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DYNAMICAL CONCENTRATION FLUCTUATIONS IN LIQUID Li₄Pb

M. Soltwisch, D. Quitmann, H. Ruppersberg and J.B. Suck

Abstract.- A measurement of the quasielastic neutron scattering from liquid ⁷Li₄Pb has been performed at a time of flight spectrometer (E₀ = 4.1 meV, ΔE₀ = 0.28 meV) for q(E=0) = 0.25...2.5 Å⁻¹. Corrections for background, absorption, self shielding, and multiple scattering were applied and the spectra were reduced to cross sections by normalization to vanadium. Since the coherent scattering lengths average to zero, the intensity observed is essentially due to the concentration fluctuations in the liquid phase by Ruppersberg and Egger /1/. A pronounced quasielastic peak around q = 1.5 Å⁻¹. The fit in terms of a sum of Lorentzians is performed which corresponds to an extrapolation of the description valid in the hydrodynamic limit. The self diffusion constant for Li is derived from the ⁷Li incoherent scattering and an interdiffusion constant from Scc(q,E).

Introduction

In a liquid binary mixture, deviations from statistical ordering of the constituent atoms in favor of AB association is often found if there are compounds in the solid state. This type of short range order is called heterocoordination and is due to the processes that go along with the heterocoordination. If one describes the pronounced heterocoordination has been demonstrated in the liquid phase by Ruppersberg and Egger /1/ using neutron scattering. In order to study the dynamical process that goes along with heterocoordination in a liquid mixture we have done a quasielastic neutron scattering measurement on Li₄Pb which is to our knowledge - the first experiment to observe directly on a microscopic scale the dynamical concentration fluctuations in a liquid with compound forming tendency. If one describes the scattering law for a binary liquid in terms of Scc(q,E), SNH(q,E), SNC(q,E) (c = concentration, N = number density) /2/, which is a rearranging of the normal set SAB(q,E), A,B = atomic species, then neutron scattering offers the possibility to isolate Scc by choosing a "zero alloy"; the mean scattering length <b> = <cA bA + cB bB > = 0, and the contributions due to SNH and SNC disappear /3/. With enriched ⁷Li (bLi = -0.229 fm) and natural Pb (bpb = +0.94 fm), the zero alloy occurs at cLi = 0.601.

Experiment and data reduction

The quasielastic scattering experiment was performed at the high resolution time of flight spectrometer IJ5 of the high flux reactor at the Institute Laue Langevin in Grenoble. A neutron wavelength of 4.09 Å was used, the detectors were positioned at 42 angles, φ = 0°...32°, so that the first peak of Scc(q) and the small q-range were scanned, 0.21 Å⁻¹ ≤ q ≤ 2.5 Å⁻¹ for energy transfers E = 0. The energy resolution, defined by the choppers, was 0.285 meV FWHM.

The sample was contained in a 15 mm i.d. Ta-container, 0.2 mm wall thickness, with an illuminated height of 4.6 cm. It was heated by a surrounding 50 μm cylindrical Mo-foil, 20 mm i.d., under high vacuum.
Measurements were performed at three temperatures, 1023 K, 1098 K and 1173 K. The measured transmission of the sample was 0.77. Based on the scattering cross section for $^7$Li and Pb, we conclude that the 23 % loss were due to 61 % scattering and 39 % absorption (about 0.1 \% $^6$Li). Here we shall restrict ourselves to the 1023 K data.

The time of flight spectra were treated in following steps:

1. Subtraction of the (small) contributions from container, oven and other surrounding objects.
2. Correction for absorption, self-shielding and energy-dependent detector efficiency.
3. Conversion to symmetrized energy spectra $I(f,E)$. - Reduction of $I(f,E)$ to absolute cross sections $\sigma_T(\alpha) (f,E)$ by vanadium normalization ($\sigma_{\text{van}} = 5.1$ b).
4. Conversion of $\sigma_T(\alpha) (f,E)$ to $\sigma_T(\alpha) (q,E)$ by a linear interpolation scheme (Fig. 1 shows $\sigma_T(\alpha) (q,E)$). - Description of $\sigma_T(\alpha) (q,E)$ by a sum of two Lorentzians, where the energy resolution (fit to the vanadium spectra with three Lorentzians) was taken into account by a convolution procedure. - The parameters obtained (smoothly extended to large $q$) were used to create the scattering law, which was taken as input for Copley's multiple scattering program MSCAT /3/.

The resultant multiple scattering was then subtracted from $S(\alpha) (f,E)$, yielding $S(1) (f,E)$. - Conversion of $\sigma_T(\alpha) (q,E)$ to $\sigma_{\text{exp}}(q,E)$ the experimental scattering law.

The energy range for which the multiple scattering was computed extended from $-3$ meV to 16 meV. The integrated multiple scattering is included in Fig. 2b. It shows the expected very slow variation with scattering angle and the mean value of $\sigma_{\text{MSC}}^2 = 0.3$ b is not far from the estimate according to Blech and Averbach /4/ which yielded 0.35 b.

The resulting energy integrals of $\sigma_{\text{exp}}(q,E)$ (note from Fig. 1 the restricted energy range accessible) can be compared with Ruppersberg's $S(q)$-measurement /5/ on Li$_4$Pb

Fig. 1 Experimentally observed neutron scattering intensity from the liquid zero alloy Li$_4$Pb for $T = 1023$ K. No multiple scattering correction is applied. The main peak is due to $S(c)$, it occurs at $q \approx 1.5$ \(\AA^{-1}\), see later figures. The increase at small $q$ is due to the incoherent scattering from $^7$Li.

using hot neutrons. As expected these data are always above the present ones. It will be interesting to find out the dynamical structure to larger energy transfers invisible in the present experiment.

Discussion

We note at the outset that in the present experiment the scattered intensity decreases monotonically with $|E|$ to very small values, i.e. diffusive motions are dominant, in the whole $q$-range accessible.

For the interpretation, we start from

$$\sigma_{\text{exp}}(q,E) = \sigma_{\text{inc}} S_{\text{Li}}(q,E) + 4\pi(b_{\text{Li}} - b_{\text{Pb}})^2 \sigma_{\text{cc}}(q,E)$$

At the lowest $q$ values $S_{\text{cc}}(q) \ll 1$, so that essentially all scattering is due to $^7$Li self diffusion. One finds from the first spectrum ($q = 0.27 \ AA^{-1}\)$ by fitting a Lorentzian FWHM = $\Gamma_{\text{Li}} = 0.17$ meV. From $\Gamma_{\text{Li}} = 2\pi q^2 D_{\text{Li}}$ one finds

$$D_{\text{Li}} = (17\pm3) \cdot 10^{-5} \text{cm}^2/\text{s}$$

at 1023 K.
For the hydrodynamic regime, small \( q \) and \( \varepsilon \), Bhatia, Thornton and March /6/ have given a theoretical treatment of the dynamical structure factors \( S_{NN}(q,\varepsilon) \), \( S_{CC}(q,\varepsilon) \) and \( S_{NC}(q,\varepsilon) \). They predict a Lorentzian shape for \( S_{CC}(q,\varepsilon) \), with a width given by the interdiffusion constant \( D^+ \), if the thermal diffusivity and the thermal diffusion ratio are small:

\[
S_{cc}(q,\varepsilon) = \frac{NK_BT}{\hbar^2 G/\partial q^2} \frac{hD^+q^2}{\varepsilon^2 + (hD^+q^2)^2} \tag{3}
\]

Since \( \frac{NK_BT}{3\hbar^2 G/\partial q^2} = S_{cc}(q=0) \), we have replaced, as a first attempt to extend eq.3 to larger \( q \), the first ratio by \( S(q) \).

In this form eq.3 resembles the Vineyard approximation. One expects therefore a second Lorentzian, and correspondingly fits to \( S\exp(q,\varepsilon) \) were performed. The second line which should represent \( S_{cc}(q,\varepsilon) \), has parameters \( f_1 \) and \( \Gamma_1 \) in the figures. We shall consider first the region \( 0.6 < q < 1.3 \). The incoherent \( Li \) contribution was extrapolated by keeping \( f_{Li} = S_{Li}(q) = 0.65b_1 \), \( \Gamma_{Li} = 2.3 \text{ meV} \cdot (qR)^2 \). In this q-region there seems to be in addition a very broad background possibly related to nondiffusive excitations. We have allowed for it by including a third Lorentzian (fig.2b). With increasing \( q \), line 1 grows rapidly as a narrow line superimposed on the \( Li \)- and background structure; the increase of its intensity with \( q \) is very similar to the increase of the total \( S_{cc}(q) \), see fig. 2a. If the theory of Bhatia et al., eq.3, is still applicable in the \( q \)-range, \( q < 1 \, \text{A}^{-1} \), then the widths \( \Gamma_1 \) imply an interdiffusion constant

\[
D^+ = 6 \cdot 10^{-5} \text{ cm}^2/\text{s} \tag{4}
\]

The self- and the interdiffusion constant are related in the limit \( q \to 0 \) by the relations /7/:

\[
D^+ = \left(c_{AB}^2 + c_{BA}^2\right) f_{th} \tag{5a}
\]

\[
f_{th} = \frac{\left(\frac{\partial^2 G/\partial q^2}{\partial q^2}\right)}{\left(\frac{\partial^2 G/\partial q^2}{\partial q^2}\right)_\text{ideal}} = \frac{c_{AB}c_{BA}}{S_{cc}(0)} \tag{5b}
\]

The region \( 1 < q < 2 \) contains the most characteristic feature of \( S_{cc}(q) \) for the present system viz. a strong peak due to very pronounced heterocoordination. The spectra can again be well described by a set of Lorentzians, of which the narrowest line, line 1, carries essentially all the intensity of the \( S_{CC} \)-peak, see fig. 2a. The width of that line does, however, not increase further with \( q \), but shows a pronounced dip in the region of the peak of \( S_{cc}(q) \), see fig. 2a. The dip was found independent of the number \( n \) of Lorentzians used to fit the data (\( n=1,2,3 \)), of the corrections applied, and of whether the \( Li \)-line parameters were extrapolated as described above, or left free in the fits. The reduction in energy width near the peak of \( S_{cc}(q) \) is considered as the de-Gennes-narrowing of the concentration fluctuations, a narrowing well known for \( S_{NN} \) in monoatomic liquids. It has been predicted in /6/, where the sum rule

\[
\langle \omega^2 \rangle = \int \omega^2 S_{cc}(q,\varepsilon) d\omega = c_{AB}c_{BA}Nk_BT q^2/\mu \tag{6}
\]

with \( 1/\mu = (1/M_A+1/M_B)c_{AB}c_{BA} \) was derived. Phrased more "anschaulich" the reduction of the width in the region of the peak of the so-called static structure factor means, that an arrangement of atoms which one finds very often in a snapshot (\( S(q) \)), does also have a very long lifetime. As was derived from \( S_{cc}(q) \) measured with hot neutrons /5/, this arrangement is an AB short range order with a periodicity extending over many atomic distances. An arrangement more like an assembly of molecules has been proposed for Li-Pb in /9/, and discussed e.g. in /10/.
Fig. 2 Results of fitting a set of three Lorentzian lines to $\sigma\cdot S(q,E)$. The area exp(f) and the width (Γ) of the line carrying most of the intensity of the main peak of $S_{CC}(q)$ is given in part a), above. The data for the lines describing the incoherent Li scattering (index Li, extrapolation from low q-values) and the third line (index 2) are presented in part b), bottom. Included are the sum of the three areas in a) and the calculated multiple scattering in b). The heavy curves for line 1 and 2 are drawn to guide the eye. From $f/2 = 5/\tau$, 1 meV corresponds to $1.32 \cdot 10^{-12}$ s.

Beyond the peak just discussed, $S_{CC}(q)$ approaches its limiting value, $S_{CC}(q + \omega) = C_{AB}$, rather rapidly. As $S_{CC} = C_{AB}$, dynamical correlations are expected to die out as well as the structural correlations do, and the scattered intensity eq.(1) will develop into

$$S(q,E) = \sigma_{\text{inc},Li} + \sigma_{\text{coh},Li} + \sigma_{\text{coh},\text{Li}}.$$  

Three Lorentzians are still suited to reproduce the general appearance of $S_{CC}(q,E)$ very well in the region $q \geq 1.8 \text{ Å}^{-1}$. The fit results included in fig. 2 show the following trend: the narrow line gets a low weight; the broader structures dominate.

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