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Electronic structures of gallium and indium across the solid-liquid transition

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Electronic structures of gallium and indium in the solid and liquid states have been investigated using photoemission and bremsstrahlung isochromat spectroscopies yielding information concerning the occupied and unoccupied parts of the density of states. Experimental results are compared with various calculations in order to obtain a detailed description. X-ray photoemission spectra of Ga $2p$ and In $3d$ core levels exhibit shifts across the solid-liquid transition, arising from changes in screening.

I. INTRODUCTION

Both Ga and In are broadband sp metals with s^2p^1 outer valence shell configuration. In these systems correlation effects are relatively less important and band structure calculations based on one-electron theories normally provide reliable descriptions of the electronic properties. Though these two elements belong to the same group (IIIA), there are some important structural distinctions between Ga and In. The stable structural phase of Ga is the orthorhombic α phase; each Ga has one close neighbor at 2.44 Å and six others between 2.71 and 2.79 Å.[1] The structure is *loosely packed* with directional bonding. Indium, on the other hand, crystallizes in a *close packed* face-centered-tetragonal structure. Liquid Ga retains a loose packed structure with about 9–10 nearest neighbors while liquid In continues to be in a close packed local structure with about 11–12 nearest neighbors.[2] The structural uniqueness of Ga results in an anomalous contraction of the volume by 2.9% on melting;[3] in contrast to most metals, exhibiting a 2–6 % volume expansion on melting. In particular, indium expands by 2.6% on melting.[3]

The nearly free electron (NFE) theory of Ziman,[4] which assumes that the conduction electrons form a free electron gas and are scattered by the ions with appropriate pseudopotentials, has been successful in explaining the transport properties of liquid metals.[5] However, it should be noted that transport properties are influenced by the density of states (DOS) at and around E_F and thus the success of the NFE theory only suggests that the DOS within a few kT of E_F has structureless NFE-like behavior. Photoemission studies have indeed shown[6–12] that the experimental spectra deviate remarkably from the expected parabolic dependence for many heavy polyvalent liquid metals. In particular, earlier photoemission work by Norris and Wotherspoon[6] on liquid Ga suggested that the spectral features between 3 and 7 eV binding energy deviate appreciably from the NFE-like behavior. They observed no major change in the ultraviolet photoemission (UP) spectra of liquid Ga recorded with $h\nu = 10.2$ eV over the temperature range of 320 K to 820 K. However, Greuter and Oelhafen[7] reported that spectral features of liquid Ga within 2 eV of E_F have no structure with a NFE-like dependence. Moreover, these authors also report an apparent increase of the DOS at E_F in Ga on melting. Recent work[8] has confirmed that UP spectra for solid and liquid Ga exhibit substantial modifications in the spectral shape near E_F in disagreement with the findings of Ref. 6. In contrast to the case of Ga, an early study of solid and liquid In by Koyama and Spicer[9] suggested hardly any change in the spectral shape on melting. In both cases, the spectra exhibit a dip around 2–3 eV binding energy. Norris *et al.*[10] also reported a similar dip between 2 and 3 eV for liquid In which has been interpreted[8,11] as the splitting of the s- and p-like spectral features. Hafner and Jank[2,13] have recently published a series of papers on the structural and electronic properties of polyvalent liquid metals. It has been pointed out that the splitting of s- and p-like states in the heavier polyvalent metals[12] is due to relativistic effects, resulting in the appearance of a dip in the density of states.

In this paper, we describe the results of x-ray photoemission (XP) and bremsstrahlung isochromat (BI) spectroscopic investigations of the electronic structures of solid and liquid Ga and In. Systematic investigations of the occupied and unoccupied parts of the DOS of liquid and solid Ga and In using XP and BI spectroscopic techniques have not been performed earlier to our knowledge. In order to understand the electronic structure of the solid in detail, we report the DOS and the various s, p, and d partial DOS's (PDOS's) of solid Ga and In calculated within the linearized muffin-tin orbital–atomic-sphere approximation (LMTO ASA).[14] From these PDOS's, we obtain theoretical XP and BI spectra, by incorporating matrix element effects.[15] Thus by comparing the calculated spectrum with the experiment, the origin of the different spectral features can be ascertained. The modifications in the DOS on melting in these systems have been studied in the past using low photon energies.[7–11] At low photon energies, however, the photoemission cross section of the s-like states is very small compared to those of the p- and d-like states.[2,13] At higher photon energies (e.g., 1253.6 eV), photoemission cross sections of these states are comparable.[2] This makes x-ray photoemission spectroscopy an effective tool to study the behavior of s-like states on melting. We have also recorded UP spectra of solid and liquid Ga as well as In with higher resolution than has been reported so far. Moreover, we also find interesting changes in the Ga $2p_{3/2}$ and In $3d_{5/2}$ core-level XP spectra across the solid-liquid transition.

II. EXPERIMENT

Commercially available Ga and In samples from Alpha Inorganics were of 99.99% purity. A clean surface was obtained by sputtering the sample surface with an argon ion gun. The surface cleanliness was monitored by recording O 1s, C 1s, and Ar 2p core-level spectral regions. The surfaces of liquid and solid Ga showed high stability against contamination from oxygen and carbonaceous products and there was no detectable signal from the contaminants even after 10–12 h in ultrahigh vacuum of the spectrometer chamber. The spectra for liquid Ga and In were measured at various temperatures up to 30 K above their respective melting points of 302.9 K and 429.6 K. Spectra on supercooled liquid Ga at 298 K were also recorded. These spectra showed no discernible dependence on temperature. The spectra for the solid Ga and In were recorded at about 120 K. The spectra were recorded using a commercial spectrometer from VSW Scientific Ltd., U.K. XP spectra were recorded using Mg $K\alpha$ radiation ($h\nu = 1253.6$ eV), UP spectra using He I radiation ($h\nu = 21.2$ eV), and BI spectra at $h\nu = 1486.6$ eV. The overall resolutions were 1.0, 0.14, and 0.8 eV for XP, UP, and BI spectra, respectively. Since the shifts observed in the core-level XP spectra were rather small, the reproducibility of our data was meticulously checked and a very high signal-to-noise ratio was achieved by accumulating large counts (typically 50 000) on the core-level peak. The binding energy shift between the solid and the liquid core-level spectra was determined by the energy shift required to superpose them on the display screen. The smallest shift at which two identical spectra appear clearly shifted provides the detection limit. In this way we could detect a shift as small as 0.03 eV.

Scalar-relativistic LMTO-ASA calculations for Ga were performed in the orthorhombic α phase with eight atoms per unit cell, the lattice constants being $a = 4.510$ Å, $b = 4.486$ Å, and $c = 7.646$ Å (Ref. 1) and for In in the face-centered-tetragonal structure with four atoms per unit cell, the lattice constants being $a = 4.588$ Å and $c = 4.938$ Å (Ref. 16). The DOS was calculated for 216 k points in the irreducible part of the Brillouin zone. The energies E_ν^l for each angular momentum partial wave were chosen to be the center of gravity of the occupied parts of the corresponding PDOS. However, in order to calculate the unoccupied parts of the DOS accurately the E_ν^l's were shifted to 5 eV above E_F. Photoemission cross sections for different angular momentum components were calculated using the converged potential obtained from the LMTO calculation, following the method of Winter *et al.*[15] In order to compare with the experimental spectra, we have included the instrumental resolution and lifetime broadenings. Thus we broaden the cross-section-weighted DOS and PDOS with a Gaussian function with 1.0 eV full width at half maximum (FWHM) for XP and 0.8 eV FWHM for BI spectra. The lifetime broadening at an energy E away from E_F was simulated[17] with a Lorentzian function having FWHM, $2\Gamma = \alpha|E - E_F|$ with $\alpha = 0.3$.

III. RESULTS AND DISCUSSION

In order to discuss the electronic structure of Ga and In in the solid and liquid states, we first show in Figs. 1(a) and 1(b) the calculated total DOS and s, p, and d PDOS's for solid Ga and In, respectively. Band structure calculations reporting the dispersion curves and the shape of the Fermi surface have been performed earlier for Ga and In.[18] Recently, Hafner and Jank[2] have published the DOS below E_F for both solid and liquid Ga and In within the LMTO ASA. The present DOS calculations for the range of energy below E_F agree well with the calculations of Ref. 2. While the DOS is highly structured, there is an overall NFE-like $E^{1/2}$ dependence within 15 eV from the band bottom in both the solids (Fig. 1). The deviation from the $E^{1/2}$ dependence above this energy range arises due to the existence of a low DOS region between p and d PDOS's, particularly noticeable in In around 10 eV above E_F [Fig. 1(b)]. The Ga DOS exhibits a pronounced dip at E_F, which has been ascribed[2] to the partial covalent bonding in the solid. The s PDOS in the case of Ga is primarily located between -11.5 eV and -4 eV with a maximum in the vicinity of -7.5 eV; however, the s PDOS is found to extend significantly above E_F and exhibit a prominent structure just above E_F. On the other hand, the p PDOS of Ga is spread out from the band bottom (-11.5 eV) to 12 eV above E_F with nearly equally high density between -2 eV and 11 eV. For indium the s band moves up, having significant intensity between -10 eV and -2 eV with a relatively broad maximum at about -5 eV. In this case also there is a significant contribution of the s PDOS above E_F. The p PDOS in indium is spread between the band bottom (~ -10 eV) and approximately 12 eV above E_F with relatively higher contribution between -2 eV and 7 eV. The d PDOS contributes states primarily above E_F and increases in intensity sharply beyond 12 eV and 10 eV for Ga and In, respectively.

In order to probe the electronic structure of these sys-

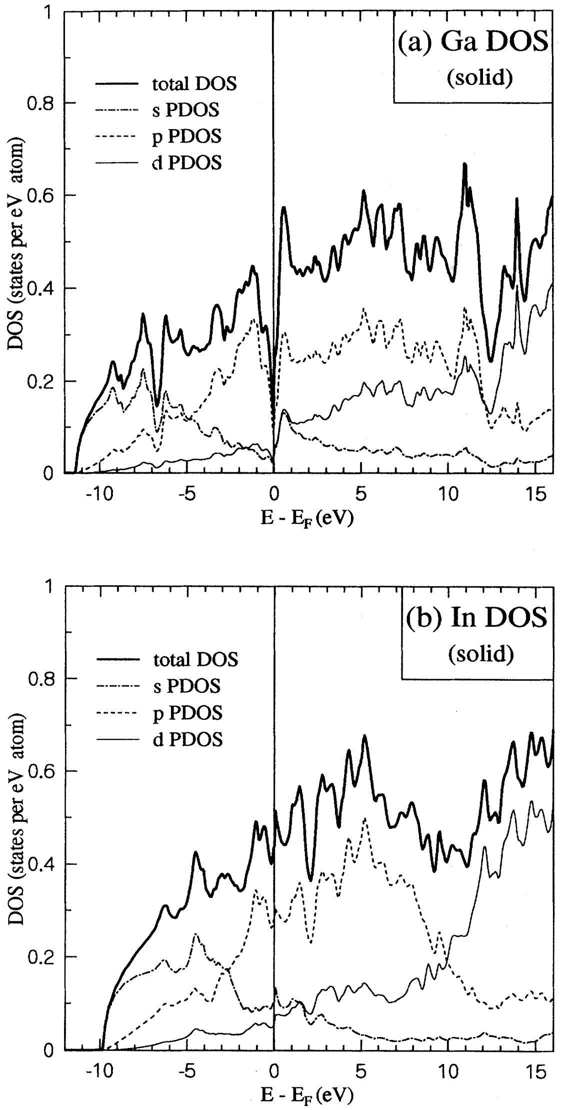

FIG. 1. The DOS and s, p, and d PDOS's for solid (a) gallium and (b) indium calculated within the LMTO ASA.

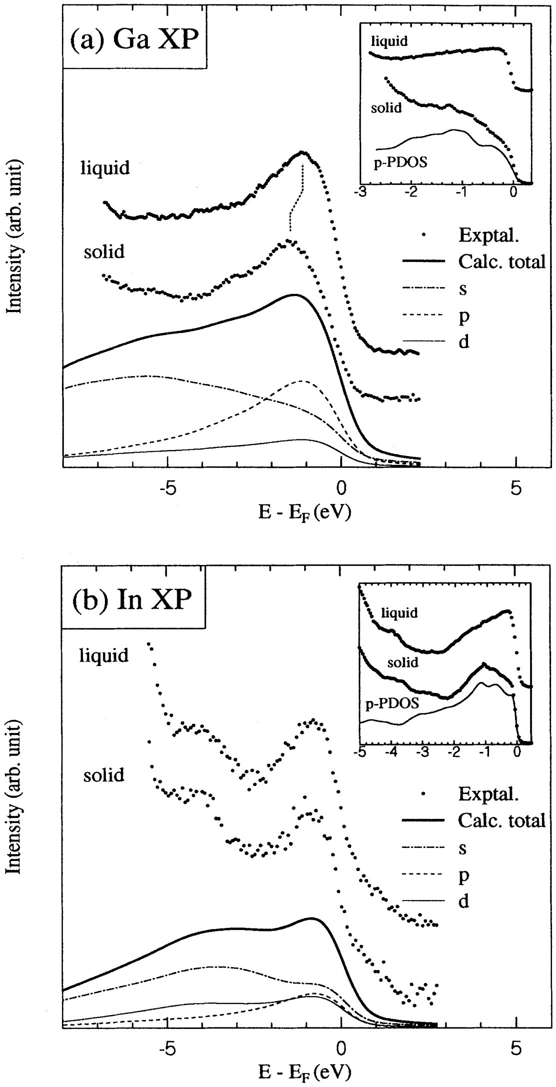

FIG. 2. The experimental XP spectra (dots) for solid as well as liquid, and the calculated XP spectrum for the solid with s, p, and d angular momentum components for (a) gallium and (b) indium. The inset shows the experimental UP spectra (dots) for solid as well as liquid and the p PDOS (solid line) for (a) gallium and (b) indium (see text).

tems experimentally, we have recorded the XP valence band spectra of solid and liquid Ga and In, shown in Fig. 2. The experimental spectra of Ga [Fig. 2(a)] exhibit a strong increase in the background below −6 eV due to inelastic scattering of electrons and the presence of the Mg $K\alpha_{3,4}$–induced photoemission signal from the Ga $3d$ core level. Independent of these effects, a comparison of Figs. 1(a) and 2(a) makes it clear that the DOS cannot be directly compared with the experimental spectrum for solid Ga, without incorporating various effects mentioned earlier, namely, the differing photoemission transition probabilities for states with different angular momentum and energy, and the resolution and lifetime broadenings. The calculated XP spectrum and its angular-momentum-projected components are also shown in Fig. 2(a). The calculated spectrum resembles the experimental spectrum well, with each of the spectral features properly reproduced. Thus the main peak in the experimental spectrum at −1.4 eV arises primarily from p-like states. On the other hand, the weak experimental feature at −3 eV is related to s- and p-like states, while the feature at −5 eV is primarily due to s-like states. However, it appears that the calculated s component is more intense than the experimentally observed feature. This suggests that the calculated matrix elements for photoemission from s-like states are somewhat overestimated compared to those of p- and d-like states in Ga. The same indication is found in the analysis of the BI spectrum corresponding to the unoccupied DOS, discussed later. We further observe that the use of a slightly lower α (~ 0.2) in defining the lifetime broadening would have improved the agreement further by defining the spectral features at -3 eV and -5 eV more clearly in the calculated spectrum. However, such a lower value of α is incompatible with the BI spectrum of Ga. Since our aim here is to identify and interpret the various experimental features with the help of calculations, rather than obtaining a very good simulation of the experimental results, we have preferred to use a single value of α for both XP and BI spectra and leave the calculated transition probabilities as nonadjustable parameters.

It is to be noticed here that the structured DOS for Ga is strongly smoothed out in the experimental XP spectrum due to poor resolution in this technique. We show a higher resolution UP spectrum (with $h\nu = 21.2$ eV) of solid Ga as an inset in Fig. 2(a). The UP spectrum of solid Ga, in the present experiment with better resolution, clearly shows several weak features. The sudden increase in the UP spectral intensity below -2 eV is due to the overlap of the Ga MVV Auger signal.[8] Since the approximations made in calculating the transition probabilities at XP energies are invalid at the low photon energies involved in UP, we cannot calculate the UP spectrum, unlike the XP spectrum. On the other hand, in the near E_F region, both the UP spectra and the DOS are dominated by p-like states[2] and so the p PDOS can be meaningfully compared with the experiment. Thus we show the occupied part of the calculated p PDOS [inset, Fig. 2(a)] including the effect of resolution broadening. The shape of the experimental UP spectrum is similar to that of the p PDOS clearly showing the low intensity at E_F. We find that the p PDOS exhibits features around -1.0 and -2.0 eV and similar features can also be seen at about the same energy positions in the experimental spectrum. Thus it appears that the experimental spectrum is in overall agreement with the calculation, though further experiments with better instrumental resolution are desirable.

The comparison of the calculated and the experimental XP spectra in the case of solid In [Fig. 2(b)] is equally favorable. Thus we find that the experimentally observed features at -0.9 eV and -4 eV are in good agreement with similar features in the calculated spectrum. The rise in the spectral signal below -5.5 eV is due to the Mg $K\alpha_{3,4}$-induced photoemission signal corresponding to the In $4d$ core level. The weak feature at about 1 eV above E_F in the XP spectrum arises from the Mg $K\alpha_{5,6}$–induced photoemission signal corresponding to the In $4d$ core level. The electron configuration of s^2p^1 in In would suggest that the experimental features at -0.9 eV and -4 eV would be interpreted as arising from p- and s-like states, respectively; this would also be justified by the PDOS shown in Fig. 1(b). However, it turns out that the calculated transition probabilities for s and d PDOS are higher than that for the p PDOS's near E_F. This leads to an interesting situation that the calculated XP spectrum has dominant contributions from s-like states over the entire energy range in contrast to Ga. Thus description of the feature at -0.9 eV as primarily In p related would be inaccurate as it has almost equal contributions from the s-, p-, and d-related states. However, the feature at -4 eV has predominant contribution from the s-like states.

We compare the UP spectrum of solid In, dominated by contribution from the p-like states, and the occupied part of the p PDOS in the inset of Fig. 2(b). The experimental spectral shape, showing a moderate dip near E_F due to higher resolution at this photon energy, is in agreement with the calculated p PDOS. The features in the p PDOS at -0.6 and -1.1 eV and a broad and weak feature around -3.0 eV have corresponding features at about the same energy positions in the experimental spectrum. The experimental spectral feature at -4 eV can be related to a similar shaped feature in the DOS appearing at -4.5 eV. Thus, in close similarity to the case of Ga, the UP and XP spectra of solid In are in fairly good agreement with the p PDOS and the calculated photoemission spectrum, respectively.

In the insets of Figs. 2(a) and 2(b), we also compare the UP spectra of liquid Ga and In with the corresponding spectra of the solids, in order to illustrate the changes in the spectral features on melting. The comparison for Ga shows that the spectrum is extensively altered on melting. Except for the sharp cutoff of the occupied density of states at E_F, all the other features observable in the spectrum of solid Ga are completely smoothed out in the spectrum of the liquid and the peak in the spectrum shifts close to E_F suggesting a higher DOS at E_F in the liquid. Thus, on melting, the pronounced dip in the DOS of the solid at E_F is wiped out; this is expected to strongly influence the low energy properties of Ga. The shift of the spectrum towards E_F on melting has been observed in earlier photoemission experiments.[7,8] It is interesting to note here that Ga shows a large change in the Knight shift on melting and this has been attributed to an increase in the DOS at E_F.[5] Thus the Knight shift data is consistent with the present photoemission results. Since the UP spectral features for Ga arise from the structures in the p-like states,[2] one can conclude that the p PDOS is strongly modified on liquefaction. Since the main peak of the solid Ga XP spectra at -1.4 eV is also dominated by p-like states [see Fig. 2(a)], we find that in liquid Ga this peak shifts closer to E_F by about 0.5 eV in agreement with the changes in the UP spectra. Comparison of the solid and liquid Ga experimental XP spectra further shows that the features at -3 eV and -5 eV in the solid are barely observable in the liquid. The dip in the solid Ga XP spectrum at -4 eV is also not present on liquefaction and the s-like states can hardly be distinguished from the p-like states unlike in the solid. The comparison of the experimental and calculated (from Ref. 2) XP spectra for liquid Ga shows a primarily p-like feature at about -1 eV in agreement with the experiment. However, the small dip around -3 eV in the calculated liquid Ga XP spectrum,[2] separating the primarily s-like feature at -5 eV from the p-like feature, is not observed in the experimental spectrum.

The valence band UP spectrum of liquid In [inset, Fig. 2(b)] also shows considerable changes compared to that of solid In, in disagreement with earlier work.[9] Our results demonstrate that the UP spectral features corresponding to *p*-like states up to -3 eV from E_F are smoothed out completely in the liquid. This also shifts the main peak in the spectrum from about -1 eV in the solid to near E_F in the liquid. The weak spectral feature at -3 eV in the UP spectrum of solid In cannot be seen in the liquid. However, the spectral feature at -4 eV, which has mainly *p* and *d* contribution and insignificant contribution from *s*-like states, is relatively unchanged on melting. The calculated[2] UP spectrum for liquid In, which exhibits a smooth spectral shape up to -3 eV, however, does not exhibit any feature at -4 eV in contrast to the experiment. Comparison of the XP spectra of solid and liquid In shown in Fig. 2(b) hardly exhibits changes in the XP spectral features on melting. In particular, the distinct feature at about -4 eV which at this photon energy has its main contribution from the *s*-like states[2] is entirely unaffected. We find that there is no discernible change in the main peak region (around -0.9 eV) as well, though the UP spectrum in this region is strongly altered on melting [see inset, Fig. 2(b)]. Considerably poorer resolution in the XP spectrum is certainly a contributing factor for this. However, we also point out that the UP spectrum up to -3 eV is dominated by *p*-like states, while the XP spectrum has comparable contributions from the *s*-, *p*-, and *d*-like states [see Fig. 2(b)]. This may also contribute to the observation of relatively unaffected XP spectral shape on liquefaction in the case of In. The calculated[2] XP spectrum for liquid In exhibits two clearly separated *p*- and *s*-like features at about -1 eV and -4 eV, in good agreement with the experiment.

It is interesting to note that, though both Ga and In are trivalent *sp* metals, the behavior of the *s*-like states on melting, as observed from the XP spectra, is different between the two. In the case of Ga, the *s*-like states become featureless along with the *p*-like states; but for In the *s*-like states are hardly affected on melting, while the *p*-like states exhibit a featureless spectrum. Comparison of liquid Ga and In XP spectra in Fig. 2 shows a clear separation of the *s*- and *p*-like states in indium while for Ga the *s*- and *p*-like states are not distinctly separated. This can be related to the stabilization of the *s* states in heavier elements due to relativistic effects.[2,13]

Having discussed the changes in the occupied DOS, we now turn to the unoccupied DOS probed by BI spectroscopy. In Fig. 3(a), we show the experimental BI spectra of solid and liquid Ga along with the calculated total and *s*, *p*, and *d* components of the theoretical BI spectrum for the solid. The corresponding spectra for In are shown in Fig. 3(b). The comparison of the calculated and experimental BI spectra of solid Ga shows that these are in good agreement. From this figure [Fig. 3(a)] it is found that the feature near E_F in the experimental spectrum of solid Ga arises primarily from the *s*- and *p*-like states, though *d*-like states also contribute significantly at these energies. The broad and weak spectral features at about 5 eV and 9 eV arise essentially from *p*-like states and the distinct rise in the spectral feature above 14 eV is due to the *d*-like states. On melting, the spectral features become still less distinct, for example, the peak near E_F and the weak features related to the *p*-like states merge into one smoothly varying spectral feature. Thus the spectral changes in the unoccupied part reflect the changes observed in the occupied part, suggesting featureless *s* and *p* spectral features over a wide energy range across E_F. The spectral feature corresponding to the *d*-like states above 14 eV does not show any modification on melting. However, this fact does not preclude the possibility of changes in the *d* component; it is to be realized that the spectral features are smoothed out, even for the solid, at such high energies due to a substantial lifetime broadening.

The calculated and experimental BI spectra of solid In [Fig. 3(b)] show good agreement except for a mismatch around 2 eV in the calculated spectrum. This is probably due to an overestimation of transition probabilities

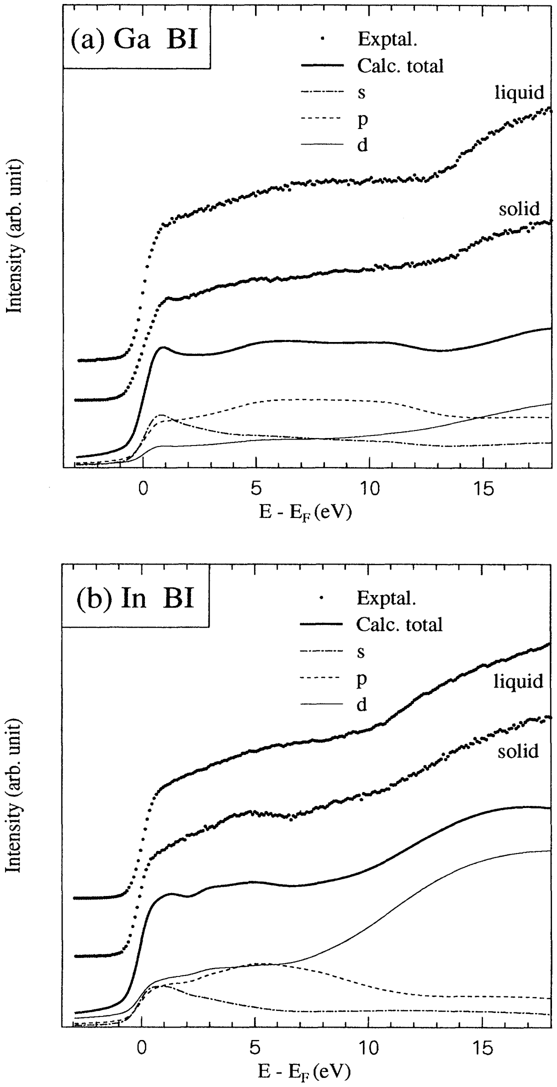

FIG. 3. The experimental BI spectra (dots) for solid as well as liquid, and the calculated BI spectrum for the solid with *s*, *p*, and *d* angular momentum components for (a) gallium and (b) indium.

of the s-like states in the calculation, as discussed earlier. The states up to 2 eV are contributed by s-, p-, and d-like states, while the broad but distinct spectral feature at about 5 eV is primarily due to p-like states. The spectrum is dominated by the d component above 8 eV. On liquefaction, the most noticeable change in spectral features is the disappearance of the peak at 5 eV; it is replaced by a smoothly varying intensity. However, we find that the spectrum above 8 eV is relatively unaffected on melting, as observed for Ga. In the above discussions we have pointed out in detail the changes in the experimental spectra on liquefaction and related these to the changes in the DOS. However, it is to be noted that we do not discuss the validity of the parabolic DOS in the liquid over an energy range, since the photoemission or BI spectral shape can be substantially different from the underlying DOS due to strong matrix element effects.

In order to probe any possible change in the core-level spectra on melting, we have recorded Ga $2p_{3/2}$ and In $3d_{5/2}$ core-level XP spectra for both the solid and the liquid states with very high signal-to-noise ratio. For clarity we show only a part of the spectra around the peaks on an expanded scale in Figs. 4(a) and 4(b). From the figure, it is clearly seen that the binding energy (E_b) shift $\Delta E\ (= E_{b\ \mathrm{liquid}} - E_{b\ \mathrm{solid}})$ is -0.08 ± 0.03 eV for Ga $2p_{3/2}$, whereas it is $+0.08 \pm 0.03$ eV for In $3d_{5/2}$. Thus the core-level binding energies for liquid Ga and In exhibit opposite behavior. In order to qualitatively understand the observed shifts across the solid-liquid transition, we note that within the Thomas-Fermi model the screening length is approximately given by $(r_s/a_0)^{1/2}/2.95$ Å, where (r_s/a_0) is the average radius of the spherical volume available per conduction electron, a_0 being the Bohr radius. If a liquid expands on melting, correspondingly r_s increases, leading to a larger screening length. Such a less compact screening leads to an apparent increase in the binding energy of the core hole on melting via the final state effect. On the other hand, a volume contraction on melting leads to a more compact screening of the core hole thereby leading to an apparent lowering of the binding energy. Thus we indeed expect that Ga, with its contraction on melting, will have lower binding energy in the liquid state, in contrast to In with a volume expansion on melting, in agreement with the observed trend (Fig. 4).

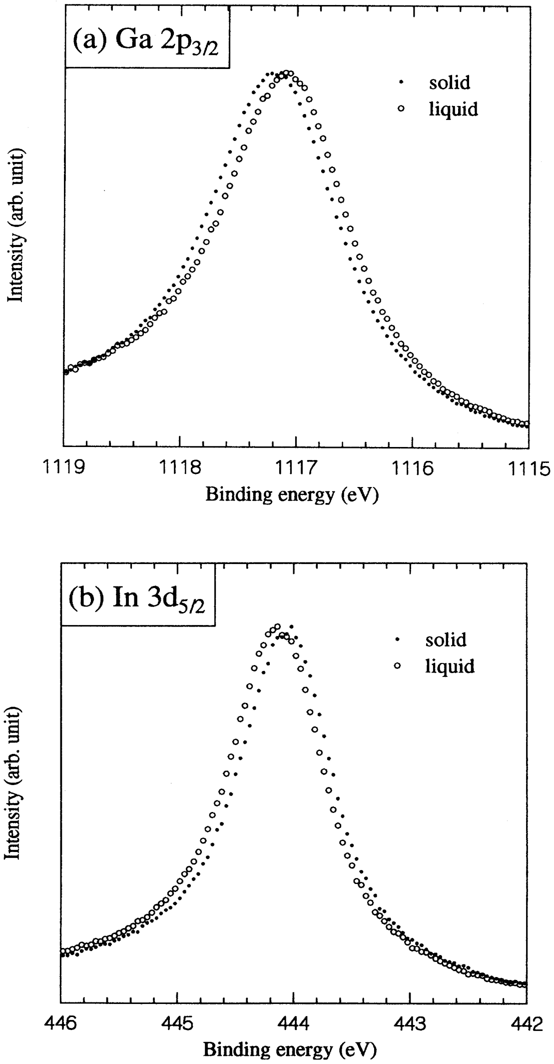

FIG. 4. The (a) Ga $2p_{3/2}$ and (b) In $3d_{5/2}$ core-level spectra for both solid and liquid states.

IV. CONCLUSIONS

We have carried out a comprehensive investigation of the electronic structure of gallium and indium, with specific reference to the effects induced on the electronic structure on liquefaction. We have analyzed in detail the valence band XP as well as BI spectra of solid Ga and In in terms of s, p, and d contributions with the help of band structure calculations. On liquefaction, various spectral features due to the s- and p-like states of Ga change considerably, giving rise to a single smoothly varying spectrum over a wide energy range below and above E_F. This leads to an increase in the DOS at E_F in the liquid due to smearing of a pronounced dip in the DOS present in solid Ga. On the other hand, the spectral weights related to primarily p and s PDOS's do not merge into one continuous spectral feature in liquid In, though the finer details in the p PDOS are smoothed in this case as well. Our studies show that matrix element effects are important in determining the spectral shape and thus, electron spectroscopic techniques cannot be directly used to determine whether a NFE parabolic DOS is obtained in the liquid state. Core-level XP spectra exhibit small binding energy shifts in opposite directions for Ga $2p$ and In $3d$ levels on liquefaction due to differing changes in screening between the solid and liquid states.

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