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Roughening of flat domain walls by random strain fields: Neutron-scattering study of twinned orthorhombic $Dy(As_xV_{1-x})O_4$

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The effects of random strain fields on the tetragonal-orthorhombic phase transition in mixed $Dy(As_xV_{1-x})O_4$ crystals have been studied by neutron scattering. In the ordered phase the diffraction peaks, which are characteristic of {110} twinning, show transverse or mosaic-type broadening, which disappears when the sample is forced into a single domain. The data are consistent with a model based on roughening of {110} domain walls, which predicts a $h^{2/3}$ dependence of broadening on random fields.

The effects of random fields on Ising phase transitions are of continuing interest, but comprehensive experimental data have been obtained only for dilute antiferromagnetic (DAF) systems.[1,2] In the presence of a uniform external field these systems belong to the same universality class as the random-field Ising ferromagnet, the most tractable model system theoretically. Analyses of the effects of random fields on cooperative ordering in this system are based on the way in which random fields roughen and pin the domain wall between a quasispherical droplet of ordered spins and a sea of oppositely ordered spins. New critical behavior as well as metastability have been predicted and observed.[1,2]

Although much has been learned from these studies, many basic questions about the effects of random fields remain open, and experimental results from other systems would be valuable. In this paper we describe a neutron-scattering investigation of a simple structural phase transition, where random strain fields arise from the size mismatch of substitutional ions. Experimental realizations of this nature were proposed by Imry and Ma[3] in their pioneering study of random-field effects. High-resolution elastic scattering was used to examine the structure and evolution of ordered domains as the composition, and hence the random-field strength, was varied. Our results show that the tendency of the pure compounds to form orthorhombic twins[4] with {110} domain walls persists in the presence of random fields. For increasing random fields, however, there is additional transverse broadening, which implies that domain walls become progressively rougher. Application of an ordering field yields a single domain, but after removal of the field the twins reform, typically with smoother walls than when first cooled through the phase transition. Thus, although this system represents in some senses a very simple example of a structural phase transition, it differs in an important way from systems previously studied in that the quenched phase has domain walls with zero average curvature. The random fields thus appear to affect not the domain sizes but only the roughness of the walls. Although some qualitative effects of random fields are anticipated to be similar to those in DAF systems, important differences are also to be expected.

Mixed single crystals of $Dy(As_xV_{1-x})O_4$ were studied. The pure parent compounds $DyAsO_4$ and $DyVO_4$ undergo tetragonal-to-orthorhombic transitions[5,6] at 11.4 and 14.6 K, respectively, driven by the coupling between nearly degenerate Dy electronic levels and B_{1g} lattice distortions. These couplings can be described by an Ising Hamiltonian in a pseudospin representation. In the mixed systems the As-V size mismatch generates random static strain fields at each site, including a B_{1g} strain component that couples to the order parameter.[7] Although the Ising interactions in the pure compounds include a coupling to a uniform strain, the observable critical exponents are found to be closer to Ising than to classical values[8,9] because of strong short-range interactions. In the mixed compounds, ultrasonic measurements showed that the susceptibility exponent γ increased significantly,[7,9] with values consistent with a change from $d = 3$ to $d = 2$. Dielectric measurements[7] showed slow equilibration and hysteresis below the transition temperature.

The neutron-scattering measurements reported here were carried out on four samples of different concentrations at the NRU reactor, Chalk River, with neutrons of λ

=1.7620 Å.[10] For high resolution we used either a double-axis spectrometer with collimations 0.15° and 0.20° before and after the sample, respectively, and a Si(331) monochromator with 0.11° mosaic spread, or a triple-axis spectrometer with collimations 0.30° and 0.40° before and after the sample and with the Si(331) monochromator and analyzer, which had somewhat larger mosaic spreads, at equal angles. The latter configuration has the advantage of providing an almost circular resolution ellipse. The samples were mounted with c axis vertical. {400}, {440}, and {600} Bragg peaks were examined above and below the transition temperature. A horizontal magnetic field could be applied parallel to the orthorhombic a or b axis to force the sample into a single domain. For typical sample sizes $2 \times 2 \times 6$ mm the maximum counting rate at a {600} peak was $\sim 400\ s^{-1}$in double-axis mode and $\sim 100\ s^{-1}$ in triple-axis mode.

The four samples studied had relative arsenic concentrations x=0.995, 0.984, 0.950, and 0.154.[11] A single Bragg peak in the tetragonal phase generally split into several peaks at low temperatures. Observations of the splittings of several peaks showed that the orthorhombic phase is twinned about {110} planes just as in the case of the pure compounds.[4,10,12] Raster scans in the vicinity of a Bragg peak were therefore necessary to allow changes in peak positions and widths to be followed. Figure 1 shows contour plots for the (600) peak in the x =0.995 sample above and below the transition temperature. Here all four peaks arising from twinning are observed, but two peaks are stronger than the others owing, presumably, to macroscopic strains favoring some distortion axes more than others. In Fig. 2, in a different sample, only three of the four allowed peaks are seen as a result of the particular strains present.

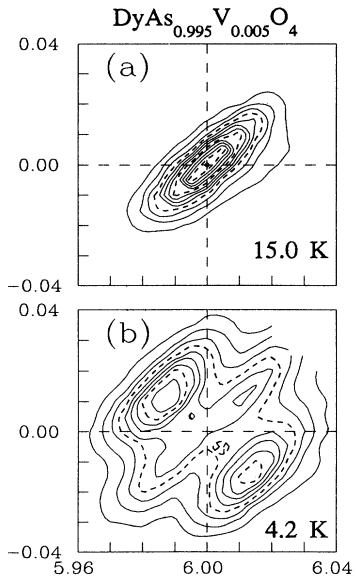

FIG. 1. Contour plots in two-axis mode for the (600) Bragg peak in the x = 0.995 sample: (a) at 15 K and (b) at 4.2 K after cooling in zero ordering field.

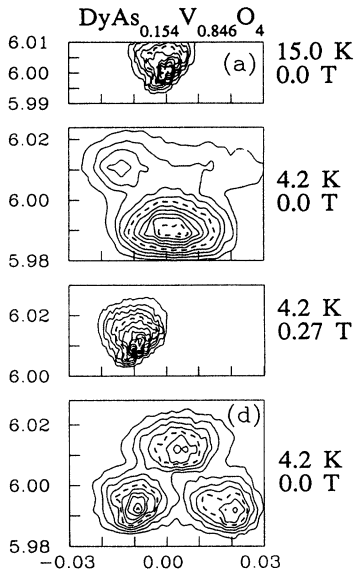

FIG. 2. Contour plots in triple-axis mode for the (060) Bragg peak in the x = 0.154 sample: (a) at 15 K, (b) at 4.2 K after cooling in zero ordering field, (c) at 4.2 K after application of an ordering field (0.27 T), and (d) at 4.2 K after removal of the field.

If the domains in the ordered phase are sufficiently small, the Bragg peaks will be broadened by finite-size effects. This would allow the direct investigation of domain sizes and their dependence on random fields by neutron scattering. In Fig. 1 it appears that any broadening below the transition temperature in the x=0.995 sample is much smaller than the resolution (for all Bragg peaks studied the widths were essentially resolution limited above the transition temperature). For the two samples with largest random fields, x=0.950 and 0.154, significant broadening was observed, but this could not be attributed to finite-size broadening. Figure 2 shows a series of contour plots for the (060) peak in the x=0.154 sample, as the temperature is reduced, and as an ordering field is applied and removed. Changes in width are apparent in the direction transverse to the scattering vector, but not in the radial direction. Broadening due to finite-size effects, however, cannot always be transverse. Measurements on peaks in different quadrants of the scattering plane confirmed the general result that Bragg peaks experience transverse broadening but little or no radial broadening. Results from the four samples show that the transverse broadening increases with impurity concentration.

The application of an ordering field progressively forces the sample into a single domain, while the peak width narrows until it is similar to that above the phase transition. Upon removal of the field the sample returns to a twinned multidomain phase, but Fig. 2 shows that this state is quite different from that reached after the initial cooling. Transverse broadening reappears but is

noticeably less than when first cooled.

Before presenting the data in detail, we point out some important qualitative implications of these results. The virtual absence of any radial broadening implies that finite domain size is not a broadening mechanism. We estimate that the domains must be larger than about 500 Å in all samples. Also the persistence of twinning in all samples indicates that the domains remain predominantly long and narrow in the basal plane, with {110} domain walls, as in the pure compounds.[4] The model of quasispherical domains used in other systems is clearly not appropriate here.

The observation of transverse broadening, which develops below the transition temperature, which disappears when a single-domain phase is induced, and which increases with impurity concentration, implies an origin for the broadening in the domain structure together with effects of random strain fields in pinning and roughening the domain walls. Transverse broadening of single-crystal diffraction peaks is usually a signature of mosaic broadening:[13] that is, the crystal axes of different regions of the crystal have a spread of orientations due to defects and inhomogeneities that are grown into the sample during crystallization. In our system we infer that in the presence of random strain fields the domains that form below the transition temperature are imperfectly aligned. This presumably occurs because the domain walls are not flat {110} crystal planes but are roughened by the random fields in such a manner that the angles between crystal axes in adjacent domains have a spread of values.

The broadening of diffraction peaks associated with domain formation was determined through least-squares fits to the observed peaks. Above the transition temperature a reasonable fit was obtained with empirical Gaussian line shapes. In some cases, most notably for the x=0.154 sample, the line shapes were distorted; this is believed to be an artifact of the spectrometer at high resolution. For this sample two circular Gaussians gave a reasonable fit. In the low-temperature phase the line shape was convoluted with transverse and radial Gaussians representing the domain broadening. This procedure gave satisfactory fits but the experimental statistics do not allow us to rule out other possible broadening functions. Figure 3 shows data for transverse scans for the two samples x=0.95 and 0.154 where the random fields are largest, and Gaussian fits to the data. The results for the broadening observed after cooling through the transition in zero applied field are shown for all four samples in Table I.

Since twinning persists for the largest random fields studied, the basic random-field Ising model, which assumes nearest-neighbor interactions J_{ij} only, cannot be an adequate model for this system. The longer-range, anisotropic elastic interactions that lead to twinning should be incorporated in J_{ij}. In this situation, it is reasonable to suppose that the random fields would act as a perturbation on a flat interface, causing roughness but not affecting the curvature or the separation between domain walls. Random-field roughening of a plane interface has been discussed in the literature as a limiting case of the spherical interface. Andelman and Joanny[14] give an expression for the maximum roughening displacement $w_{\max}(b)$ of a domain wall of length b, which in three dimensions is

$$w_{\max}(b) = \left(\frac{h\sigma}{g}\right)^{2/3} b^{2/3}, \tag{1}$$

where h is the random-field strength, σ is the order parameter, and g is an interaction parameter. Since twin boundaries typically have the same length scale as the sample size L, the characteristic angular misorientation between twins will be

$$\gamma \approx w_{\max}(L)/L \sim h^{2/3}L^{-1/3}. \tag{2}$$

The resulting mosaic spread over the whole sample can then be estimated from a random walk argument as $\theta = n^{1/2}\gamma$, where $n \approx L/t$ is the number of domains in the

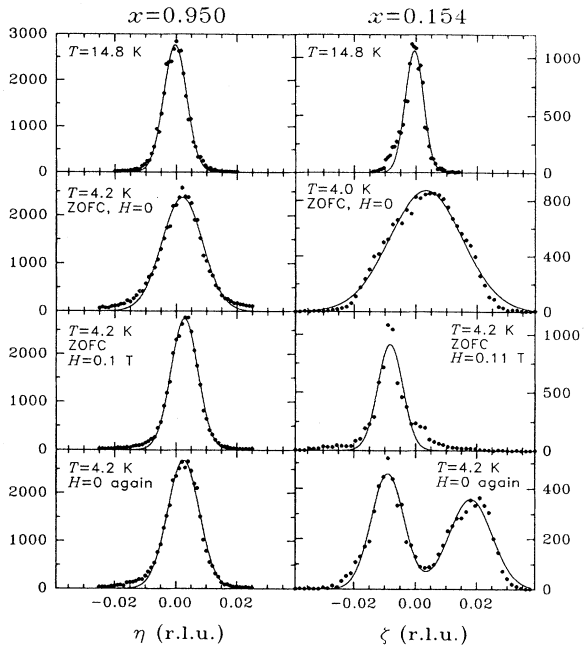

FIG. 3. Transverse scans through (060) Bragg peaks for the samples with strongest random fields. Sequences from top to bottom are as in Fig. 2, with values as indicated. Lines are Gaussian fits.

TABLE I. Transverse resolution width (Σ_r) and broadening (Σ_t) of diffraction peaks at 4.2 K. Data for Σ are full width at half maximum in 10^{-3} reciprocal lattice units.

x	$x(1-x)$	Σ_r	Σ_t
0.995	0.0050	14.0±0.3	9.0±5.8
0.984	0.0157	14.7±0.5	10.8±3.5
0.950	0.0475	9.0±0.2	13.0±0.4
0.154	0.130	7.0±0.3	23.3±0.3

sample and t is the average domain thickness. Thus,

$$\theta \sim L^{1/6} h^{2/3} t^{-1/2}. \quad (3)$$

This mosaic spread θ is directly related to the transverse broadening observed in neutron scattering. Note the weak dependence on sample size, and the $h^{2/3}$ dependence on random-field strength. The latter can be compared with the data of Table I if h is assumed to scale with concentration as $x(1-x)$.

Figure 4 shows that the observed transverse broadening is consistent with a $[x(1-x)]^{2/3}$ relationship, at least for the two samples where the broadening is most clearly evident. For the two samples with the lowest impurity concentrations the broadening appears to be larger than predicted. We have not, however, taken account of roughening due to the strain fields of residual impurities, vacancies, etc., nor the broadening due to the variation in unit cell parameters close to domain boundaries. It is hoped that future results from both experiments and numerical simulation will confirm the relationship between random strain fields and transverse broadening.

It is of interest to note from Figs. 2 and 3 that after removal of the ordering field from a single-domain sample at low temperatures a twinned phase reappears in which the domain walls are rough but less rough (according to the transverse broadening) than when cooled in the presence of the random field but in zero ordering field. This suggests that rough domain walls are characteristic of the ground state of this system.

In summary we have identified a random-field system with attractively simple features. Twinning forces constrain the domain walls to be flat on average, but they are progressively roughened by increasing random-field strength. The degree of roughening is directly revealed by neutron scattering through a novel transverse "mosaic" broadening of diffraction peaks.

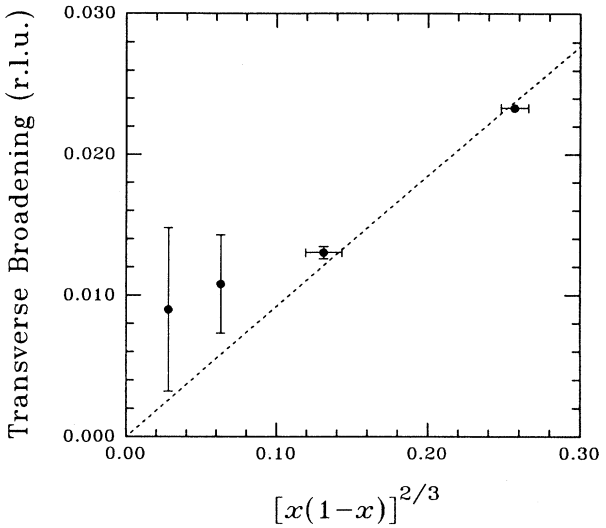

FIG. 4. Transverse broadening for the four sample concentrations. The dashed line is a fit to $[x(1-x)]^{2/3}$.

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