Also gilt der

Satz 5: Aus einem Vakuumfeld, das eine nicht lichtartige hyperflächennormale Isometrie zuläßt, kann mit den Methoden (6), (8) oder (9) eine Schar exakter Lösungen der EINSTEIN–MAXWELL-Gleichungen konstruiert werden. Sämtliche Lösungen der Klasse (7) können so gewonnen werden.

Die Beweise sowie weitere Literaturangaben sind vom Autor in [4] gegeben.

Für die Anregung zu dieser Arbeit sowie die Unterstützung bei der Durchführung danke ich den Mitgliedern des Hamburger Seminars für allgemeine Relativitätstheorie, insbesondere den Herren Dr. TRÜMPER und Dr. KUNDT. Mein besonderer Dank gilt Herrn Prof. Dr. PASCUAL JORDAN.

Refractive Index Measurements of Molten Salts with Wave-Front-Shearing Interferometry

II. $LiNO_3$, $NaNO_3$, KNO_3, $RbNO_3$, and $CsNO_3$

LENNART W. WENDELÖV, SILAS E. GUSTAFSSON, NILS-OLOV HALLING, and ROLF A. E. KJELLANDER

Institute of Physics, Chalmers University of Technology, Göteborg, Sweden

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A wave-front-shearing interferometer has been used to determine the refractive index of the alkali nitrates $LiNO_3$, $NaNO_3$, KNO_3, $RbNO_3$, and $CsNO_3$ from the melting point to a temperature just below the decomposition point. The accuracy of these measurements has been estimated to $\pm 3 \cdot 10^{-5}$ which should be compared with $\pm 3 \cdot 10^{-3}$, being the estimated error in earlier determinations. The refractive index is found to depend almost linearly on temperature. For most of the investigated liquids, however, one gets a better fit to the measured values if a second order dependence is assumed.

As part of a larger program to apply optical techniques to the study of transport properties of molten salts it has been necessary to remeasure the refractive index of these liquids. The accuracy of the methods used in earlier determinations is much too low, which can easily be seen if one tries to get a reliable value of (dn/dt), where n is the refractive index and t the temperature. This quantity must be known within one percent when measuring thermal conductivity whilst the differences between recent published data are sometimes of the order of 50 percent [1, 2]. The methods applied up to now are based upon two different principles. In the first one the minimum deviation of a light beam passing through a hollow prism containing the melt is measured [1, 3] and in the second one the familiar "bent stick" principle is utilized, where a direct reading of the angles of incidence and refraction can be made [1, 2, 4, 5].

The reason why the accuracy of these methods is limited is that the refractive index is calculated from the ratio of two trigonometric functions containing measured angles. Even if the readings of the angles are very accurate the errors are still rather big. In order to avoid this difficulty we are using a wave-front-shearing interferometer which combines two light beams, one passing through the liquid and the other through a rotatable quartzplate (fused quartz) inside the liquid. Since we are using the refractive index of the quartz plate as a reference one may consider it a relative method but it is equally easy to determine the refractive index of quartz relative to vacuum and thus making the method an absolute one. A detailed description of the method is given elsewhere [6]. The construction of a container with optically flat windows for the liquid and a thermostat which allows the light to pass without distortion of the wavefront is discussed in reference [7].

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[6] L. W. WENDELÖV, L. E. WALLIN, and S. E. GUSTAFSSON, Z. Naturforschg. **22 a**, 1180 [1967].
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I. Experimental

The chemicals $LiNO_3$ (J. T. Baker), $NaNO_3$ and KNO_3 (E. Merck) were of analytical reagent quality. $RbNO_3$ (E. Merck) and $CsNO_3$ (Hopkin & Williams) were not commercially available with higher purity than C. p. grade but all the chemicals gave colorless clear melts. The salts were melted in an auxiliary furnace from which the liquid could be introduced directly into the main thermostat. The melts could be kept under a protective atmosphere of argon, which was used when handling $RbNO_3$ and $CsNO_3$. We could not detect any changes of the melts when keeping them under different atmospheres. The temperature was determined with Chromel-alumel thermocouples calibrated at the melting points of tin, lead and zinc. The e.m.f. (E) was assumed to vary according to the equation

$$E = a + b\,t + c\,t^2$$

where t is °C. The voltage was measured with a precision potentiometer (Croydon P10) with a sensitivity of $\pm 5 \cdot 10^{-7}$ volts, which made it possible to measure changes in the temperatures of the order of 0.05 degrees. The temperature of the liquid could be kept constant within ± 0.05 degrees during one particular measurement, which was accomplished by supplying the thermostat with stabilized AC voltage.

The optical system consisted of a wave-front-shearing interferometer with two Savart plates giving a vertical shear in the cell plane of approximately 2.5 mm [8]. The difference between the present arrangement and the one described in ref. [6] was that we did not use any mirror to reverse the light in the optical system. This was not necessary because a helium-neon gas laser ($\lambda = 6330$ Å) was used as a light source which removed the problem of coherence.

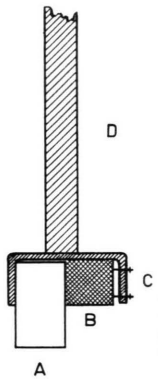

Fig. 1. Rotatable holder of the quartz plate. A. Fused quartz plate. B. Aluminum cube for compensating the thermal expansion of the holder (C). D. Stainless steel rod.

The arrangement for supporting the quartz plate in the liquid is shown in Fig. 1. The holder was supported by a large leveling plate placed just above the thermostat. In order to protect the quartz plate from slipping out of the holder a piece of aluminium was inserted to compensate the expansion of the holder. The aluminium could be kept just above the surface of the liquid, thereby avoiding any contact with the melt. In order to adjust the quartz plate perpendicular to the optical axis we used the principle of autocollimation. The thickness of the glassplate was in all measurements about 20 mm and the refractive index (n) of the quartz plate was taken to $n = 1.45730 + 9.9 \cdot 10^{-6}\,t$, where t is deg. C [9]. A value of $5.6 \cdot 10^{-7}$ deg.$^{-1}$ was accepted as the thermal expansion of fused quartz.

II. Results and Discussion

The determination of the refractive index of molten salts has not received very much attention, probably due to the experimental difficulties involved. The methods developed up to now have had a rather limited accuracy compared with methods used at room temperature. With the present technique the accuracy of the high temperature measurements is comparable with that of other precision methods and work is in progress to further improve the accuracy at least ten times.

The experimental results are given in Table 1, where the refractive index at one particular temperature has usually been computed for between five and ten different angles of rotation of the quartz plate. The standard deviation (s), calculated from the formula

$$s^2 = (k-1)^{-1} \sum_{1}^{k} (\bar{n} - n_\nu)^2,$$

is given in the third column showing the internal consistency of one particular series of measurements. The molar refractivity (R) is computed using the Lorentz–Lorenz equation

$$R = [\,(n^2-1)/(n^2+2)\,]\,(M/\varrho) \qquad (1)$$

where n is refractive index, M is molecular weight, and ϱ is the density given in Table 2. There is a slight temperature dependence of this quantity for all the investigated salts. This may be within the limits of experimental uncertainty for the density determination, but from point of view of refractive index the tendency is significant. The only conclusion that can be made from the data so far is that the molar refractivity or the polarizability of all the measured alkali nitrates changes by about 0.6 percent over a temperature range of 100 degrees.

[9] Landolt-Börnstein, Zahlenwerte und Funktionen, 6th ed., vol. II.

[8] O. Bryngdahl and S. Ljunggren, J. Phys. Chem. **64**, 1264 [1960].

Temp. °C	Refractive index	Standard deviation $\times 10^5$	Molar refractivity cm^3
	$LiNO_3$		
277.0	1.46413	3	10.76
295.4	1.46170	2	10.78
313.9	1.45913	—	10.79
336.5	1.45606	5	10.81
365.9	1.45221	5	10.83
	$NaNO_3$		
316.3	1.42373	2	11.42
332.5	1.42129	3	11.43
351.4	1.41853	2	11.45
370.4	1.41580	1	11.47
395.1	1.41229	2	11.49
405.8	1.41070	2	11.50
428.2	1.40760	1	11.52
	KNO_3		
341.7	1.41088	3	13.44
348.9	1.40974	3	13.45
369.6	1.40639	4	13.46
402.6	1.40120	3	13.48
410.0	1.40001	2	13.49
429.8	1.39696	3	13.50
456.7	1.39273	3	13.53
	$RbNO_3$		
356.8	1.41417	4	15.13
402.9	1.40656	8	15.16
421.9	1.40350	—	15.18
447.4	1.39925	6	15.20
473.0	1.39517	2	15.22
497.0	1.39152	3	15.25
	$CsNO_3$		
420.7	1.42832	2	17.85
433.0	1.42603	2	17.86
441.4	1.42456	2	17.86
454.9	1.42211	2	17.87
470.8	1.41941	3	17.89
481.8	1.41729	3	17.90

Table 1. Refractive index and molar refractivity of fused alkali nitrates at different temperatures and at a wavelength of 6330 Å relative to vacuum.

Because of the constancy of the molar refractivity it would yield interesting information to make systematic studies of the refractivity of a large number of salts containing one common ion. From such information it would be possible to estimate the effect of ionic interaction in the different salts and to see how one particular ion is influenced by the presence of other ions. This would be particularly interesting because in molten salts we do not have any solvent present which may influence the results.

In Table 2 the temperature dependence of the refractive index is computed assuming both a linear and a quadratic relation. As seen from the c'-values there may exist a slight deviation from a linear dependence. The accuracy of the c'-values is naturally rather low but since they all have the same sign and are of the same order of magnitude they may have a physical significance.

WAGNER [4] has suggested an equation from which it would be possible to calculate the temperature dependence of the refractive index (the b-values in Table 2)

$$\frac{dn}{dt} = \frac{(n^2-1)(n^2+2)}{6n} \cdot \frac{1}{\varrho} \cdot \frac{d\varrho}{dt} \qquad (2)$$

where ϱ is the density. This equation is simply obtained by differentiating the LORENTZ–LORENZ formula assuming that the molar refractivity is a constant. The values calculated from this equation at 400 °C are listed in the last column of Table 2 and the agreement between the calculated and the experimental values (the theoretical values are all about 20 percent too high) is surprisingly good. This is actually a good test of the LORENTZ–LORENZ equation showing its validity in spite of the rather elementary reasoning behind it.

Salt	a	$-b \times 10^4$	a'	$-b' \times 10^4$	$c' \times 10^8$	Density	$-b \times 10^4$ from Eq. (2)
$LiNO_3$	1.50141	1,346	1.50390	1.505	2.52	$1.919 - 0.546 \cdot 10^{-3} \cdot t$	1.66
$NaNO_3$	1.46915	1,439	1.47489	1.750	4.18	$2.125 - 0.715 \cdot 10^{-3} \cdot t$	1.78
KNO_3	1.46480	1.579	1.46875	1,781	2.56	$2.116 - 0.729 \cdot 10^{-3} \cdot t$	1.81
$RbNO_3$	1.47189	1.621	1.47971	1.990	4.32	$2.783 - 0.972 \cdot 10^{-3} \cdot t$	1.88
$CsNO_3$	1.50409	1.802	1.50843	2.005	2.38	$3.1670 - 1.6605 \cdot 10^{-3} \cdot t$	2.23

Table 2. Temperature dependence of refractive index expressed by means of the two equations $n=a+b\,t$ and $n=a'+b'\,t+c'\,t^2$, where t is °C. The densities are taken from ref. [10].

[10] G. J. JANZ, F. W. DAMPIER, and P. K. LORENZ, Molten Salts: Electrical Conductance, Density and Viscosity Data, Rensselaer Polytechnic Institute, Troy 1966.

As to the errors of the absolute values of the refractive index one must realize the difficulty to give them within $\pm 3 \cdot 10^{-5}$ even if the method used is capable of such an accuracy. The reason for this difficulty is that there does not exist any really good analytical method to measure the purity of the salt in the molten state. A refractive index determination is of course such a method but in order to give the refractive index of an "absolutely" pure melt, it would be necessary to try a large number of different purification techniques. This was not done because it was outside the scope of this investigation but it seems to be a rather urgent work. All possible precautions were taken not to contaminate the melt and as mentioned above they were all clear and colorless and no attack of any kind could be seen either on the cell walls or on the quartz. Another difficulty is to measure the temperature with sufficient accuracy which means that the reading should be correct to ± 0.1 degrees. This may sometimes be difficult in high temperature work unless a special calibration of the thermocouples is performed.

As has been shown above a systematic investigation of a large number of molten salts with a method of high precision would give interesting results from many points of view and would not only be of importance when using optical techniques to study transport properties.

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Quantenstatistik eines Vielteilchensystems mit Coulomb-Wechselwirkungen

(Methode der reduzierten Dichtematrizen)

D. KREMP und G. SCHMITZ

Institut für Theoretische Physik der Universität Rostock

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Aus der BOGOLJUBOW-Hierarchie für die reduzierten Dichteoperatoren wird die Zweiteilchen-Dichtematrix bis zur Ordnung e^2 für ein System geladener Teilechn im Gleichgewicht berechnet. Mit dieser Funktion wird dann für den Fall $n \lambda^3 \ll 1$ die Korrelationsenergie und die freie Energie bis zur Ordnung e^4 bestimmt.

Ein wichtiges Problem in der Theorie der Vielteilchensysteme ist die Berücksichtigung der Wechselwirkungen zwischen den Teilchen bei der Berechnung der Mittelwerte dynamischer Größen und den thermodynamischen Funktionen, d. h., die Erfassung der Korrelationseffekte. Dieses Problem führt bei der Behandlung von Systemen mit COULOMB-Wechselwirkungen wegen des weitreichenden Charakters der COULOMB-Wechselwirkungen und den daraus resultierenden Divergenzen zu besonderen Schwierigkeiten.

Der Formalismus der Quantenstatistik gibt im Prinzip zwei Möglichkeiten zur Berechnung von thermodynamischen Funktionen. Die erste Methode besteht in der Berechnung der thermodynamischen Funktionen über die Zustandssumme. Methoden zur Auswertung der Zustandssumme wurden von MATSUBARA [1] und von MONTROLL und WARD [2] entwickelt, unter Benutzung der in der Quantenelektrodynamik entwickelten Störungstheorie und des WICKschen Theorems.

An die Methode von MATSUBARA schließt die Arbeit von WEDENOW und LARKIN [3] an. In dieser Arbeit wird unter der Bedingung $n \lambda^3 \ll 1$ und $e^2/k T \lambda \ll 1$ die freie Energie mit Berücksichtigung von Austauscheffekten bestimmt.

Die Methode von MONTROLL und WARD wurde von DE WITT [4] weiter entwickelt und auf Systeme mit COULOMB-Wechselwirkungen angewandt. Von DE WITT wurde ebenfalls die freie Energie unter den obigen Bedingungen, aber ohne Austauschterme, berechnet.

Neben den quantenfeldtheoretischen Methoden

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