Effects of Surface Magnetization on the Surface Phonons of Fe(110) by Helium Atom Scattering

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The temperature dependence of Rayleigh waves in Fe(110), measured by helium atom scattering in the range of 150 to 905 K ($0.91T_c$), is shown to provide new information on surface magnetization. The magnetic shifts of the surface phonon frequencies exhibit a large anisotropy, with the [1$\bar{1}$0] direction showing the expected decrease of frequency for increasing temperature, while the [001] direction shows an anomalous increase with temperature. The results are interpreted in terms of a simple model.

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Surface ferromagnetism is an important subject not only from a fundamental point of view but also for technical applications, e.g., in magneto-optic information-storage devices [1]. A basic, extensively investigated but still open question is how much the surface effective exchange interactions differ from the bulk values.

Whereas there is some evidence that magnetoelastic effects lead to an anomalous temperature dependence of bulk phonon frequencies [2,3], little is known about magnetic forces at the surface. Surface magnetization in Fe(110) is known to develop at the same Curie point as in the bulk ($T_c = 1044$ K), but with a different critical behavior [4-6]. For $T \rightarrow 0$, surface magnetization was shown to fulfill the Bloch $T^{3/2}$ law [7-9] as for the bulk, but with an anomalous Bloch coefficient which is 3 times larger than the bulk value. According to Mathon and Ahmad's theory [10] such an anomaly is the signature of a strong softening of the exchange between the first and second surface layers as confirmed by surface hysteresis measurements of Allenspach *et al.* [11] and Siegmann and Bagus [12] for Fe(100).

In this Letter we report helium scattering data on Fe(110) which show a strong temperature dependence of the Rayleigh wave (RW) frequency. The results are interpreted in terms of a significant reduction of the derivatives of the surface exchange interaction with respect to the bulk values. For the [1$\bar{1}$0] direction (the surface easy direction), the observed change is between 30% and 80% but even larger along [001] (the bulk easy direction) leading to negative surface exchange derivatives. This dramatic anisotropy in the temperature effect could be easily observed in Fe(110) because surface spins are pinned along [001] and are thus not affected by the domain structure.

The helium atom scattering (HAS) time-of-flight (TOF) apparatus used in these experiments has been described elsewhere [13] and had a fixed angle of 90° between incident and final beams. To clean the surface we have followed a multistep procedure similar to Kirschner's [14] and described elsewhere [15]. Helium intensities were found to be very sensitive to surface contamination and were used to monitor the surface in addition to Auger spectroscopy and LEED. The temperature dependence of the inelastic HAS TOF spectra measured along the [001] and [1$\bar{1}$0] directions is shown in Fig. 1 for incident angles near $\Theta_i = 38°$. The Θ_i were adjusted so that the phonon wave vector **Q** for the RW peak (↑) was about the same at all temperatures. As observed for the transition and noble metals [13], the spectra also show a second inelastic peak, attributed to a surface longitudinal resonance which will not be discussed further here. The RW peak positions at high temperatures were determined

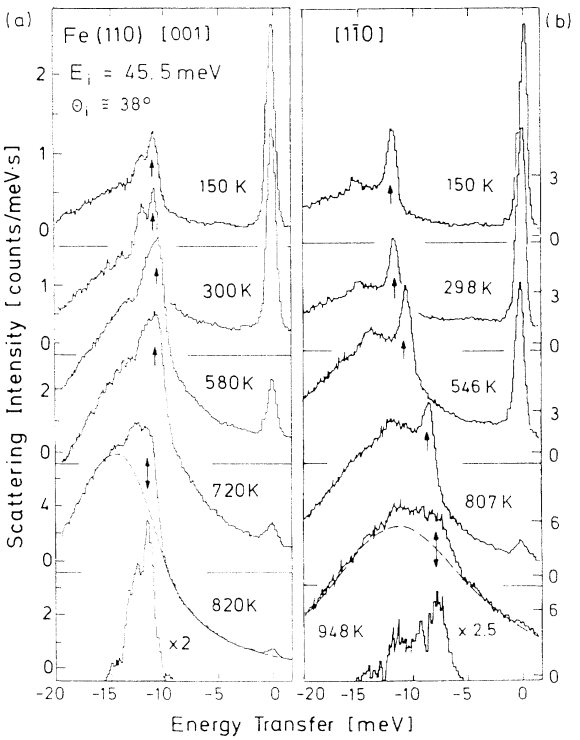

FIG. 1. Inelastic He atom scattering spectra from the Fe(110) surface for different surface temperatures showing (a) an anomalous shift along the [001] direction and (b) a normal shift of the Rayleigh wave peak (↑) along the [1$\bar{1}$0] direction. The high-temperature spectra are also shown after subtraction of the multiphonon background. The incident energy was 45.5 meV.

by subtracting off the multiphonon background, which could be very well fitted by a sum of two Gaussians, $A_c \exp[-\alpha(\omega-\omega_m)^2]+A_i \exp(-\alpha\omega^2)$, where A_c, α, ω_m, and A_i are fitting parameters for the coherent inelastic and incoherent elastic parts, respectively, as suggested by recent theoretical work [16]. For values of Q less than $\frac{3}{5}$ of the zone boundary the RW dispersion curve could be accurately determined for both symmetry directions and different surface temperatures (Fig. 2).

In the $[1\bar{1}0]$ direction [Figs. 1(b) and 2(b)] the RW peak shifts to lower frequency with increasing temperature. The RW peak frequencies, interpolated to a constant $Q_0=(\frac{1}{4},-\frac{1}{4},0)(2\pi/a)$, are indicated by a vertical line in Fig. 2 ($a=2.87$ Å is the lattice constant). These and additional data are also plotted in Fig. 3(b), for comparison with the analogous temperature dependence of the neutron data for the z-polarized TA bulk mode (TA_2) at the N point $(\frac{1}{2},\frac{1}{2},0)$ [2] [Fig. 3(a)]. This bulk TA mode has the same propagation direction as the surface RW and approximately the same polarization. The significant change of slope at T_c in the bulk data indicates that the magnetic contribution to the temperature dependence of the force constants is a least comparable to that of anharmonicity.

The data along the $\bar{\Gamma}\bar{H}\equiv[001]$ direction [Figs. 1(a) and 2(a)] show an entirely different behavior. At any fixed wave vector $Q\geq 0.2$ Å^{-1} and for increasing temperature the RW frequency reaches first a minimum around 580 K and then increases with temperature. This anomaly disappears at large wavelengths ($Q\leq 0.1$ Å^{-1}) where the frequency shows now a monotonous softening with temperature. This indicates that the anomaly disappears for deeply penetrating RWs and must be a surface effect. The anomalous temperature shift adjusted to a fixed $Q_0=(0,0,\frac{3}{8})(2\pi/a)=0.82$ Å^{-1} [vertical line in Fig. 2(a)] is compared in Fig. 3(b) with the corresponding results along $[1\bar{1}0]$.

The effects of magnetization on the force constants

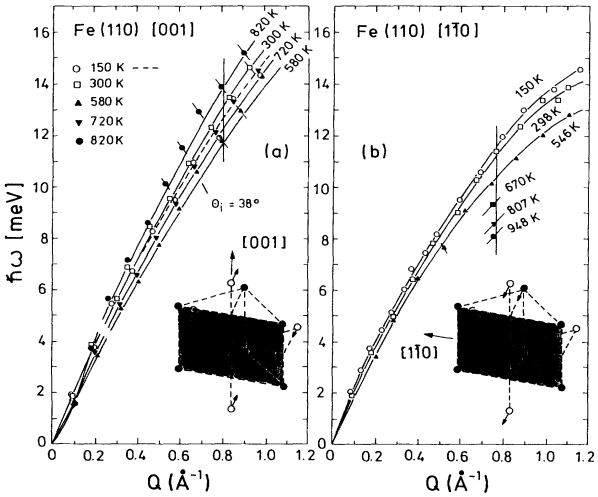

FIG. 2. Experimental Rayleigh wave (RW) dispersion curves at different temperatures for the two symmetry directions. The curves are sine functions except for small Q along [001] where deviations are observed for the higher values of T. Insets: RW displacement patterns at Q_0. Solid and open circles are first- and second-nearest neighbors to the surface atom S, respectively. The dark area represents the (110) surface.

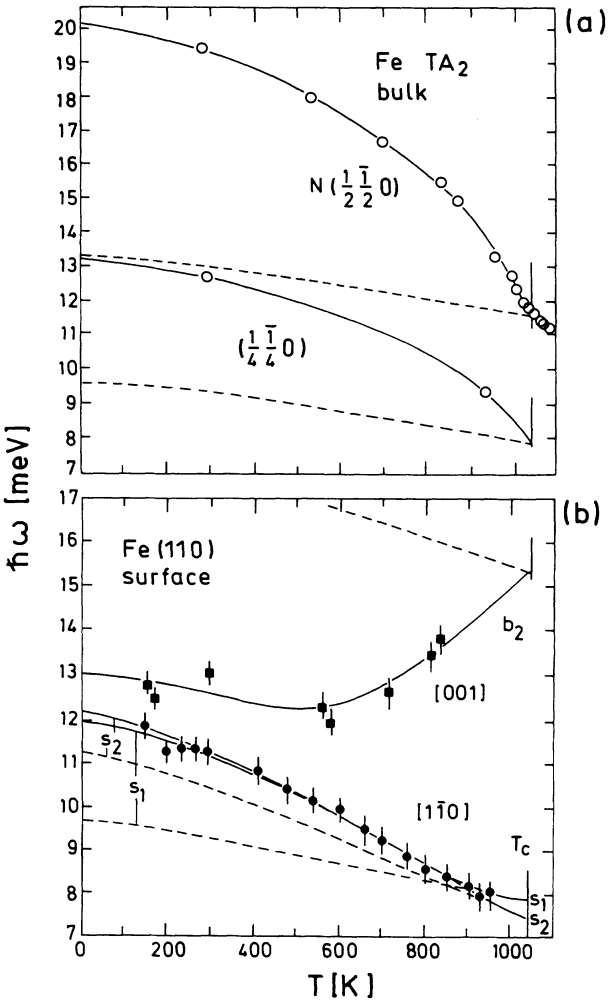

FIG. 3. (a) Experimental $[1\bar{1}0]$-polarized transverse frequency for bulk iron as a function of temperature at the N point, $Q=(\frac{1}{2},-\frac{1}{2},0)(2\pi/a)$ (neutron data from Satija, Comès, and Shirane [2]), and at $Q_0=(\frac{1}{4},-\frac{1}{4},0)(2\pi/a)$ (neutron data from De Vallera [3]) and theoretical fitting curves. Broken lines show the expected behavior without magnetic interaction due only to anharmonicity. (b) Experimental Rayleigh wave frequency for the wave vector Q_0 at one-half of the Brillouin zone along $[1\bar{1}0]$ (below) and [001] (above) symmetry directions as a function of temperature. The theoretical curves for the $[1\bar{1}0]$ direction are based on surface magnetization and either bulk (s_1) or surface (s_2) anharmonicity; the one for the [001] direction (b_2) is based on bulk magnetization and surface anharmonicity. Broken lines show the expected behavior without magnetic interaction due only to anharmonicity.

TABLE I. Saturation magnetic shifts for bulk TA_2 phonons and Rayleigh waves (RW) for different fitting conditions.

Magnetization / Anharmonicity	Bulk Bulk	Surface Bulk	Bulk Surface	Surface Surface
$TA_2(\frac{1}{2}\ \frac{1}{2}\ 0)$	225	...	...	...
$TA_2(\frac{1}{4}\ \frac{1}{4}\ 0)$	84	...	...	...
$RW(\frac{1}{4}\ -\frac{1}{4}\ 0)$	57	21	49	17
$RW(00\ \frac{3}{8})$	−120	−197	...	...

have been investigated theoretically by Hausch [17] for localized spins, and by Wohlfarth [18] for itinerant spins. Though iron belongs to the class of itinerant magnets, and displays anisotropy effects at the surface [2], the change in magnetic energy induced by small atomic displacements is fairly well described in a local scheme [12,18] starting from a Heisenberg Hamiltonian $H_m = -\sum_{ij} \epsilon_{ij}$, where $\epsilon_{ij} = J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$ are functions of the distance between spins S at sites i and j. The derivatives of ϵ_{ij} with respect to distance r_{ij} describe the magnetic part of the force constants. The change with temperature of the magnetic force constants occurs via magnetostriction [17,18] and is proportional to the square of the magnetization $M(T)$. Thus we analyze the temperature-induced frequency shifts of both bulk (j=TA) and surface (j=RW) phonons by means of the same phenomenological expression

$$\omega_j^2(T) = \omega_{0j}^2 - A\omega_{0j}^2(2n_{0j}+1) + B_j M^2(T)/M^2(0), \quad (1)$$

where ω_{0j} is the harmonic phonon frequency at zero magnetization, A is the anharmonicity constant [19], and B_j is the magnetic shift at saturation (T=0). The anharmonic shift expressed by the second term on the right-hand side is that of a single anharmonic oscillator, where $n_{0j} = [\exp(\hbar\omega_{0j}/kT) - 1]^{-1}$ is its occupation number. A is proportional to the T=0 vibrational mean-square displacement $\langle u^2 \rangle_0$. The surface anharmonicity A_s is greater than its bulk value since it involves the larger surface mean-squared displacements [20]. For surface modes with increasing penetration into the bulk, A_s and $M_s(T)$ will tend to the respective bulk limits.

In order to fit the experimental frequencies as a function of temperature we have represented the relative magnetization $M(T)/M(0)$ by an analytic expression. As shown in Fig. 3(a), Eq. (1) gives an excellent fit of the temperature dependence of the bulk TA_2 mode at N with A=0.0193 and $\hbar^2 B_{TA}(\frac{1}{2}\ \frac{1}{2}\ 0)$=225 meV^2. The parameter A agrees with the value extrapolated from the neutron data of De Vallera for Fe(Si) above T_c [3]. DeVallera's work also provides the TA_2 bulk frequencies at $Q_0 = (\frac{1}{4}, \frac{1}{4}, 0)(2\pi/a)$, for T=296 and 933 K [Fig. 3(a)]. With A=0.0193 [20], Eq. (1) now yields $\hbar^2 B_{TA}(\frac{1}{4}\ \frac{1}{4}\ 0)$=84 meV^2.

Equation (1) also provides a good description of the RW temperature dependence at Q_0. The calculated curves s_1 and s_2 [Fig. 3(b)] are based on surface magnetization and two extremes of surface anharmonicity, $A_s = A$ or $A_s = 2A$, respectively [20]. For s_1, we obtain $\hbar^2 B_{RW}$=49 meV^2, and for s_2, $\hbar^2 B_{RW}$=17 meV^2. Lower-quality fits are obtained assuming bulk magnetization, with $\hbar^2 B_{RW}$=57 meV^2 for $A_s = A$, and $\hbar^2 B_{RW}$=21 meV^2 for $A_s = 2A$. In all cases the surface B_{RW} is significantly smaller than the corresponding bulk value $B(\frac{1}{4}\ \frac{1}{4}\ 0)$ (see Table I).

The anomalous shift along [001] can only be fitted with Eq. (1) [Fig. 3(b)] assuming bulk magnetization. No acceptable fit can be obtained with surface magnetization. The best fit for $A_s = 2A$ and bulk magnetization leads to a negative value of $\hbar^2 B_{RW} = -197$ meV^2. A fair fit is also obtained for $A_s = A$ and also leads to a negative value of $\hbar^2 B_{RW} = -120$ meV^2. Along the same direction in the bulk the phonon frequencies do show a regular decrease for increasing temperature [15].

We propose the following explanation for the striking anisotropy in the surface magnetic force constants. Looking at the RW displacement patterns at one-half of the Brillouin zone (insets of Fig. 2), the *in-plane* exchange interactions exerted by nearest neighbors (nn, solid circles) on any surface atom are modulated by the RW displacement in the same way for both symmetry directions. On the contrary, the *in-plane* exchange interactions exerted on a surface atom by second-nearest neighbors (2nn, open circles) are modulated by the RW in the [001] direction, whereas in the [1$\bar{1}$0] direction they are not. Along this direction 2nn exchange modulation comes only from *out-of-plane* interactions, i.e., between spins in the first and second layers. Thus, the experimental results can be explained if the in-plane 2nn exchange is strongly reduced in the surface plane. In this case the exchange attraction would be insufficient to compensate the in-plane repulsion induced by volume magnetostriction. As a result the shear vertical modes such as the RW are softened in the presence of magnetization as observed along [001]. Such an effect depends on bulk magnetostriction, in agreement with the conclusion drawn from the fit of the data along [001].

The important conclusion of this work is the demonstration that surface phonons can work as a sensitive, geometrically selective probe of surface magnetic interactions through an accurate study of the temperature dependence.

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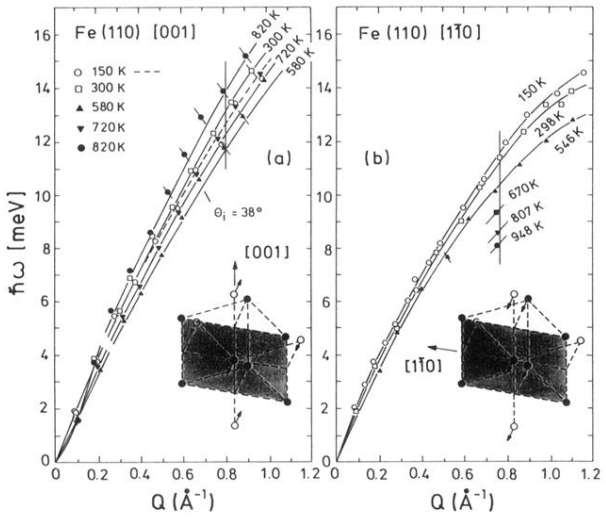
[20] S. K. S. Ma, F. W. de Wette, and G. Alldredge [Surf. Sci. **78**, 598 (1978)] have determined the bulk and surface mean-squared displacements of Fe(001) from the improved Johnson (IJ) potential which gives a good description of both thermal expansion and surface relaxation. They find $\langle u^2\rangle_0 = 0.16\times10^{-18}$ cm^2, and a surface-to-bulk ratio of the mean-squared displacements normal to the surface $\langle u^2\rangle_{0s}/\langle u_z^2\rangle_0 = A_s/A = 1.38$. A is practically constant over most of the Brillouin zone, with sizable deviations only around Γ: see, e.g., Fig. 7 in A. Larose and B. N. Brockhouse [Can. J. Phys. **54**, 1990 (1976)] for copper, where one finds $A = 0.021 \pm 0.002$. For comparison electron-energy-loss-spectroscopy data for the open surface Cu(110) [A. P. Baddorf and E. W. Plummer, Phys. Rev. Lett. **66**, 2770 (1991)] are well fitted with $A_s = 0.045 \pm 0.002$, which gives a ratio A_s/A slightly larger than 2. We present elsewhere [G. Benedek and J. P. Toennies (to be published)] a discussion of surface anharmonicity enhancement as found in copper and aluminum surfaces by HAS.



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