeared to fall to zero at T_D much more abruptly than H_t. Quantitative results were, however, difficult to obtain because the differential response becomes very small for large ordering fields.

Increasingly realistic models for the motion of domain walls pinned by random fields have been developed[20,21] and used to interpret metastable properties in previous experiments.[22] Rather little work has been done in analyzing the effects of ordering fields and finite cooling rates, however, and hence only a qualitative explanation of the behavior described above can be given. When an Ising system is cooled in a random field, it is believed that the system does not reach its equilibrium state which has long-range order, but enters a metastable phase with domains of both orientations whose walls are pinned by the random fields. Relaxation to the equilibrium state is logarithmically slow,[23] so that the domain state persists for all accessible times. When the system is quenched to a temperature $T < T_D$, domains with a range of characteristic curvatures or dimensions (radii in the case of spherical domains) are initially present. The potential barriers for domain-wall motion are a function of radius, so that on a laboratory time scale domains of radii $R < R_{min}(T)$ thermalize and disappear, while domains with R

$> R_{min}(T)$ are essentially unaffected.[23] Assuming, as Andelman and Joanny suggest,[21] that $R_{min}(T)$ decreases from the value $R_{min}(T_D)$ for quenches to $T < T_D$, our observation of a nonzero H_t implies that in practice the sample is not cooled rapidly enough to prevent partial thermalization of the domains. As a result, the distribution of domain sizes present at T is depleted for $R_{min}(T) < R < R_{min}(T_D)$. Andelman and Joanny[21] also show that $R_{min}(T,H)$ increases with H, so that the application of an ordering field allows the thermalization of domains with $R < R_{min}(T,H)$. No appreciable effect will therefore be expected until H reaches that value H_t at which $R_{min}(T,H_t)$ becomes equal to the effective minimum radius present.

For larger fields, Andelman and Joanny[21] have found that all domains are thermalized for a critical field $\Delta^2\sigma/k_BT$. This defines a line of critical fields separating the metastable phase from the equilibrium state, analogous to the de Almeida–Thouless line between the ferromagnetic and spin-glass phases.[24] Our experimental values for $H_{eq}(T)$ are reasonably consistent with this expression, but confirmation is not yet possible owing to limited sensitivity and complications due to the pinning of domains by macroscopic crystal imperfections.

Previous experiments on dilute antiferromagnets[22] showed no recovery towards the domain state from a state of greater long-range order. This is consistent with the belief that the ordered phase has lower free energy, and that domains of opposite polarity, having disappeared, should not reappear. According to the data of Fig. 1 and similar data using much larger fields, this is not the case for our system where substantial recovery from an ordering field occurs at all but the lowest temperatures. There is some evidence from numerical simulations[7] that the domain state has lower free energy than the ordered state in a limited range of temperature below T_D, but results obtained in this way generally have to be viewed with caution. On the other hand, the observed recoveries seem physically reasonable considering the probable nature of real random-field distributions and real domains. The latter are likely to have complicated geometries, strongly pinned in some regions by structural defects which could nucleate domain expansion after removal of an ordering field. At sites where local fields exceed any exchange field, it is also very probable that the fields at neighboring sites are not random, but will be similar in size and direction. It may be necessary to take account of this fact in theoretical models of domain motion before any quantitative description of our results can be given.

Ultrasonic experiments have also been carried out in these systems to obtain information on the critical behavior, in particular on the susceptibility exponent γ. While the theoretical description of the effect of random fields on critical exponents continues to be actively debated,[25–31] experiments on dilute antiferromagnets[8] and numerical simulations[32] are for the most part consistent with random fields causing a reduction in dimensionality from three to two. Accurate measurements are required to distinguish between theories which predict a dimensionality reduction of $\rho = 1$,[33] of $\rho \neq 1$,[26,27] or alternatives which introduce an additional exponent.[28–31] Because nonequilibrium behavior is expected below some temperature close to T_D, only $T > T_D$ exponents can be measured with any confidence.

Early $DyVO_4$ ultrasonic measurements[34] of the soft elastic constant $(C_{11}-C_{12})/2$, which near T_D is proportional to the inverse susceptibility, were unable to determine the susceptibility exponent because of strong ultrasonic attenuation for [110] transverse waves near T_D. We accordingly measured C_{11} using [100] longitudinal waves[35] and subtracted from it the constant contribution of $(C_{11}+C_{12})/2$ to the ultrasonic velocity. The sample used was $Dy(As_{0.15}V_{0.85})O_4$, in which the random fields should be sufficiently strong ($T_D = 7.9$ K) to ensure a large random-field power-law regime.[32]

Figure 3 shows a log-log plot of $(C_{11}-C_{12})/2$, obtained in the manner described,[35] versus reduced temperature t. Over the range $0.01 < t < 0.1$ the data give $\gamma = 1.6 \pm 0.3$. This result has to be viewed with some caution due to uncertainties in the fitting procedure and possible effects of concentration gradients and departures from equilibrium. Nevertheless, γ seems to be significantly larger than the 3-d Ising value 1.25, and to be consistent with the value 1.75 expected for effective dimensionality two and observed in recent experiments,[8] and with the value 2.0 ± 0.5 found in the most recent simulations.[32] Above $t \approx 0.1$, Fig. 3 shows a range of temperature for which the data are consistent with $\gamma = 1.25$, suggesting a crossover to pure Ising behavior at large t. Since these data probably lie outside the usual critical range, however, our evidence for such a crossover is not firm at present.

In summary, our capacitance and ultrasonic experiments show that the mixed Jahn-Teller compounds $Dy(As_xV_{1-x})O_4$ may be model systems in which to study the effects of random fields on Ising phase transitions. Our observations of metastability, history dependence, and modified critical behavior include some properties of random-field systems not previously considered. Similar experiments with improved resolution and new measurements using birefrigence techniques are in progress to elu-

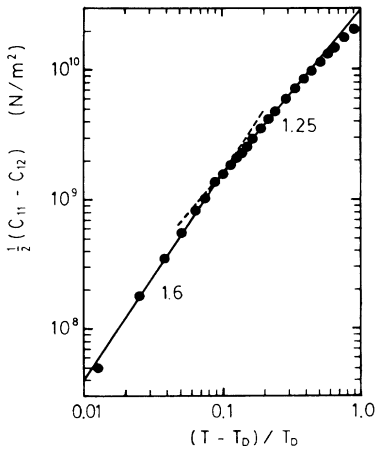

FIG. 3. Elastic constant $(C_{11}-C_{12})/2$ vs reduced temperature for $Dy(As_{0.15}V_{0.85})O_4$. The straight lines have slopes as indicated.

cidate these properties. This process would be assisted by the availability of further theoretical and numerical work on the response of such systems to ordering fields.

Valuable experimental assistance was provided by E. Zwartz, C. Stratas, and J. Storr. Collaboration with J. D. MacArthur and his colleagues in the PIXE analysis, and with R. D. Heyding in the x-ray diffraction analysis, is gratefully acknowledged. The crystals were grown by B. E. Watts of the Clarendon Laboratory. Research support was provided by the Natural Sciences and Engineering Research Council of Canada.

---

*Current address: Cavendish Laboratory, Cambridge CB3 0HE, England.

†Permanent address: Physics Department, University of Manitoba, Winnipeg, Canada R3T 2N2.

‡Permanent address: Physics Department, University of Essex, Colchester C04 3SQ, England.

[1]Y. Imry and S. Ma, Phys. Rev. Lett. **35**, 1399 (1975).

[2]G. A. Gehring, S. J. Swithenby, and M. R. Wells, Solid State Commun. **18**, 31 (1976).

[3]D. R. Taylor, E. Zwartz, J. H. Page, and B. E. Watts, J. Magn. Magn. Mater. **54–57**, 57 (1986).

[4]S. Fishman and A. Aharony, J. Phys. C **12**, L729 (1979).

[5]See, for example, A. R. King and D. P. Belanger, J. Magn. Magn. Mater. **54–57**, 19 (1986); V. Jaccarino and A. R. King, J. Appl. Phys. **57**, 3291 (1985); D. P. Belanger, A. R. King, and V. Jaccarino, Phys. Rev. B **31**, 4538 (1985); H. Yoshizawa, R. A. Cowley, G. Shirane, and R. Birgeneau, *ibid.* **31**, 4548 (1985).

[6]D. A. Huse and C. L. Henley, Phys. Rev. Lett. **54**, 2708 (1985).

[7]C. Ro, G. S. Grest, C. M. Soukoulis, and K. Levin, Phys. Rev. B **31**, 1682 (1985); T. Nattermann, Phys. Status Solidi (b) **129**, 153 (1985).

[8]A. R. King and D. P. Belanger, J. Magn. Magn. Mater. **54–57**, 19 (1986).

[9]G. A. Gehring and K. A. Gehring, Rep. Prog. Phys. **38**, 1 (1975).

[10]J. H. Page, D. R. Taylor, and S. R. P. Smith, J. Phys. C **17**, 51 (1984).

[11]R. Folk, H. Iro, and F. Schwabl, Phys. Lett. **57A**, 112 (1976).

[12]G. A. Gehring and M. C. Marques, J. Phys. C **13**, 3135 (1980).

[13]R. T. Harley and R. M. Macfarlane, J. Phys. C **8**, L451 (1975).

[14]T. Schneider and E. Pytte, Phys. Rev. B **15**, 519 (1977).

[15]B. M. Wanklyn and B. E. Watts, Mater. Res. Bull. **19**, 825 (1984).

[16]D. R. Taylor, S. R. P. Smith, and J. H. Page, J. Phys. C **18**, 3285 (1985).

[17]G. A. Gehring, A. P. Malozemoff, W. Staude, and R. N. Tyte, J. Phys. Chem. Solids **33**, 1499 (1972).

[18]A. Kasten and P. J. Becker, Int. J. Magn. **5**, 157 (1973).

[19]N. Bontemps, J. Rajchenbach, and R. Orbach, J. Phys. (Paris) Lett. **44**, L47 (1983).

[20]For a brief review, see G. Aeppli and R. Bruinsma, J. Magn. Magn. Mater. **54–57**, 25 (1986).

[21]D. Andelman and J. -F. Joanny, Phys. Rev. B **32**, 4818 (1985).

[22]D. P. Belanger, S. M. Rezende, A. R. King, and V. Jaccarino, J. Appl. Phys. **57**, 3294 (1985).

[23]G. Grinstein and J. F. Fernandez, Phys. Rev. B **29**, 6389 (1984).

[24]J. R. L. de Almeida and D. J. Thouless, J. Phys. A **11**, 983 (1978).

[25]A. Aharony, J. Magn. Magn. Mater. **54–57**, 27 (1986).

[26]M. Schwartz, J. Phys. C **18**, 135 (1985).

[27]Y. Shapir, Phys. Rev. Lett. **54**, 154 (1985).

[28]A. J. Bray and M. A. Moore, J. Phys. C **18**, L927 (1985).

[29]A. P. Young and M. Nauenberg, Phys. Rev. Lett. **54**, 2429 (1985).

[30]D. S. Fisher, Phys. Rev. Lett. **56**, 416 (1986).

[31]J. Villain, J. Phys. (Paris) **46**, 1843 (1985).

[32]A. T. Ogielski and D. A. Huse, Phys. Rev. Lett. **56**, 1298 (1986).

[33]A. Aharony, Y. Imry, and S. Ma, Phys. Rev. Lett. **37**, 1364 (1976). The main result giving $\rho=2$ has since been discredited, but an argument giving $\rho=1$ is also presented.

[34]R. L. Melcher and B. A. Scott, Phys. Rev. Lett. **28**, 607 (1972).

[35]J. H. Page, M. C. Maliepaard, and D. R. Taylor, in *Phonon Scattering in Condensed Matter V,* Springer Series in Solid-State Sciences, Vol. 68, edited by A. C. Anderson and J. P. Wolfe (Springer-Verlag, Berlin, 1986), p. 275.