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Temperature influence on the valence Compton profiles of aluminum and lithium

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We present temperature-dependent valence Compton profiles of single-crystalline Al and Li measured with 30 keV incident energy and 173° scattering angle with momentum space resolution of 0.1 a.u. The valence profiles for both samples measured at low temperature are above the high-temperature ones at momentum $p_z \approx p_F$, the Fermi momentum, and below at $p_z = 0$ a.u., which corresponds to a narrowing of the valence Compton profiles with increasing temperature. This fundamental temperature dependence can be attributed to the variation of the lattice constant and thus the variation of the Fermi momentum with temperature when the experimental results are compared with jellium calculations of the valence Compton profiles utilizing a correlation corrected occupation number density. In addition the Li experiment shows a significant temperature dependence even for $p_z > p_F$, which is assigned to the diminished contribution of higher momentum components to the valence Compton profile with increasing temperature. The Li results are in good agreement with calculations using an empirical temperature-dependent local pseudopotential.

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I. INTRODUCTION

Experimental studies on simple metals are suited for the study of fundamental problems like electron-electron correlation in solid-state physics. These metals are model systems to test theoretical calculations and the limits of different theoretical approaches.

Recent high-resolution Compton profile (CP) measurements of Al[1,2] show good overall agreement between experiment and Korringa-Kohn-Rostoker (KKR)–local-density-approximation (LDA) theory by introducing electron-electron correlation utilizing a model for the occupation number density $N(k)$ where the renormalization constant z is the only free parameter.[3] The value of z is estimated to be approximately 0.75, which agrees with the result from coincidence Compton measurements.[4]

In contrast, CP measurements on Li[3,5,6] and LiMg alloys[7] show significant discrepancies between experiment and KKR–LDA theory, in which the electron-electron correlation is included via the Lam-Platzman correction.[8] The experimental valence profiles are above the theoretical ones at $p_z > p_F$ and below near the center of the profile. Calculations by Kubo,[9] where the *GW* approximation is utilized, show much better agreement with experiment and yield the renormalization constant z to be 0.25 averaged over all calculated crystallographic directions. But it was emphasized by Schülke[10] that Kubo's calculations exhibit an unphysical behavior of the imaginary part of the self-energy at the Fermi level. Schülke calculated z to be 0.75 and roughly the same result, namely, 0.72, was determined by Eguiluz *et al.*[11] Recent quantum Monte Carlo calculations for solid Li disagree also with Kubo's predictions and indicate that the electron-electron correlation in the case of Li accounts only for 30% of the discrepancy between experiment and theory.[12] The disagreement between theory and experiment seems to prevail, and Barbiellini[13] has criticized the fact that all these theoretical calculations[5,10–12] use many-body wave functions within the free fermion nodal structure. Most recent full-potential linear augmented plane-wave (LAPW) calculations, correlation corrected within the Lam-Platzman formalism, show a somewhat better agreement with the experimental Li valence CP's and its first derivatives than the KKR–LDA theory.[14] However, the directional differences are still overestimated, which is traced back to neglecting anisotropic electron-electron correlations when using the Lam-Platzman scheme.

A different approach was used by Dugdale and Jarlborg[15] to explain the discrepancies in the case of Li. They simulated thermal disorder by introducing static disorder within a supercell calculation using a self-consistent linear muffin-tin orbital (LMTO) scheme. This resulted in a better agreement between experiment and theory in the sense of an increasing momentum space delocalization of the CP with increasing temperature. This approach seems reasonable, especially because LDA calculations usually neglect the influence of temperature on the momentum space density. Chen *et al.*[16] measured Li CP's at 90 K and 300 K and found that the difference at $p_z = 0$ a.u. has the same sign but a much smaller amplitude than that predicted by Dugdale. This diminished amplitude is explained to be the result of neglecting the variation of the lattice constant with temperature in the LMTO calculation. But Chen *et al.*[16] do not present calculations to quantify how the change of p_F with temperature might influence their experimental results, especially the oscillations of the experimental difference in the range 0 a.u. $> |p_z| > 1.5$ a.u. Therefore, this experiment cannot be considered to be in favor of the predictions of the thermal disorder model of Dugdale and Jarlborg.

The aim of our study is to examine the validity of the supercell LMTO model by measuring the temperature dependence of the valence CP's for two different systems, namely, Al and Li. The electron momentum density of Al including its lattice induced higher momentum components (HMC's) is nearly isotropic,[17] so that the directional CP differences are found to be small compared to Li[18] and the main contributions of the HMC's cannot be assigned to a single directional valence CP. The total spectral weight outside the Fermi sphere (as a fraction of the number of conduction electrons) is hardly smaller in Li than in Al.[19] However, the electron momentum density of Li exhibits a strong lattice induced contribution strictly centered around $\mathbf{p}=(0.6,0.6,0)$ a.u.,[17] so that the corresponding valence CP measured with $\mathbf{q}\|[110]$ is much more affected by the HMC contributions than the directional CP's with $\mathbf{q}\|[100]$ and $[111]$.[3,5,12] The choice of these two systems gives the possibility to distinguish between the fundamental influence of temperature on the valence CP for an electron gas and the influence due to the change of the crystal potential with temperature.

II. EXPERIMENT

High-resolution Al and Li Compton profile measurements were performed at the beamline ID15 of the ESRF for different temperatures with a scattering angle of 173° and 30 keV incident energy.[20] The Li CP's for momentum transfer $\mathbf{q}\|[110]$ were measured at temperatures of 295 K and 95 K, which is above the martensitic phase transition of Li at 75 K,[21] with a momentum space resolution of 0.1 a.u. at the Compton peak. Al CP measurements were performed at 15 K and 560 K for $\mathbf{q}\|[111]$ where the momentum space resolution was 0.09 a.u. The Li sample was etched just before the measurements and retained the metallic shine until the end of the experiment. The samples were fixed into a scattering chamber evacuated to 10^{-5} mbar to avoid oxidation, and the temperature was measured utilizing a thermocouple. For both the cooling with the closed cycle cryostat and the heating with a resistance heater a temperature controller was used. The experimental valence electron CP's were evaluated as described elsewhere.[20,22]

The temperature differences $J(p_z,15\,\mathrm{K})-J(p_z,560\,\mathrm{K})$ determined for Al and $J(p_z,95\,\mathrm{K})-J(p_z,295\,\mathrm{K})$ for Li presented in Fig. 1 are given in percent of the corresponding low-temperature valence CP maximum $J(p_z=0\text{ a.u.},15\,\mathrm{K})$ and $J(p_z=0\text{ a.u.},95\,\mathrm{K})$, respectively. The experimental differences have only significant contributions in the p_z regime where LDA theory predicts contributions from the valence electrons to the CP. No temperature dependence of the core electron CP's could be detected within the experimental error.

III. CALCULATIONS AND DISCUSSION

The experimental results are compared with a temperature-dependent free electron calculation of the valence CP's using a model for the correlated occupation number density $N(k)$, where the renormalization constant z is the only free parameter:

$$N(k)=(1-a)-\frac{1}{2}(1-a-z)\left(\frac{k}{p_F}\right)^8,\quad k<p_F$$
$$=\frac{1}{2}(1-a-z)\left(\frac{p_F}{k}\right)^8,\quad k>p_F. \tag{3.1}$$

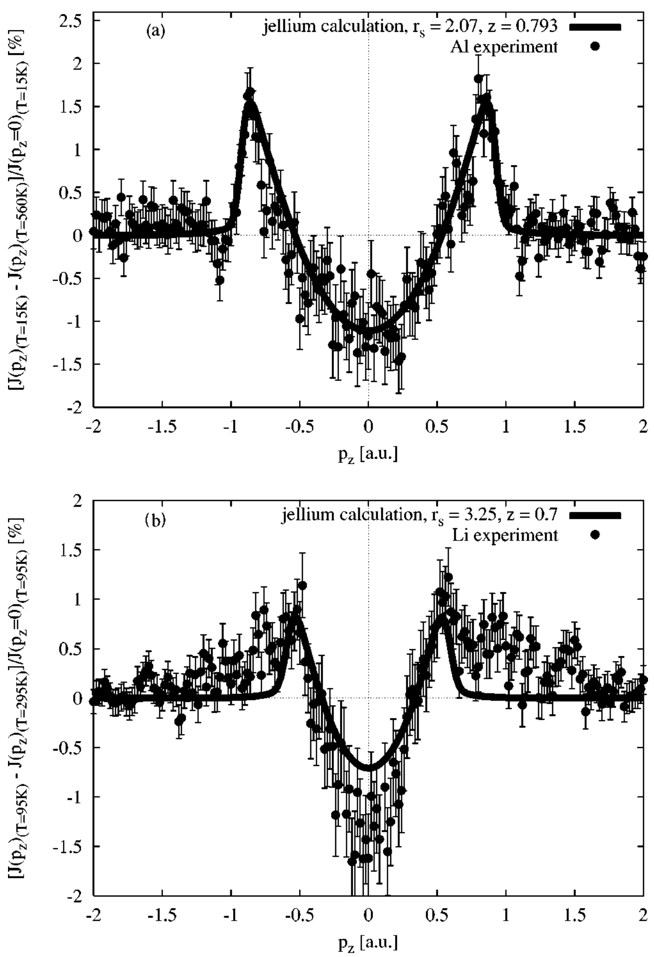

FIG. 1. Experimental valence CP temperature differences for Al [(a)] and Li [(b)] compared with a jellium calculation utilizing a model occupation number density $N(k)$ with a value for the renormalization constant z of 0.793 (Al) and 0.7 (Li).

The constant a equals to $\frac{9}{64}(1-z)$ due to the normalization condition.[3] z is estimated to 0.793 for Al and 0.7 for Li by an interpolation of the occupation function $N(k/p_F)$ of Takada and Yasuhara[23] calculated for $r_s=1$, 3, and 5, where r_s is the radius of the sphere occupied by one electron, in units of the Bohr radius (0.529 Å). The theoretical profiles are convoluted with the experimental resolution function. The influence of temperature is introduced into the jellium calculation by using temperature-dependent lattice constants l. The change of z with temperature, estimated from the $N(k/p_F)$ calculations[23] by taking into account the temperature dependence of r_s, is found to be negligible. The values of l, z and r_s as a function of temperature are presented in Table I. In the case of Al the temperature difference is well described within this model plotted as a solid line in Fig. 1(a). A chi-square test was performed yielding $\chi^2=0.97$ with the definition $\chi^2=1/N\Sigma_{k=1}^{N}(\Delta J_k^{exp}-\Delta J_k^{calc})^2/\sigma_k^2$ where N denotes the number of datapoints, ΔJ_k^{exp} and ΔJ_k^{calc} the experimental and calculated values of the valence CP differences, and σ_k the statistical error of the experimental difference. In contrast to the Al results the experimental temperature difference in the case of Li disagrees significantly with

TABLE I. Temperature-dependent lattice constant, free electron gas parameter, renormalization constant, and Debye parameter of Al and Li.

	Al		Li	
T (K)	15	560	95	295
l (Å)	4.0313	4.0770	3.4848	3.5104
r_s (a.u.)	2.0642	2.0876	3.2424	3.2662
z	0.794	0.792	0.699	0.701
B (Å^2)	0.15	2.08	1.56	4.84

the jellium model ($\chi^2=2.1$). In Fig. 1(b) one can clearly see that the difference exhibits large contributions at $p>p_F$. This deviation from the behavior of Al can be traced back to the decrease of the HMC contributions to the valence CP for $\mathbf{q}\|[110]$ between 1.4 a.u.$>|p_z|>p_F$ when the temperature increases. Therefore, it is necessary to include the effects of temperature on the crystal potential within a calculation of the CP of Li. But, nevertheless, both samples show the same principal behavior, which is in contrast to the predictions of Dugdale and Jarlborg[15] and different from the results of Chen *et al.*[16]

Calculations using an empirical local pseudopotential scheme were performed to separate the effects of the change in lattice constant from those arising from the HMC contributions. The pseudopotential coefficients were determined by fitting the calculated directional differences to experimental differences from Ref. 3. Only the pseudopotential coefficients of the $\langle 110\rangle$ and $\langle 200\rangle$ type were necessary to fit the room temperature CP differences with $V_{110}(T=295\,\mathrm{K})=0.1$ a.u. and $V_{200}(T=295\,\mathrm{K})=0.02$ a.u. To simulate the influence of temperature on the crystal potential due to thermal disorder the pseudopotential coefficients were multiplied by a Debye-Waller factor

$$V_{\mathbf{g}}(T)=V_{\mathbf{g}}(T=0\ \mathrm{K})\,e^{-B(T)(|\mathbf{g}(T)|^2/(16\pi^2))}, \tag{3.2}$$

with the reciprocal lattice vector $\mathbf{g}$ and the Debye parameter $B(T)=B_0+B_T=8\pi^2/3\langle u^2\rangle$ derived from results of recent experimentally determined phonon density of states measurements,[24] where $\langle u^2\rangle$ denotes the mean-square vibrational displacement of the atoms, B_0 the zero-point energy parameter, and B_T the thermal Debye parameter. The total Debye parameters presented in Table I are somewhat different from the outdated values utilized in Ref. 20. This method is routinely used to include temperature effects into pseudopotential calculations concerning the determination of semiconductor band gaps,[25] and it was successfully applied in the calculation of the influence of thermal disorder to the dynamic structure factor of Al.[26] $V_{110}(T=95\,\mathrm{K})$ and $V_{200}(T=95\,\mathrm{K})$ were determined to be 0.114 a.u. and 0.026 a.u. using Eq. (3.2). The calculated pseudopotential CP's were corrected for electron-electron correlation using the difference between the isotropic $N(k)$ model of Eq. (3.1) with ($z=0.7$) and without correlation ($z=1.0$), which is close to the Lam-Platzman correction. Since the influence of the crystal potential was shown to have only a minor effect on the renormalization constant z,[10,11] the choice of the isotropic correlation model seems to be justified and the temperature influence due to thermal disorder on the correlation correction is neglected. The CP's were convoluted with the experimental resolution and the temperature differences were normalized to the maximum of the 95-K profile as done with the experimental ones. Within this calculation the variation of the lattice constant with temperature and therefore the change of p_F was also included. In Fig. 2(a) the experimental temperature difference $J(p_z,95\,\mathrm{K})-J(p_z,295\,\mathrm{K})$ for Li is compared to the calculated one (solid line). The theory agrees well with the experiment ($\chi^2=0.89$) especially when the p_z regime dominated by the HMC contributions is considered. To separate the part of the difference that is due to the change of the HMC contribution to the valence CP a second pseudopotential calculation was performed where only the temperature dependence of the lattice constant and therefore of the Fermi energy was included, whereas the

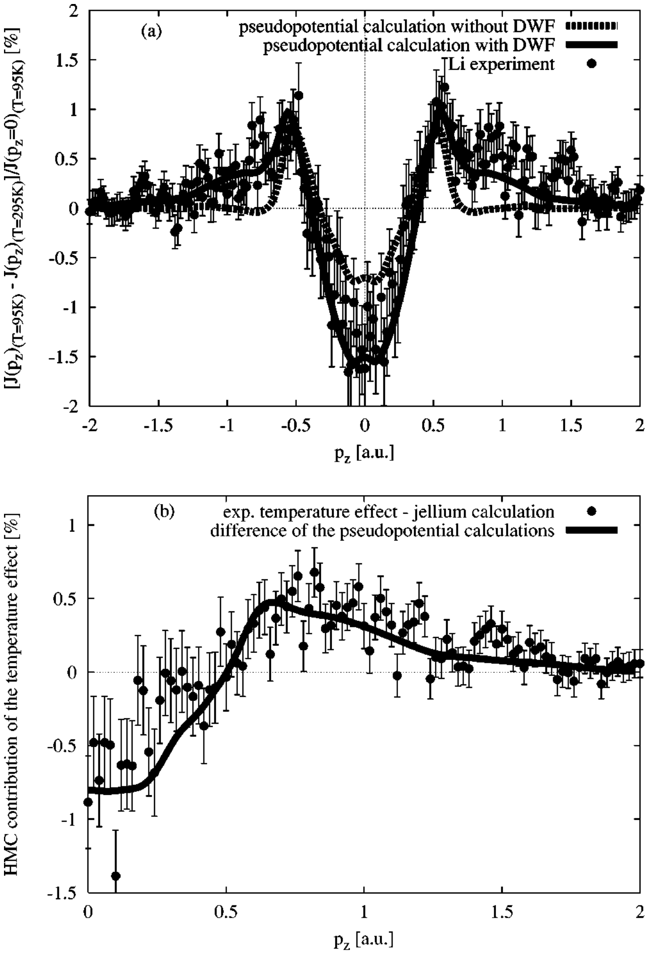

FIG. 2. (a) The experimental temperature difference for Li compared with a pseudopotential calculation with (solid line) and without (dashed line) consideration of the temperature influence to the crystal potential via Debye-Waller factors. The part of the temperature dependence that is due to the contributions of the HMC's to the valence CP is presented in (b) by calculating the difference between the symmetrized experimental temperature effect and the jellium calculation (points) compared with the difference between the pseudopotential calculation with and without Debye-Waller factor (solid line).

pseudopotential coefficients were chosen to be those at room temperature for both temperatures. Figure 2(a) shows the result ($\chi^2=2.2$, dashed line), which is almost identical to the jellium calculation. In Fig. 2(b) the difference between the symmetrized experimental temperature difference and the jellium calculation for $z=0.7$ is shown presenting the part of the temperature effect that is not attributed to the variation of the lattice constant. This is compared with the difference of the pseudopotential calculations with and without temperature-dependent crystal potential. The difference exhibits a good overall agreement and confirms the assignment of the contributions in the experimental temperature differences for $p>p_F$ to the temperature dependence of the HMC's. With increasing temperature momentum density is transferred back to the primary Fermi sphere of the extended zone scheme, and the valence CP becomes more and more free electron like. This interpretation is in agreement with the experimental results of positron annihilation measurements on potassium[27] showing that the contributions of the HMC's decrease with increasing temperature. Within the limits of the present experiment, it is not possible to measure directly the effect of the zero-point lattice motion on the valence CP. Nevertheless, the zero-point lattice motion should also cause an additional diminishing of the HMC contributions to the valence CP and is usually neglected in standard CP computations. Since the zero-point motion in the case of light elements is rather large, $B_0=0.96\,\text{Å}^2$ for Li,[28] it should be included into the CP calculations of those elements.

IV. CONCLUSION

In conclusion, measurements of the temperature dependence of Al and Li valence CP's are presented. The high-temperature valence CP's are above the low-temperature profiles at $p_z=0$ a.u. and below at $p_z\approx p_F$. This general behavior, that the CP's are narrower at high temperatures, is traced back to the variation of the lattice constant with temperature when the experiment is compared with temperature-dependent jellium calculations using a correlated occupation number density. The Al temperature difference is well described within this model, whereas, for Li, large contributions in the experimental temperature difference at $p_z>p_F$ are found. These additional contributions could be assigned to the temperature dependence of the HMC's. Good agreement with empirical local pseudopotential calculations is obtained, where the influence of temperature to the crystal potential due to thermal disorder is considered by using Debye-Waller factors within the pseudopotential scheme. In contrast to Li the directional CP differences in Al are found to be small, so that the main part of the HMC contribution to the valence CP cannot be assigned to a special directional CP. Moreover, the variation of the lattice constant with temperature amounts 1.1% for Al compared to 0.7% for Li (see Table I), whereas the change of the Debye parameter is $1.93\,\text{Å}^2$ for Al and $3.28\,\text{Å}^2$ for Li (see Table I). Therefore, in Al the temperature effect due to the lattice expansion dominates and the influence of thermal disorder on the valence CP is estimated to be within the experimental error. Due to the fact that the measured temperature differences are opposite in sign to the LMTO calculations of Dugdale and Jarlborg[15] it can be ruled out that the discrepancy between Lam-Platzman corrected KKR–LDA calculations and experiment is due to thermal disorder. The experimental results suggest that the discrepancy between theory and experiment will be enlarged, when thermal disorder is considered within the band calculations. This might encourage a more careful look into the reasons for the discussed discrepancies by going beyond the LDA and the isotropic Lam-Platzman correction.

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