Fe on the periodic table enter the Fe_{II} site exclusively, but different elements show different near-neighbor preferences in iron-rich off-stoichiometric samples. On the basis of these investigations, we conclude that an additional parameter which specifies the selective site occupation in Fe_3Si when transition-metal impurities are added could shed some light on the ternary phase diagrams[9] of these systems.

The regularity of these results suggest a direct relationship to the large class of magnetic Heusler alloys.[10] If one writes Fe_3Si as $(Fe_{II})_2Fe_ISi$ the similarity to the Heusler structure, A_2BC, is clear.[11] In the known Heusler alloys, the transition metals most to the left in the periodic table prefer the B site, while those to the right enter the A site. Our results that V and Mn enter the Fe_I site whereas Co, Ru, Rh, Os, and Ir enter the Fe_{II} site suggest a basis for the systematics of the transition-metal site occupancy of the known Heusler alloys. An interpretation of these results based on size and valency factors is actively being pursued.

During the course of this investigation, a similar conclusion for the $(Fe_{3-x}+Mn_x)Si$ system was reached on the basis of a neutron experiment which concluded that Mn entered the Fe_I site.[12]

We would like to thank Dr. J. H. Wernick for providing the master ingots used in the initial phases of this study, Dr. S. Pickart for his helpful collaboration, and Dr. S. Skalski for his comments.

*Work supported in part by the National Science Foundation.

†Work supported in part by a Fordham Faculty Research Grant.

‡Work supported in part by the University of Connecticut Research Foundation.

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Anomalous Small-Angle Magnetic Scattering from Amorphous $TbFe_2$ and YFe_2†

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(Received 24 June 1974)

Small-angle quasielastic neutron scattering measurements have revealed an intense magnetic component at low temperatures in amorphous $TbFe_2$ and YFe_2, in addition to a weak critical divergence at T_c in $TbFe_2$. These observations are interpreted as evidence that spatial fluctuations remain "frozen in" below the Curie point of $TbFe_2$, and that only short-range order is achieved in YFe_2.

Recent neutron scattering measurements on sputtered, amorphous magnetic alloys have provided information on the atomic and spin correlation functions[1] and excitation spectra[2] of these novel materials. Small-angle quasielastic scattering provides additional information about the longer-range, spatial fluctuations in the magnetization, particularly in the critical region near the transition temperature. We report here the observation by this method of an intense, strongly temperature-dependent small-angle component of magnetic origin in amorphous $TbFe_2$ and YFe_2, accompanied by a weak divergence near T_c in $TbFe_2$. We believe that these phenomena provide insight into the anomalous nature of the phase transition in amorphous magnets.

The measurements were taken at the National Bureau of Standards reactor with a double-axis

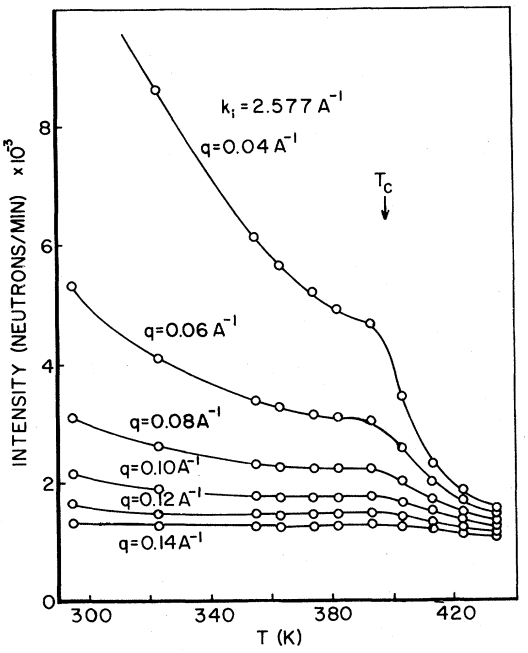

FIG. 1. Small-angle neutron scattering from amorphous $TbFe_2$ in the critical region, corrected for absorption and instrumental background. (Data taken for $q = 0.02$ Å^{-1} would be off scale and are not plotted for convenience, while data at higher q continue to decrease slightly and are essentially flat with T.) The indicated T_c is the average derived from Ref. 3.

spectrometer using a 20′-10′-10′ collimator sequence. This allows observations without excessive background contamination down to a momentum transfer $q \approx 0.02$ Å^{-1}, with the incident wave vector of 2.577 Å^{-1} obtained from a curved graphite monochromator.

Data obtained in the critical region for $TbFe_2$ are presented in Fig. 1. Two interesting features are visible in these data: a weak "critical" anomaly near T_c and a further precipitous rise as T decreases below T_c.

Measurements at closer intervals than indicated in the figure at a fixed q of 0.04 Å^{-1} demonstrate that the anomaly is not at all sharp, as expected in a normal ferromagnetic second-order phase transition, but rounds off and transforms smoothly into the unexpected small-angle component. If the high-temperature asymptotic level of the scattering is subtracted (a somewhat arbitrary procedure because the highest safe temperature to avoid recrystallization does not reach into the completely paramagnetic regime), the shape of the angular dependence above and immediately below T_c in Fig. 1 is closely Lorentzian. The correlation length obtained by fitting the resolution-corrected intensity increases from ≈ 15 Å at the highest T to ≈ 70 Å just below T_c. This slower than normal divergence, plus the rounded character of the anomaly, suggest that the fluctuations are "frozen in" at T_c and never become long range.

On the other hand, the angular dependence of the small-angle component below T_c is far from Lorentzian. It is strongly temperature dependent, increasing at $q = 0.02$ Å^{-1} by over 2 orders of magnitude as T falls from room temperature to 4 K. It is found to scale very nearly with the square of the spontaneous magnetization,[3] which suggests an interpretation in terms of magnetic inhomogeneities or clusters, i.e., the magnetic analog of particle size broadening effects.[4] Since the forward beam, the (000) reflection, is the only in-phase component in the scattering from an amorphous medium, it is the only region in scattering space that will reflect inhomogeneities on a scale large compared to the interatomic spacing. It is important to note, however, that the intensity far above T_c shows no rapid falloff with q; thus, since the nuclear and magnetic cross sections are comparable, there is no similar small-angle scattering of *nuclear* origin. Hence these magnetic clusters are apparently *not* connected with chemical or structural inhomogeneities.

We have attempted to analyze the small-angle scattering below T_c by the methods[4] of Guinier and Porod; although these theories apply strictly only to noninteracting particles, a sufficiently random distribution may minimize interference effects. For a collection of N identical particles with moment μ and radius R the intensity is

$$I(q) \sim N\mu^2 \exp(-q^2R^2/3),$$

where the factor in the exponent, but not the Gaussian dependence, is modified by resolution corrections. We find on plotting the intensity on a logarithmic scale versus q^2 that the curves have a continuous upward curvature at small q, thus indicating a distribution of radii and effectively preventing determination of an upper limit to R by extrapolation to $q = 0$. We find, however, that for temperatures below room temperature the data exhibit a q^{-n} dependence with $n = 2.4$, in remarkable agreement with Porod's limiting formula[4] for a distribution of particle sizes with total surface area S and magnetization density m,

$$I(q) \sim 2\pi m^2 S/q^4,$$

where the q^{-4} dependence is reduced to $q^{-2.6}$ after correction for vertical and horizontal resolution. Using the theoretical magnetization density (rare-earth and iron spins antiparallel) we obtain from the absolute intensity at $q = 0.02$ Å^{-1} a specific surface area of ≈ 4 Å^2/ atom, almost exactly the same value as a spherical particle with a diameter equal to the correlation length above T_c. The agreement is probably fortuitous, since we have no idea of the shape and distribution of the particles, but does lend credence to the model.

In order to investigate the effect of substituting a nonmagnetic rare earth, we have also measured diffraction patterns and small-angle scattering from sputtered YFe_2, which is nonmagnetic at room temperature. Fourier transforms of the nuclear scattering observed at 300 K are strikingly similar to our previous $TbFe_2$ data,[2] with peaks corresponding to combinations of the ionic radii of Y and Fe pairs and clusters, as expected for a dense random-packing model.[5] Small-angle scattering data exhibited a temperature-dependent component in this material as well (see Fig. 2), but less intense than in $TbFe_2$ and with a Lorentzian angular dependence at all temperatures. The correlation length ranges from ≈ 6 Å at 175 K to ≈ 8 Å at the lowest temperatures. These results suggest that YFe_2 is not ordered magnetically on a long-range basis, as confirmed by subsequent magnetization measurements.[3] The broad peak at ~40 K for $q = 0.04$ Å^{-1} corresponds to the appearance of hysteresis in the magnetization, and may result from anisotropy effects.

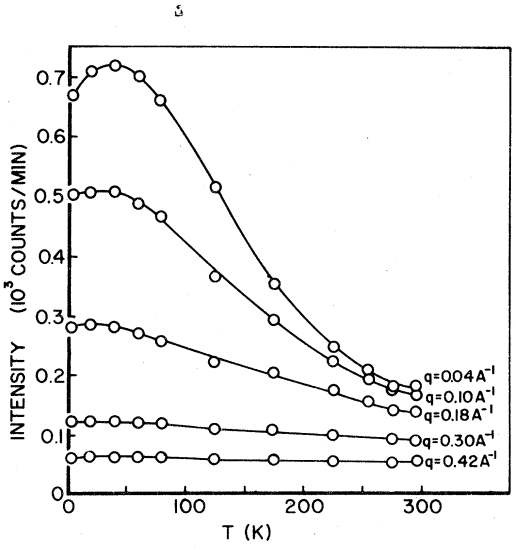

FIG. 2. Small-angle scattering observed in amorphous YFe_2 as a function of temperature.

A question naturally arises as to the inelasticity of this small-angle scattering, as could happen for instance if the counter angle is at all temperatures below the spin-wave cutoff given by $\theta_c = \hbar^2/2mD$, where D is the spin-wave stiffness. Under these conditions, if D renormalizes as $T \to T_c$, the spin-wave cone opens up and the intensity decreases because of the finite vertical collimation. There are two pieces of evidence against this interpretation. First, our previous[2] elastic and total scattering measurements on $TbFe_2$ indicate that the energy-integrated inelastic scattering decreases with T, and, in fact, is hardly observable at 4 K. Second, with a strongly temperature-dependent D one would expect renormalization effects near T_c to be visible; however, data taken on a triple-axis spectrometer (shown in Fig. 3), although extremely limited in energy range by geometric factors, show no evidence of energy broadening. We therefore conclude that the small-angle scattering is primarily elastic.

As a result of these data, we have arrived at the following tentative model for the qualitative nature of the phase transition in these amorphous magnets. Fluctuations begin to build up as T approaches T_c from above in the normal manner,

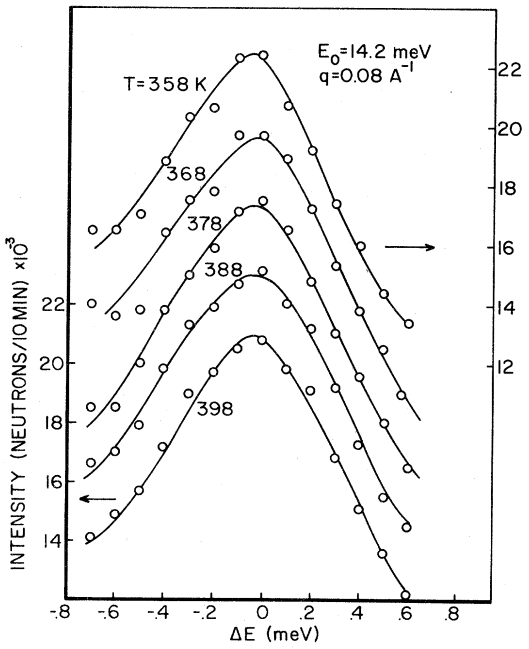

FIG. 3. Energy dependence of the small-angle scattering component in $TbFe_2$ in the critical region. The collimation was greatly relaxed (40′ throughout) from the data in Fig. 1. Since the scans overlap, the scale is shifted up progressively by one ordinate unit.

but are interrupted by the spatial disorder of the lattice and are "frozen in" at the ordering temperature with some finite mean correlation length, thus preventing the wavelength-dependent susceptibility from diverging.[6] These frozen-in fluctuations must in some manner be stabilized by the rare-earth–iron interaction, since in the absence of a magnetic rare earth the fluctuations are of much shorter range and never spontaneously order. We are undertaking experiments on other rare-earth–iron compositions to corroborate this model for the amorphous magnetic transition and determine whether the exchange or crystal field interactions are predominantly responsible for the anomalous behavior.

We are grateful for helpful discussions on these results with Dr. J. Cullen and Dr. A. Clark. The samples were fabricated by Battelle Northwest under ARPA support.

†Work supported by the Naval Ordnance Laboratory Independent Research Fund, Office of Naval Research, and Naval Air Systems Command.

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Polycritical Points and Floplike Displacive Transitions in Perovskites

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(Received 29 April 1974)

The critical behavior occurring at displacive phase transitions in anisotropically stressed perovskite crystals is examined. It is shown that, under various conditions, the asymptotic critical behavior may be of Ising, XY-model, or Heisenberg type. The existence of a "spin-flop"-like transition (at zero stress) between two differently ordered phases is predicted. An explanation of the discrepancy between the measured exponents and those predicted theoretically is proposed, and several new experiments are suggested.

It is well known that stressed crystals undergoing displacive phase transitions exhibit phase diagrams with interesting complexities.[1,2] In this Letter we show that, under different stress conditions, perovskite crystals may display a variety of types of critical behavior, including *tricritical and bicritical points, crossover phenomena,* and *floplike transitions* of the type proposed recently for anisotropic antiferromagnets.[3,4] The analysis raises the interesting possibility that the discrepancy between recent theoretical predictions[5-7] and measurements of the critical exponents characterizing the structural transitions in the perovskites $SrTiO_3$ and $LaAlO_3$[8] arises through the existence of systematic residual strains in the crystals studied. We show that these (conjectured) strains precipitate a crossover from the Heisenberg-like (or cubiclike) behavior, previously predicted,[5-7] to an Ising-like behavior. We use scaling theory to study this crossover, and propose several experiments which should elucidate the situation.

Our conclusions are based on an analysis of an effective Hamiltonian that is a natural extension of the Landau-type potential used in previous mean-field investigations of the 105°K phase transition in $SrTiO_3$.[2,9] The Hamiltonian embodies a coupling between the local rotational coordinates of the characteristic perovskite octahedra, $Q_\alpha(\vec{x})$ ($\alpha = 1, 2, 3$), in which the primary ordering occurs, and the elastic strain coordinates $e_i(\vec{x})$ ($i = 1, \ldots, 6$ in the Voigt notation). Allowing for an applied stress T_i ($i = 1, \ldots,$