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The kinetic energy dependent effective Debye temperature for CoS$_2$ (100)

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Small lattice distortions could have a profound influence on the spin asymmetry near the Fermi level in highly polarized materials, as has been suggested for both CoS$_2$ [1] and NiMnSb [2]. For CoS$_2$, small displacements of the sulfur atom in the unit cell affect the position of the spin minority bands [1]. The placement of these bands with strong sulfur weight, with respect the Fermi level, can dramatically alter the polarization [1]. Furthermore, since the vibrational structure at both surfaces and interfaces can have a profound effect on the polarization [3] and polarization injection [4], low Debye temperatures, particularly at interfaces, are generally undesirable for spin filters and spin injection. Cobalt disulfide (CoS$_2$) has been measured to be highly spin polarized [5] with a Curie temperature in the range of 116–120 K [6], but the role of dynamic motion on the band structure and polarization has not yet been clearly established.

The Debye temperature is a key descriptive parameter of the dynamic motions of atoms on the surface, as well as in the bulk. The surface Debye temperature of single crystal materials can be investigated by low energy electron diffraction (LEED) [7–12], X-ray photoemission spectroscopy (XPS) or valence band photoemission (PES) [11–16], inverse photoemission [17] as well as atom beam scattering and other surface sensitive techniques. With LEED and the various electron spectroscopies, the electron mean free path plays a key role in establishing the effective Debye temperature [11, 12], representative of motion along the surface normal. Generally, in electron scattering and electron spectroscopy techniques it is assumed, in the absence of surface phase transitions, that the emerging electron beam intensity depends exponentially on the sample temperature [7–17]

$$I = I_0 \exp(-2W)$$  \hspace{1cm} (1)

where $W$ is Debye–Waller factor given by

$$2W = |\Delta k|^2 (u_0)^2$$  \hspace{1cm} (2)
where $\Delta k$ is the wave vector transfer and $\langle u_i^2 \rangle$ is the mean square displacement of the atoms. In the Debye model of thermal vibration, in the case of isotropic vibration, $W$ is described as

$$2W = \frac{3T(h\Delta k)^2}{mk_B\theta_D^2}$$

(3)

where $T$ is the sample temperature, $h\Delta k$ is the electron momentum transfer, $m$ is the mass of the scattering center, and $\theta_D$ is the effective Debye temperature. This Debye temperature is dominated by dynamic motions normal to the surface in almost all experiments and typically does not contain significant in plane or anharmonic contributions to the true Debye temperature.

In this Letter, we investigate the Debye temperature of CoS$_2$ (100) by LEED as a function of electron kinetic energy, comparing the data to temperature dependent XPS, and LEED I(V) analysis. Because of the different scattering geometries, we estimate the electron momentum transfer differently for LEED and XPS. For LEED, the momentum transfer is

$$|\Delta \vec{k}| = |\vec{k}_f - \vec{k}_i| = \left| 2k\cos\frac{\theta}{2} \right|$$

(4)

where $\theta$ is the angle between surface normal and diffracted electron beam [9, 10, 15]. For the case of CoS$_2$, as with other multicomponent crystals [7, 11, 12], the mass of the scattering center in LEED is the average mass calculated from one cobalt atom and two sulfur atoms. Due to geometry of our LEED experiments here, the scattering vector is close to the surface normal, so $\theta$ is very small. For XPS, the momentum transfer is the momentum of the emitted photoelectron [11–16]. Since the photoelectrons were collected normal to the surface ($\theta = 0$), the vibrational motions normal to the surface are again the dominant contribution to the Debye–Waller factor. In XPS, the element of origin for emitted photoelectron determines the mass of the scattering centers [11, 12, 15]. In our experiment, we monitored the photoelectron intensity from the 2p$_2/3$ shell of the cobalt atoms and the 2p shell of the sulfur atoms (using MgK$_\alpha$ radiation at 1253.6 eV). The X-ray photoelectron spectroscopy (XPS) studies were performed with a Gammaxdata Scienta SES-100 electron energy hemispherical analyzer and a SPEXS X-ray source. LEED intensity versus voltage data, when complemented by dynamical scattering calculations (i.e. dynamical scattering analysis of the I(V) curves for multiple diffraction beams) can also be used to obtain a layer by layer estimate of the effective Debye temperature [7]. Such LEED I(V) analysis has already been used to determine the structure of the CoS$_2$ (100)-(1×1) surface [18] using an automated tensor LEED program [19, 20].

The success of this work depends on a surface stoichiometry that is well characterized and not susceptible to surface segregation under experimental conditions. The surface of CoS$_2$ has been established, with the surface stoichiometry preserved under our experimental conditions [18]. The preparation of the surface structure, schematically shown in the inset to Figure 2, was made possible by the cleavage of sufficiently large CoS$_2$ (100) single crystals (millimeters in diameter), prepared by chemical vapor transport, as detailed elsewhere [5]. These crystals, when cleaved, provide low energy electron diffraction (LEED) patterns characteristic of the highly ordered 1×1 surface [18].

Figure 1 shows the temperature dependent LEED intensities, after background ($I_{bg}$) subtraction and normalization to the value $I_0$ at the lowest temperature, for two different electron energies ($107$ eV and $121$ eV). Multiple sets of data were taken at six different incident electron energies ($89$, $107$, $121$, $167$, $213$ and $222$ eV). The effective Debye temperatures were derived from the data to be $326 \pm 9$ K (at $89$ eV incident electron energy), $405 \pm 8$ K (at $107$ eV), $460 \pm 7$ K (at $121$ eV), $542 \pm 21$ K (at $167$ eV), $595 \pm 23$ K (at $213$ eV) and $612 \pm 24$ K (at $222$ eV), using Equation (1). These different Debye temperatures have been plotted against electron energies in Figure 2 (panel (a)). As the incident electron energy increases so does the electron mean free path and effective probing depth [10] and [21]. Thus a smaller electron kinetic energy should be more surface sensitive, and larger electron kinetic energy would be more dominated by the bulk.

The inelastic mean free path $\lambda$ can be roughly described as [21–23]:

$$\lambda = \frac{E}{E_p^2[\beta \ln(\gamma E) - (C/E) + (D/E^2)]}$$

(5a)

where $E$ is electron kinetic energy, $E_p = 28.8(N_e\rho/M)^{1/2}$ is roughly the free electron plasmon energy, $N_e$ is the number of valence electrons per atom, $M$ is the atomic or molecular weight, $\rho$ is the density and $\beta$, $\gamma$, $C$ and $D$ are fitting parameters that can be expressed as:

$$\beta = -0.1 + 0.944/(E_p^2 + E_g^2)^{1/2} + 0.069\rho^{0.1},$$

(5b)

$$\gamma = 0.191\rho^{-0.5},$$

(5c)

$$C = 1.97-0.91U,,$$

(5d)

$$D = 53.4-20.8U,,$$

(5e)

$$U = N_e\rho/M = E_p^2/829.4$$

(5f)

where $E_g$ is the bandgap energy. This ensemble of equations (sometime known as TPP-2M) [22, 23], may be used to assess the electron mean free path in the surface region of CoS$_2$ exploiting the NIST Electron Inelastic Mean Free Path database (version 1.1) [24]. The effective attenuation length (EAL) has been calculated using the approach of Seah [25]:

$$EAL = \lambda(1-0.028Z^{0.5}[0.501+0.068\ln(E)])$$

(6)

where $\lambda$ is the inelastic mean free path, $Z$ is the atomic number of the compound and $E$ is the electron kinetic energy. We have to divide this effective attenuation length by factor of 2 because the collected electrons from LEED experiments go through the surface region twice (in and out), and this is partly the basis for the much greater surface sensitivity of LEED than XPS for a given energy. The change of inelastic mean free path (IMFP) and effective attenuation length (EAL), for CoS$_2$ (100), as a function of the kinetic energy of incident electrons are summarized in Figure 2(b) for several choices of the number of valence electrons per chemical formulae unit (7, 4, and 1).

Caution should be used in interpreting these numbers, not simply because this is an approximation but also be-
cause this equation describes effective attenuation length from overlayer-film samples that are measured by photo-emission techniques. Admittedly, this is an imperfect model for calculating effective attenuation lengths as discrepancies are very evident between the slope of fitting curve in Figure 2(a) and that of probing depth in Figure 2(b). This comparison between experiment and theory indicates that a calculation of attenuation length based on the valence electron count is fraught with uncertainty and that a better method for calculation attenuation lengths needs to be derived, particularly at lower electron kinetic energies. The modeling methodologies need to be better than just a plasmon loss model based on electron count for compound systems. Compound systems like Fe$_3$O$_4$ (also a high polarization ferromagnet) can exhibit a more dramatic logarithmic dependence on electron energy than other metals [26]. What exactly is the electron count contributing to inelastic electron losses due to plasmons and what are the matrix elements for the other various loss mechanisms is not clear nor well defined [27]. We have been able to show already that the core can play a role in the plasmon structure for poor metals [28]. Experiment must be the ruler.

As the effective attenuation length is generally experimentally seen to be a logarithmic function of the electron kinetic energy [25] and [26], we have fitted the extracted experimental effective Debye temperature, as a function of electron kinetic energy, to a logarithmic function, as shown in Figure 2(a). Therefore there should be a layer dependence of the Debye temperature, and under no conditions for the work here is LEED perfectly sensitive to the surface or bulk alone. Nonetheless, the general trend is clear from Figure 2, and there is general agreement with our other measurements of the Debye temperature.

Our effective surface Debye temperature of 326 ± 9 K obtained at 89 eV incident electron energy, which should be more representative of the surface, is reasonably consistent with the surface Debye temperature values of 350 K and 460 K for cobalt and sulfur respectively, obtained from the LEED I(V) analysis for data taken at room temperature alone, as partly described elsewhere [18]. These estimates for the Debye temperatures, obtained from the LEED I(V) analysis, consider multiple scattering, and we note that there are associated complications that may affect the value and accuracy of the Debye temperature estimated in this fashion. The Debye temperature extracted from the LEED I(V) analysis employs the experimental data taken at room temperature and the effective Debye temperature is just an adjust parameter in the LEED I(V) analysis and obtained from an optimization procedure. In the kinematic limit, the Debye–Waller formalism applies and the Debye temperature extracted in this manner depends on the temperature itself. In the case of surfaces, the Debye temperature will also depend on anisotropic vibrational contributions and also have some layer dependence. Regrettably, the thermal
Table 1. \( \text{CoS}_2 (100) \) Debye temperatures

<table>
<thead>
<tr>
<th>Method and analysis technique</th>
<th>Surface Debye temperature</th>
<th>Bulk Debye temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>LEED scattering intensities versus temperature</td>
<td>326±9 K</td>
<td>612±24 K</td>
</tr>
<tr>
<td>Tensor LEED I(V) analysis: cobalt</td>
<td>350 K</td>
<td>600 K</td>
</tr>
<tr>
<td>Tensor LEED I(V) analysis: sulfur</td>
<td>460 K</td>
<td>800 K</td>
</tr>
<tr>
<td>XPS intensities versus temperature: cobalt</td>
<td>555±21 K</td>
<td></td>
</tr>
<tr>
<td>XPS intensities versus temperature: sulfur</td>
<td>511±26 K</td>
<td></td>
</tr>
<tr>
<td>Bulk heat capacity</td>
<td>489±5.1 K</td>
<td></td>
</tr>
</tbody>
</table>

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than the values for the bulk Debye temperature of 489±5.1 K, obtained from heat capacity measurements (as has been done for polycrystalline samples [6]) taken from \( \text{CoS}_2 \) single crystals in the temperature range 1.8 to 200 K. These latter values of the Debye temperature should be less than those obtained from LEED and XPS, as the measurement should include contributions along other crystallographic directions and significant anharmonic motion. The bulk heat capacity measurement is one outlier in the bulk Debye temperature but the heat capacity measurement is measuring an overall Debye temperature, is not just measurement characteristic of normal motion along (100). This comparison of Debye temperature values is summarized in Table 1.

When comparing the Debye temperatures for the surface and the bulk, we may use a simple assumption that the surface vibration amplitudes \((\sigma u)^2\) in Equation (2) are enhanced when the number of nearest atoms surrounding surface atoms is halved compared with neighbor atoms of bulk atoms [10]. The negative correlation between vibration amplitudes and Debye temperature indicates that the Debye temperature for bulk is \(\sqrt{2}\) times greater than that for surface. Considering the uncertainties in the absolute values and accuracy of the derived Debye temperature, these Debye temperatures for the surface and the bulk differ by far more than the expected simple geometrical factor of \(\sqrt{2}\) [10]. For a close packed surface, these general arguments imply that the Debye temperatures for the surface and the bulk differ by less than a simple geometrical factor of \(\sqrt{2}\).

Effective surface and bulk Debye temperature differ dramatically when the composition of the surface is vastly different from the bulk. This might explain the prior results for \( \text{La}_{0.35} \text{Pb}_{0.65} \text{MnO}_3 (100) \) [12], but such an explanation cannot be applied here or in the case of \( \text{ErAs} (100) \) films [11], as the stoichiometry of the surface is that of the bulk. What these results tend to indicate is that there is a surface layer relaxation for \( \text{ErAs} (100) \) [11] and \( \text{CoS}_2 (100) \), which although small [18], permits the surface atoms to exhibit large amplitude soft vibrational modes of low energy along the surface normal.

Because of plasmon–magnon and magnon–phonon interactions, the spin injections will also clearly be dependent upon electron energy, particularly in the hot electron regime, without even the additional considerations necessary due to the details of the electronic structure at the interface of \( \text{CoS}_2 \) and a semiconductor. Strong inelastic scatter-
of the electron from particle–hole and collective excitations (plasmons) will shorten the mean free paths that can be spin dependent [29–33]. Furthermore, understanding of the spin dependence of the inelastic mean free path is critical to the interpretation of results from spin-polarized electron spectroscopies since plasmon–magnon coupling can occur [34]. In high polarization materials, magnon–phonon coupling can also occur [35], and is seen in materials with Debye temperatures little different (where known) from CoS$_2$, as reported here. Particularly pertinent to the discussion here, we note that in high polarization materials there is a delicate balance of energies to maintain the high values of electron polarization at the Fermi level, as small adjustments in atomic positions may have profound effects upon the density of states in the minority spin channel. Such lattice distortions can occur with anharmonic vibrational motion of the lattice so that the low Debye temperature may implicate a phonon mediated reduction to spin injection and spin polarization in this and related materials. Clearly a simple plasmon model for estimating the electron effective attenuation length is insufficient, as is demonstrated here.

In conclusion, we have found the effective Debye temperature for CoS$_2$(100) single crystals varies roughly as the logarithm of the incident electron kinetic energy, or proportional to the expected functional for the elastic mean free path. The experimental values obtained from temperature dependent LEED are in general agreement with expectations from LEED I(V) analysis, from data taken from room temperature alone, temperature dependent XPS and heat capacity. While there are few experimental determinations of the surface Debye temperature for compound systems, usually because of problems with surface characterization and preparation, we have also been able to estimate a Debye temperature descriptive of motion largely along the surface normal for CoS$_2$(100).

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