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The ^{7}Li Knight Shift of Liquid Li-Au Alloys; Properties of the Solid Compound LiAu*

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Abstract

Measurements have been performed of the ^{7}Li Knight shift of liquid Li-Au alloys, both as a function of composition and of temperature. The Knight shift decreases markedly when Au is added to liquid lithium, and is practically independent of temperature. The results are in agreement with a simple tight-binding model in which Li 2s, Au 6s and Au 6p states are taken into account. Additionally, some attention was paid to the solid equiatomic compound LiAu. The ^{7}Li Knight shift and UPS spectra were measured at room temperature. The results are compared with recent band structure calculations on LiAu.

Introduction

During the last ten years the liquid alloy system Cs-Au has been subject of much interest /1/. In this system a metal-nonmetal transition takes place about the equiatomic composition. Recent tight-binding calculations /2,3/ demonstrated that both electron charge transfer from Cs to the much more electronegative Au and the relatively narrow partial Au s band in the equiatomic alloy are essential for this MNM transition. In liquid LiAu the Au partial bands are expected to be broader because the Li atom is smaller than the Cs atom. Indeed, tight-binding calculations

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on liquid Li-Au alloys predicted that this system is metallic for all concentrations /2,3/. This prediction finds some support in the observation that the electrical resistivity of equiatomic liquid LiAu is definitely within the metallic regime /4/. We investigated the validity of the aforementioned tight-binding calculations more extensively by measuring the ^{7}Li Knight shift in liquid Li-Au alloys, as it gives information about the character of the wave functions at the Fermi level.

The solid equiatomic alkali-gold compounds exhibit interesting properties as well: LiAu is definitely a metal whereas CsAu is a semiconductor (references in /5/). We measured the ^{7}Li Knight shift of LiAu at room temperature. Furthermore we performed UPS (ultra-violet photoemission spectroscopy) measurements on LiAu as it provides a picture of the band structure which can be compared directly with the calculated density of states of /5/.

Experimental, results and discussion

For a description of the techniques used for the Knight shift measurements above room temperature we refer to /6/; LiF was used as reference material. For the Knight shift measurements at room temperature a dilute LiCl solution was used as reference material; the chemical shift of the Li^+ ions in this solution is negligible /7/. The apparatus used for the UPS measurements is described in /8/.

The ^{7}Li Knight shift K of liquid Li-Au alloys is plotted as a function of concentration in Fig. 1. The total experimental error is estimated at ± 3 ppm. Within the investigated temperature range, typically from 600°C to 750°C, no temperature dependence was observed.

The total density of states at the Fermi level $N(E_F)$ of liquid Li-Au is calculated as a function of concentration in /2/ using a tight-binding model in which Li 2s and Au 6s states were taken into account. We repeated these calculations using the same values for the parameters and determined also the partial density of states at E_F,$N_i(E_F)$ (i=Li or Au). Assuming a random distribution of the atoms, i.e. short range order parameter $\sigma_{sr} = 0$ (definition of σ_{sr} in /9/), and assuming /9/ that the ^{7}Li Knight shift is proportional to $N_{Li}(E_F)$ we obtained, by scaling to the experimental Knight shift of pure liquid Li at 600°C, the dotted curve in Fig. 1. The concentration dependence of the calculated Knight shift is rather different from the experimental data. Using the self-consistently determined values of σ_{sr} from /2/ we obtained, within 10%, the same results. In order to investigate the origin of this discrepancy we carried out a similar calculation in which also the Au 6p energy level was included. Energy levels and hopping integrals were adopted from /2,9/. The Au s-p splitting was taken from atomic spectroscopy data /10/. $N_{Li}(E_F)$ was calculated as a function of concentration for σ_{sr} = 0 (random mixture) and for σ_{sr} = -0.9 (nearly complete order). The results, scaled to the experimental Knight shift of pure liquid lithium, are also shown in Fig. 1. The Knight shifts calculated in this way are in agreement with the experimental data; concentration and temperature dependence are reproduced. Apparently it is essential to include Au 6p states.

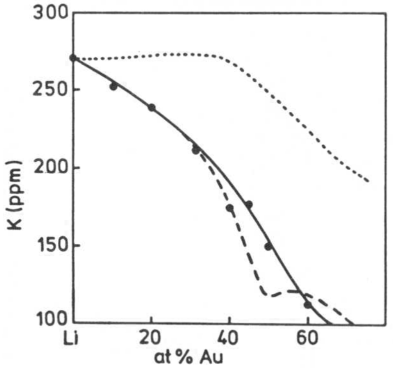

Figure 1. ^{7}Li Knight shift in liquid Li-Au alloys plotted as a function of concentration. Full dots: experimental points. Dotted curve: from tight-binding calculation in which only Li 2s and Au 6s states were taken into account and σ_{sr} = 0 was assumed (see text). Full curve: t.-b. calculation including Li 2s, Au 6s and Au 6p states, σ_{sr} = 0. Dashed curve : t.-b. calculation including Li 2s, Au 6s and Au 6p, σ_{sr} = -0.9.

Next we will consider measurements on the solid equiatomic compound LiAu. The ^{7}Li Knight shift measured at several temperatures between 500°C and the melting point (645°C) is 122 ± 2 ppm independent of temperature. This value is close to the aforementioned calculated value obtained for σ_{sr} = -0.9 (dashed curve in Fig. 1). At room temperature the ^{7}Li Knight shift of LiAu is much lower: K = 60 ± 6 ppm. For experimental reasons we were not able to measure K continuously as a function of temperature between room temperature and 500°C. According to DSC (differential scanning calorimetry) and resistivity measurements carried out recently LiAu exhibits a phase transition at 260 ± 3°C; possibly also the Knight shift changes discontinuously at this temperature. The low value of the Knight shift at room temperature - despite the metallic character of LiAu - is probably due to strong p-character of the electron states at the Li sites /5/.

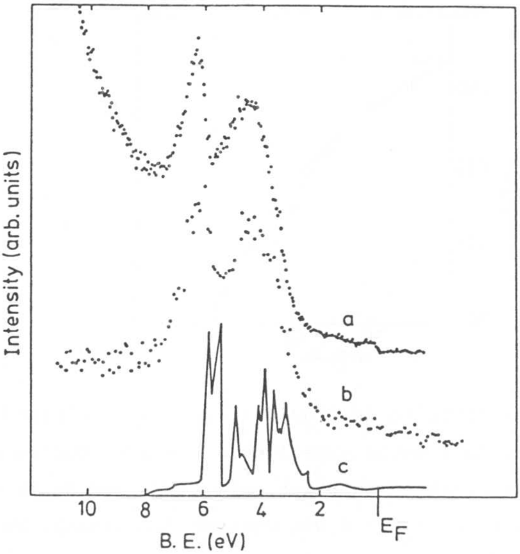

Figure 2. Curves a and b: intensity of the emitted photo electrons plotted as a function of their binding-energy. Curve a: using He I photons. Curve b: using He II photons.

Curve c: density of states of LiAu as calculated in /5/.

Preliminary UPS measurements on LiAu have been performed at room temperature. The obtained energy distribution curves of the emitted photoelectrons are shown in Fig. 2. The upper curve was obtained using a He I light source (E = 21.2 eV),the lower curve, b, using He II photons (E = 40.8 eV). The bands at 4.5 and 6.3 eV binding energy correspond to the $d^{5/2}$ and $d^{3/2}$ components of the Au d-band. The He I and He II spectra are similar apart from a different $d^{3/2}/d^{5/2}$ intensity ratio. As measuring at different photon energies samples the d-bands in different parts of the Brillouin zone, one expects a strong photon energy dependence of the observed line shape like in pure Au /11/. The absence of such a photon energy dependence may be caused by a disorder induced breakdown of momentum selection rules, or a small interatomic d-d transfer matrix element resulting in narrow impurity like d bands. The density of states of LiAu, obtained from recent band structure calculations /5/, is also shown in fig. 2 (curve c). The Fermi level of the calculated density of states and the measured EDC (curve a) were aligned. The calculated Au 5d states are approximately 0.7 eV shifted upward with respect to the experimental results; the calculated spin-orbit splitting of the Au 5d level is in reasonable agreement with experiment.

References

(1) Hensel F, Adv. Phys. 28 555 (1979).
(2) Holzhey C, Brouers F and Franz J R, J. Phys. F: Metal Phys. 11 1047 (1981).
(3) Holzhey C, Brouers F, Franz J R and Schirmacher W, J. Phys. F: Metal Phys. 12 2601 (1982).
(4) Nicoloso N, Schmutzler R W and Hensel F, Ber. Bunsenges. Phys. Chem. 82 621 (1978).
(5) Koenig C, Christensen N E and Kollar J, Phys. Rev. B 29 6481 (1984).
(6) Van der Marel C and Van der Lugt W, J. Phys. F: Metal Phys. 10 1177 (1980).
(7) Dickinson W C, Phys. Rev. 81 717 (1951).
(8) Bosch A, Feil H and Sawatzky G, J. Phys. E: Sc. Instr. 17 1187 (1984).
(9) Franz J R, Brouers F and Holzhey C, J. Phys. F: Metal Phys. 10 235 (1980).
(10) Moore C E, Atomic Energy Levels, NSRDS-NBS 35, Washington (1958).
(11) Freeouf J, Erbudak M and Eastman D E, Sol. St. Comm. 13 771 (1973).