Origin of the Second Length Scale above the Magnetic-Spiral Phase of Tb

P. M. Gehring,[1] K. Hirota,[2] C. F. Majkrzak,[1] and G. Shirane[2]
[1] *National Institute of Standards and Technology, Gaithersburg, Maryland 20899*
[2] *Brookhaven National Laboratory, Upton, New York 11973*
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High q-resolution neutron-scattering measurements of the critical scattering in Tb above the magnetic-spiral phase transition temperature T_s exhibit a two-component line shape, as recently documented in Ho. This implies the existence of a second length scale. By using a narrow beam only 300 μm wide, and then translating the crystal through the beam, we have established that the origin of the second length scale lies within the near-surface volume or "skin" of the Tb crystal. This is manifested by a large enhancement of the scattering intensity at the c-axis face of the cube-shaped crystal.

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The unexpected observation of a second, and very narrow, component in the quasielastic scattering profiles of several different systems, just above their respective critical temperatures T_c, has renewed considerable interest in the critical fluctuations associated with phase transitions in recent years. An additional component implies the existence of a second length scale, and runs counter to our current understanding of second order phase transitions in which only one divergent length scale, which describes the size of fluctuating regions, is present above T_c. This anomalous feature was first seen in the perovskite $SrTiO_3$ above its cubic-to-tetragonal structural phase transition temperature using x-ray scattering techniques [1]. Much more recently, high q-resolution neutron-scattering measurements on Ho just above its magnetic-spiral phase transition temperature revealed a similar two-component line shape [2]. Taken together, these two seminal results suggest that the narrow component may be a feature common to all phase transitions in condensed matter systems. Indeed, two-component line shapes have also been documented in both $RbCaF_3$ and $KMnF_3$ [3,4]. Studies on other systems are in progress.

Central to all of these investigations has been the question concerning the origin of the narrow component. X rays, which probe crystal surfaces to a depth of order 1 μm, cannot tell if the narrow component is absent in the crystal bulk. Neutrons, which do probe the bulk, have not yet been able to separate surface and bulk contributions. In this Letter we present the answer to this question through high q-resolution neutron-scattering measurements of the quasielastic scattering in Tb which, like Ho, exhibits a transition to a magnetically ordered spiral phase [5]. By use of a 300 μm wide beam, we have been able to isolate thin slices of the Tb crystal. Our finding is that the origin of the narrow component lies in the near-surface volume or "skin" of the Tb sample, and not in the bulk. In this context the meaning of skin is distinct from that of surface since the narrow component is spread over several hundred μm and not just one or two. Moreover, we also find that not all skins are equivalent. The intensity of the narrow component scattering is greatest in those faces which are orthogonal to the c-axis face.

The single crystal specimen of Tb used in this study was grown and prepared by B. Beaudry of the Materials Preparation Center at Ames Laboratory, and has been extensively studied using x rays [6]. The sample is a $7.1 \times 6.4 \times 7.1$ mm^3 cube with faces cut normal to the [100], [010], and [001] directions (orthorhombic indexing) corresponding to lattice constants of a=6.2371, b=3.6010, and c=5.6936 Å. Thus each face is associated with a specific crystal plane. The sample was polished on all sides with 0.5 μm alumina and electropolished in a mixture of methanol and perchloric acid. This procedure removes layers damaged by the cutting process and leaves behind a passive coating one to two monolayers thick of an oxychloride of Tb that prevents subsequent oxidation of the Tb surface. The miscut of the [00l] face was determined directly by measuring the mirror reflection from the Tb c-axis surface. This crystal surface does not have a perfect mirror finish as the mirror reflection was quite broad. However, the reflection was very sharply peaked at a position corresponding to a miscut of only 0.25°.

In order to resolve both narrow and broad quasielastic components it is necessary to have extremely good in-plane q resolution. To this end, Thurston *et al.* exploited the long-wavelength magnetic-spiral structure of Ho which has satellite peaks at $\mathbf{G}_{hkl} \pm (0, 0, \delta)$, where $\mathbf{G}$ is any nuclear Bragg peak [2]. This allowed momentum scans to be made about the forward direction (small scattering angle), where the transverse q resolution is finest, without significant contamination from the main beam. The same method was applied to our study of Tb which has a slightly longer wavelength spiral structure than does Ho.

The neutron scattering experiments were performed on the BT7 reflectometer at the NBSR research reactor at the National Institute of Standards and Technology [7]. This reflectometer is ideally suited to this study because the incident horizontal beam width can be varied from

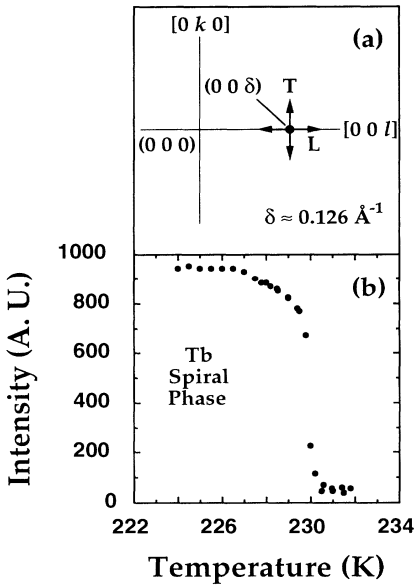

FIG. 1. (a) Tb reciprocal lattice. (b) Temperature dependence of the integrated intensity derived from longitudinal scans across the $(0, 0, \delta)$ satellite peak position.

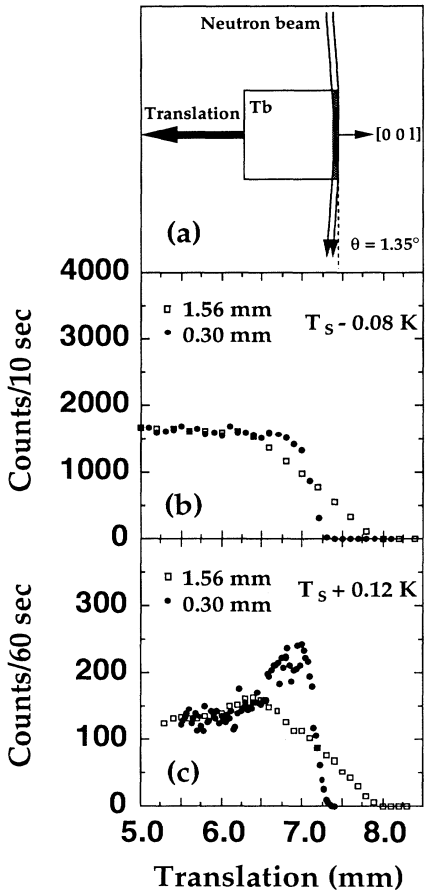

FIG. 2. (a) Schematic diagram of scattering geometry. The Bragg angle θ_B has been slightly exaggerated for clarity. (b) Translation scans below T_s at beam widths of 0.30 mm and 1.56 mm. Intensities have been normalized to those for the narrower beam. (c) Identical scans above T_s showing the enhancement at the c-axis face.

zero to several mm (with an accuracy of ± 0.01 mm) using motorized slits positioned upstream from the sample. By narrowing the width of the incident beam to as little as 300 μm (0.3 mm), the near-surface volume of the Tb crystal can be probed preferentially by translating the crystal face into the beam. It should be emphasized that this capability requires the incident beam to be essentially parallel to the crystal face, as is the case when working in the forward direction. Operating at a fixed incident wavelength of 2.35 Å^{-1}, the scattering angle θ_B is only 1.35°. In the same fashion, scattering from the bulk can be isolated by translating the center of the crystal into the beam and reducing the spatial extent of the scattered beam with exit slits and appropriate collimation. Beam widths of 0.30, 0.80, and 1.45 mm were used in these experiments. To avoid confusion, all widths represent the measured beam full width at half maximum (FWHM) at the sample position. With a horizontal beam width of 0.80 mm, the half widths at half maximum (HWHM) for transverse and longitudinal q scans at $(0, 0, \delta)$ are 0.000 03 Å^{-1} and 0.0020 Å^{-1}, respectively. By comparison, the Tb crystal mosaic at $(0, 0, \delta)$ is 0.17° (HWHM) which converts to 0.0004 Å^{-1}.

Figure 1(a) shows the reciprocal lattice for Tb in the vicinity of the magnetic satellite peak at $(0, 0, \delta)$. The arrows depict the orientation of both transverse (T) and longitudinal (L) scans relative to $(0, 0, \delta)$. Figure 1(b) shows the q-integrated intensity obtained from longitudinal scans at $(0, 0, \delta)$ as a function of temperature. The rapid change in intensity over a very narrow temperature range suggests the transition is first order. This identification is further supported by significant hysteretic effects which have been documented on the same sample using resonant magnetic x-ray scattering techniques [6]. The approximate value for the spiral transition temperature is 229.5±0.1 K. A thermal stability of ±0.01 K over several hours was obtained during these measurements.

The experimental scattering geometry is shown schematically in Fig. 2(a). The Tb crystal was mounted with the [100] axis vertical. The [001] direction was aligned along the translation axis of a motorized goniometer stage so that the narrow neutron beam could selectively probe thin slices of the Tb crystal, as depicted by the shaded area. Figure 2(b) shows two such translation scans below T_s for two different beam widths of 1.56 mm and 0.30 mm, with the spectrometer fixed at the $(0, 0, \delta)$ satellite peak position. The translation scale was set so that zero corresponds to the front face of the crystal. The intensity scale for the wider beam setting has

been normalized to that for the narrower beam setting to better contrast the markedly different profiles at the crystal edge. Because the absorption is constant as the crystal is translated through the beam, the peak intensity remains constant until it drops to zero when the crystal moves out of the beam. Figure 2(b) shows how much sharper this dropoff becomes with a narrower beam.

Identical scans are shown above T_s in Fig. 2(c). In this case, as the beam approaches the crystal c-axis face the intensity does *not* remain constant. Instead, a truly remarkable enhancement of the intensity is observed, persisting over a limited range of 0.2 K above T_s. The enhancement is broad and weak for the wider beam setting which is nearly one-quarter of the full crystal width. But at the narrowest beam setting, the enhancement becomes sharper and larger. This is an extremely important point because it demonstrates that the quasielastic scattering is concentrated near the face of the crystal rather than in the bulk. The narrower the beam, the greater the enhancement. At the narrowest setting, the width over which this enhancement takes place is of order 0.75 mm. Taking into account the effect of the finite beam width, crystal miscut, and scattering angle leaves an effective enhancement width of order 0.3 mm. The large size of this width clearly distinguishes this effect from those studied recently by grazing-incidence diffraction of x rays or neutrons, which probed crystal surfaces to a depth of just 50 to 100 Å [8,9].

The cause of the enhancement becomes apparent by comparing transverse-q scans at the same temperature taken at two different translations, one slightly displaced from the crystal face where the enhancement is maximum (6.75 mm), and one at the crystal center (3.50 mm) [10]. These are shown in Figs. 3(a) and 3(b) which are drawn on the same scale. Slits with a vertical opening of 3 mm were placed 140 mm after the sample, then carefully centered. In addition, a 40′ collimator was placed between the slits and the detector to limit the vertical divergence of the scattered beam. This configuration effectively eliminated scattering from no less than the top and bottom 0.6 mm of the sample. To measure the full extent of the broad component properly the transverse scans covered a range of $\theta_B \pm 13°$. A wider beam width of 0.80 mm was used because of intensity considerations. In both cases the distinctive two-component line shape is present. Whereas the peak intensity of the broad component differs by only 6% in the two scans, that of the narrow component changes by over 70%. The constant background is the same within 4%. The anomalous enhancement is therefore due to a striking increase in the intensity of the narrow component within the skin of the Tb crystal face, as is obvious from Fig. 3(b).

The reason why a small, but finite, narrow component is still present in the line shape shown in Fig. 3(a) is that the incident beam is now illuminating square-shaped portions of the skin at the points where the beam enters

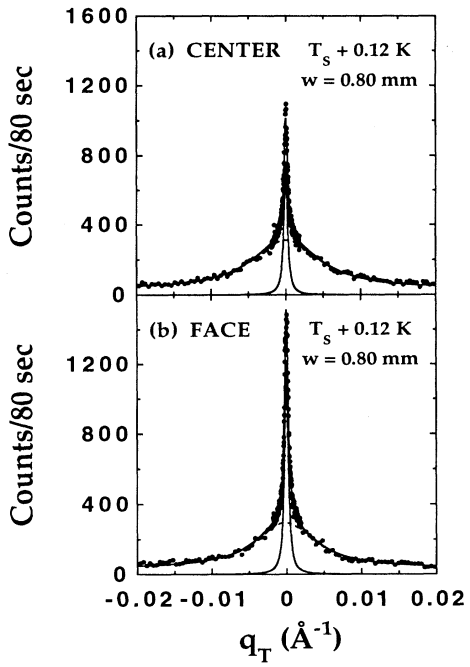

FIG. 3. (a) Transverse-q scan just above T_s at the crystal center (3.50 mm). (b) Identical scan taken at the crystal face (6.75 mm) showing enhanced narrow component.

and exits the crystal on the two faces orthogonal to the c-axis Tb face. Therefore these faces contribute a narrow component as well. Although it is still possible the bulk contributes to the total narrow-component intensity at both translation settings, the translation scans presented in Fig. 2(c) show that the skin, and not the bulk, is the predominant source of this feature. Assuming for the moment that all faces are equivalent, and that the narrow component is absent from the bulk, their contribution in Fig. 3(a) should be proportional to $2hws$, where h is the vertical height of the beam, w=0.80 mm is the effective beam width at the sample position, and s is the skin depth. This contribution should also be present in Fig. 3(b) except that now there is the added contribution from the face of the crystal which should scale as dhs, where d=7.1 mm is the width of the crystal. Therefore the ratio of the narrow-component intensities should vary as $1 + d/2w$, independent of the skin thickness and beam height. This simple geometrical model predicts an intensity ratio of 5.2±0.2 between the crystal center and face. However, the experimental ratio is 1.7±0.1. This indicates that each face orthogonal to the c-axis face contributes roughly 6 times more to the total narrow-component intensity than does the c-axis face itself. Such an anisotropy is easily motivated on physical grounds. In the spiral phase of Tb, all spins lie within the basal plane (c-axis face). Thus it is not unreasonable to expect that the strength of the narrow component in the

c-axis face will differ from that in faces which are orthogonal to the easy plane of the spins. This idea could be tested by repeating these experiments on a cube-shaped single crystal of erbium which exhibits a conical spiral structure.

In summary, we have convincingly demonstrated that the origin of the anomalous narrow component in Tb lies in the near-surface volume or skin of the Tb crystal face. Recent experiments on $SrTiO_3$ also strongly suggest that the origin of the narrow component lies in the skin of the crystal [11]. However, the microscopic explanation for the second length scale is as yet unknown. One model put forth is based on the presence of extended defects such as dislocations which mediate the large scale fluctuations [3]. Given the present results, these defects would have to be populated most heavily in the skin of the crystal, and in an anisotropic fashion. Another intriguing possibility is that the second length scale results from the boundary condition imposed by the crystal surface on the interaction driving the phase transition. In the case of Tb, the fact that the spins are confined to the basal plane below T_s could then easily account for the observed anisotropy between crystal faces.

The skin thickness of 0.3 mm for Tb is rather large. Other systems, such as the perovskites, appear to have a significantly thinner skin inasmuch as neutrons have not been able to detect a narrow component. Moreover, the relationship between skin thickness and crystal perfection is not yet understood. Prior theoretical work on the critical behavior of semi-infinite spin systems predicts a new transition in which the bulk orders at a temperature below the surface ordering temperature [12]. However, in light of our present result we require a theory which models the depth dependence of the correlation length.

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