Dielectric constants and molar polarizabilities of saturated and compressed fluid nitrogen*

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In this paper we present accurate, wide range measurements of the dielectric constant of saturated and compressed fluid nitrogen. Measurements were made from 65 to 125 K along the saturated liquid boundary and along selected liquid and gaseous isotherms ranging from 92 to 300 K at pressures to 34.5 MPa. Densities ranged from the dilute gas to nearly three times the critical density. Molar polarizabilities, thought to be accurate to better than 0.10%, were calculated by combining the dielectric constant measurements with densities obtained from least-squares analyses of experimental pVT data. A correlation function based on selected experimental data is given for the saturated liquid densities. Dielectric virial coefficients, derived from the calculated molar polarizabilities, are also presented.

I. INTRODUCTION

In this paper, we report measurements of the dielectric constant of saturated and compressed fluid nitrogen. Unlike most previous measurements for nitrogen[1-3] the dielectric constant was measured over a wide temperature and pressure range: from 65 to 125 K along the saturated liquid boundary and along selected isotherms from 92 to 300 K and at pressures ranging from approximately 0.5 to 34.5 MPa. The density range extends to nearly three times the critical density at the lower temperatures.

We also report values of the molar polarizability which we shall denote by the symbol M. This quantity is not directly experimentally measurable, but it can be derived by combining the measured dielectric constants with high precision density data via the well known Clausius–Mossotti relation

$$M = [(\epsilon - 1)/(\epsilon + 2)]\rho^{-1} = 4\pi N\alpha/3, \tag{1}$$

where ϵ is the static dielectric constant and α, ρ, and N are the mean molecular polarizability, density, and Avogadro's number, respectively. This quantity is of much greater interest than ϵ itself for two reasons: (1) An accurate knowledge of the temperature and density dependence of M offers a potentially useful and accurate method of density gauging through dielectric constant measurements and (2) deviations from Eq. (1), which are usually analyzed in a truncated virial type expansion of the form

$$M = A_D + B_D(T)\rho + C_D(T)\rho^2 + \ldots , \tag{2}$$

where A_D $(= 4\pi N\alpha/3)$, $B_D(T)$, $C_D(T)$, $\ldots$, are the so-called dielectric virial coefficients, can provide information on the nature of intermolecular forces.[4-8] We include, therefore, values of M and the first three dielectric virial coefficients for the isotherms studied. Also, the values of A_D and $B_D(T)$ are compared with the results of other investigations.[2,3]

II. EXPERIMENTAL

The dielectric constant was determined by measuring the capacitance C of a highly stable cylindrical capacitor[9] with the fluid contained between the plates. A sub-

sequent measurement of the capacitance C' of the evacuated capacitor then provides the dielectric constant directly as the ratio C/C'. The capacitances were measured on a commercial three terminal capacitance bridge capable of six figure resolution. Uncertainty in the dielectric constants thus obtained is estimated to be less than 0.002 percent at the high pressures, increasing to approximately 0.003 percent at the lowest pressures considered. The nitrogen used in the experiment was a commercial 99.997 percent pure grade and it was passed through a molecular sieve to further ensure the absence of any water.

Temperatures were measured on the IPTS-1968 using a platinum resistance thermometer which had been calibrated by the National Bureau of Standards. Uncertainties in measured temperatures were estimated to be 0.005 K at the lower temperatures, increasing to 0.030 K at 300 K.[10] Pressures were measured by referencing the system pressure to oil pressures derived from an oil dead weight guage.[11] The estimated accuracy of the pressure measurement was 0.01 percent. The experimental apparatus and procedures were identical to those used for dielectric constant measurements on oxygen,[12] fluorine,[13] and methane,[14] and have been described in detail.

III. RESULTS

The Clausius–Mossotti relation, Eq. (1), is shown as a function of density for the saturated liquid and compressed fluid in Fig. 1. The estimated uncertainty in these polarizabilities is 0.1 percent. It is seen that the molar polarizability initially increases with increasing density then decreases, in qualitative agreement with theoretical models[4-8] and experimental results for other nonpolar fluids.[12-16] The corresponding dielectric constants, pressures, densities, and derived molar polarizabilities are listed in Table I. The isotherms were selected to be identical to experimental pV isotherms to permit a more accurate determination of the molar polarizability. The methods used for the determination of the appropriate densities are discussed in detail in the next section.
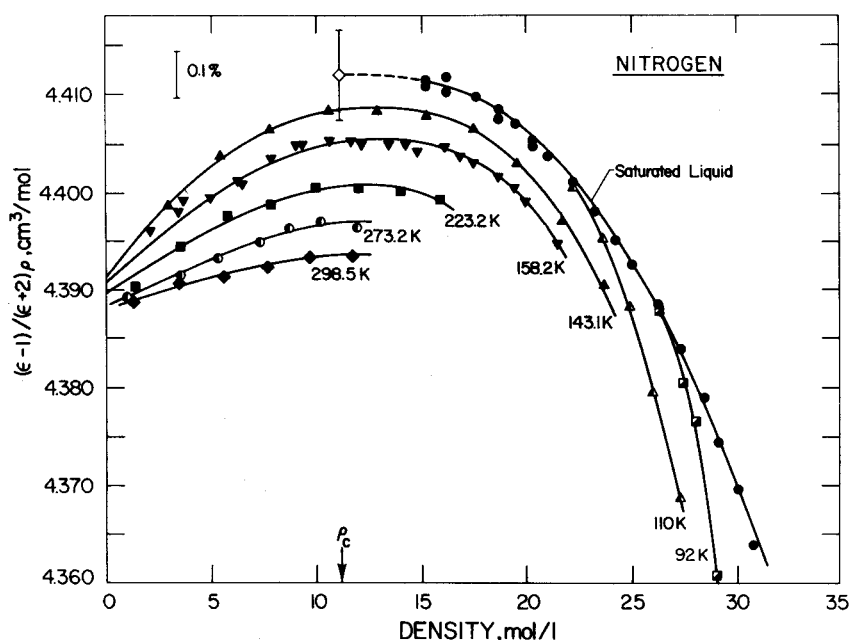
FIG. 1. Calculated molar polarizabilities for saturated liquid and compressed fluid nitrogen. The value of the molar polarizability at the critical point was obtained by extrapolation, as explained in the text.

The measured dielectric constants for the saturated liquid are shown plotted against temperature in Fig. 2. The dielectric constants at the triple and critical points were calculated by extrapolating values of the molar polarizability of the saturated liquid from Fig. 1. The polarizability at the triple point was taken to be 4.3615 ±0.0044 cm^3/mol at a density of 30.998±0.031 mol/ℓ, resulting in a dielectric constant of 1.46876 ±0.00084. A similar calculation at the critical point with M = 4.4120±0.0044 cm^3/mol and ρ = 11.20±0.01 mol/ℓ, yielded a dielectric constant of 1.15595±0.00033. Table II lists the dielectric constants, densities, and calculated molar polarizabilities for the saturated liquid.

Dielectric virial coefficients for those isotherms which exhibit a well-defined maximum in polarizability were obtained from a free floating fit of Eq. (2) (the value of A_D was allowed to vary with temperature) to the derived polarizabilities. The coefficients for the 273.2 and 298.5 K isotherms were obtained by constraining Eq. (2) to exhibit a maximum at densities of 11.5 and 10.2 mol/ℓ, respectively. The results obtained are listed in Table III. The estimated accuracy of these coefficients is discussed in the next section.

IV. DISCUSSION

The accuracy of the molar polarizability at moderate to high densities is determined primarily by the accuracy of the densities used in Eq. (1). As can be seen from Fig. 1, the molar polarizability deviates from the Clausius–Mossotti relation by less than one percent over the entire temperature and pressure range considered. This behavior has been qualitatively observed for almost all other nonpolar fluids.[12-16] For this reason, the calculation of molar polarizabilities from experimental dielectric constant data places severe demands on the pre-

cision, accuracy, and empirical representation of the experimental pVT data used to obtain the densities. Thus, the isotherms studied were selected to coincide exactly (in temperature) with existing experimental pV isotherms. In spite of this precaution, initial attempts to obtain the required densities from existing equations
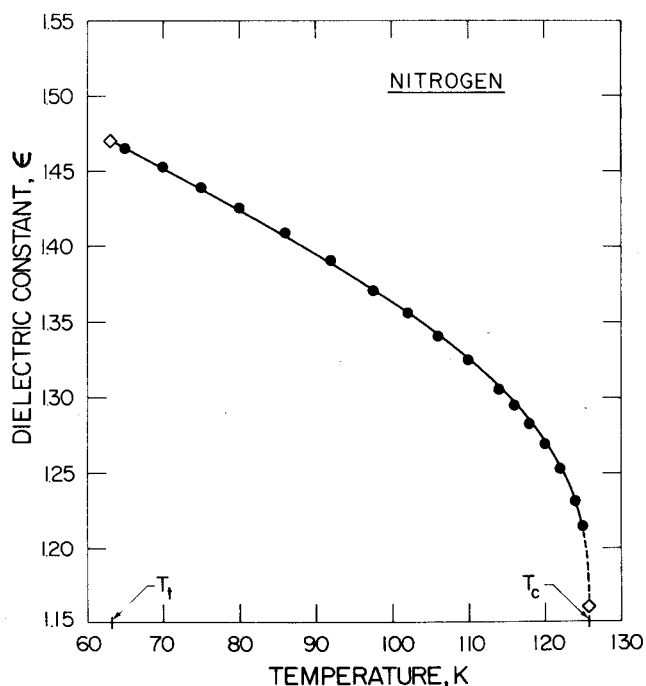

FIG. 2. Dielectric constant of saturated liquid nitrogen as a function of temperature. The open symbols denote dielectric constants obtained by extrapolating the saturation curve in Fig. 1 to the triple and critical points.

TABLE I. Values of the dielectric constant ϵ and derived molar polarizability M along gaseous and liquid nitrogen isotherms. At a given temperature T and pressure p, the density was calculated from Eq. (3) using the appropriate coefficients listed in Table IV.

T, K	p, MPa	ρ, mol/ℓ	ϵ	M, cm^3/mol
92.00	25.620	28.912	1.43276	4.3604
	17.230	28.156	1.42164	4.3766
	10.727	27.532	1.41144	4.3806
	0.436[a]	26.224	1.39012	4.3883
110.00	32.783	27.311	1.40640	4.3684
	20.194	26.006	1.38561	4.3796
	11.943	24.831	1.36688	4.3884
	5.968	23.624	1.34760	4.3954
	1.466[a]	22.170	1.32435	4.4010
143.10	34.972	23.722	1.34879	4.3906
	22.938	21.757	1.31737	4.3972
	14.939	19.555	1.28266	4.4033
	10.711	17.465	1.25014	4.4067
	8.263	15.213	1.21564	4.4081
	6.922	12.925	1.18126	4.4084
	6.056	10.592	1.14696	4.4087
	5.221	7.978	1.10930	4.4061
	4.261	5.505	1.07455	4.4041
	2.826	3.020	1.04039	4.3987
158.20	31.031	21.425	1.31182	4.3945
	24.527	20.054	1.29028	4.3993
	22.091	19.409	1.28017	4.4006
	19.892	18.732	1.26961	4.4020
	16.575	17.456	1.24978	4.4031
	15.386	16.888	1.24106	4.4042
	14.034	16.136	1.22955	4.4050
	12.138	14.812	1.20935	4.4041
	11.564	14.326	1.20205	4.4048
	10.653	13.445	1.18886	4.4050
	9.531	12.138	1.16946	4.4050
	9.199	11.698	1.16301	4.4055
	8.514	10.713	1.14861	4.4056
	7.608	9.283	1.12791	4.4052
	7.472	9.058	1.12468	4.4051
	6.748	7.860	1.10758	4.4040
	5.855	6.423	1.08727	4.4011
	5.802	6.341	1.08613	4.4011
	4.849	4.946	1.06673	4.3992
	3.841	3.649	1.04895	4.3997
	3.671	3.448	1.04618	4.3971
	2.446	2.123	1.02827	4.3962
223.20	34.459	15.926	1.22604	4.3994
	27.275	13.952	1.19620	4.4000
	21.828	12.000	1.16725	4.4005
	17.305	9.977	1.13777	4.4007
	13.436	7.929	1.10841	4.3987
	9.783	5.777	1.07820	4.3970
	6.273	3.631	1.04865	4.3945
	2.680	1.495	1.01982	4.3904
273.20	31.002	11.953	1.16637	4.3960
	25.284	10.294	1.14224	4.3973
	20.514	8.695	1.11924	4.3967
	15.962	6.975	1.09486	4.3945
	11.810	5.254	1.07088	4.3927
	7.913	3.544	1.04742	4.3907
	3.973	1.772	1.02351	4.3881
298.50	34.730	11.747	1.16326	4.3935
	26.841	9.724	1.13388	4.3933
	20.207	7.703	1.10505	4.3920
	14.152	5.590	1.07549	4.3911
	8.723	3.510	1.04697	4.3914
	3.389	1.371	1.01816	4.3886

[a]Saturation boundary.

ration boundary and isotherms close to critical (especially at 143.1 and 158.2 K) showed large oscillations (on the order of 0.5 percent at 143.1 K). Since these oscillations were orders of magnitude greater than the estimated error in the dielectric constant measurements and since the molar polarization of other nonpolar fluids is known to be smooth and generally well behaved even in the critical region,[13] a reanalysis of the existing experimental pVT data was performed. It should be mentioned that this situation is not unique to nitrogen[14,15] nor does it necessarily imply that the wide range pVT correlations frequently used are unreliable. It simply arises from the fact that in the construction of an equation of state, some of the accuracy in the isothermal pV fits is often lost when the coefficients for all isotherms are fitted to a function of T.

The sources of the isothermal pVT data used in the analysis are as follows: Michels et al.[19] 298.5 K; Canfield et al.[20] and Crain,[21] 143.1 to 273.2 K; Crockett et al.[22] and Street and Staveley,[23] 110.0 K; and Weber,[24] 92.0 K. The average uncertainty in these data was estimated to be less than 0.15 percent. The data were analyzed by weighted least squares fitting a polynomial in density to the experimental compressibility factor, the functional form being given by

TABLE II. Dielectric constant ϵ and derived values of the molar polarizability M in saturated liquid nitrogen as a function of temperature. The saturation densities were calculated from Eq. (4).

T, K	ρ, mol/ℓ	ϵ	M, cm^3/mol
63.15[a]	30.998	1.46803	4.3615[c]
65.00	30.757	1.46509	4.3640
70.00	29.982	1.45228	4.3696
75.00	29.185	1.43905	4.3743
80.00	28.362	1.42543	4.3791
86.00	27.326	1.40830	4.3839
92.00	26.224	1.39013	4.3884
	26.224	1.39012	4.3883
98.00	25.028	1.37055	4.3926
102.00	24.161	1.35642	4.3952
106.00	23.217	1.34118	4.3981
110.00	22.170	1.32437	4.4011
	22.170	1.32435	4.4008
114.00	20.973	1.30528	4.4038
116.00	20.293	1.29453	4.4053
	20.293	1.29450	4.4049
118.00	19.535	1.28261	4.4072
120.00	18.664	1.26898	4.4086
	18.664	1.26892	4.4076
122.00	17.615	1.25267	4.4099
124.00	16.211	1.23110	4.4120
	16.211	1.23101	4.4104
125.00	15.190	1.21548	4.4117
	15.190	1.21545	4.4110
126.20[b]	11.200	1.15595	4.4120[c]

[a]Triple point; the dielectric constant is calculated from an extrapolated value of M.
[b]Critical point; the dielectric constant is calculated from an extrapolated value of M.
[c]Extrapolated value of M obtained from Fig. 1.

of state[17,18] based on these same isothermal data, yielded "unreasonable" values for the molar polarizability. To be more specific, the derived values of M for the satu-

TABLE III. Dielectric virial coefficients appearing in Eq. (2).

T, K	A_D,cm^3/mole	B_D,cm^6/mole^2	C_D,cm^9/mole^3
This work:			
143.10	4.3898	3.22	−132.4
158.20	4.3905	2.49	−103.6
223.20	4.3874	2.18	−90.4
273.20	4.3881	1.80	−88.2
298.50	4.3885	0.87	−37.0
Cole *et al*[a]			
242.00	4.389(±0.003)	4.2(±1.0)	
296.00	4.381(±0.002)	2.0(±1.0)	
306.00	4.384(±0.002)	1.8(±1.0)	
322.00	4.388(±0.002)	0.65(±0.3)	
...		0.83(±0.2)	
344.00	4.382(±0.001)	0.0(±0.8)	
	4.382(±0.001)	1.5(±2.5)	

[a]See Refs. 2 and 3. The numbers in parentheses are the estimated errors.

$$Z - Z_{\text{ref}} = \sum_{n=1} a_n(\rho - \rho_{\text{ref}})^n, \qquad (3)$$

where $Z = p/\rho RT$ and R is the gas constant. The reference point was chosen to be the ideal gas for temperatures above critical and the saturation boundary for temperatures below critical. The coefficients thus obtained are given in Table IV. Figure 3 shows typical deviations of the calculated densities from those measured experimentally for three isotherms: 143.1, 158.2, and 298.5 K. The results are quite good with all deviations being less than the estimated experimental error except at the highest densities on the 143.1 K isotherm. Even in this case the deviations seem to be random.

The situation with the saturation densities is slightly different from the isothermal case. Here, attempts both to use an equation of state, and to correlate all available data, yielded a molar polarizability curve that oscillated above 110 K. This behavior was attributed to
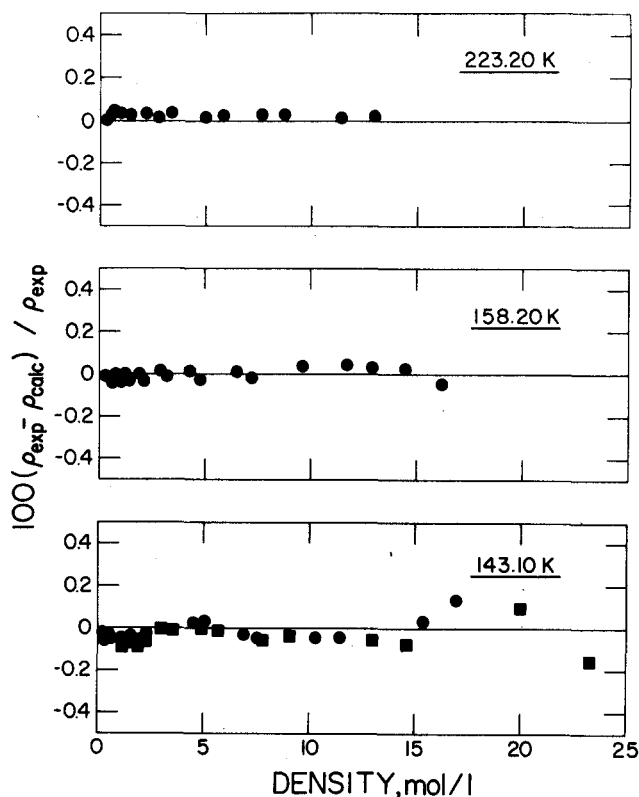

FIG. 3. Typical deviations observed between the experimental isothermal densities and those calculated with Eq. (3). ● (Ref. 20) and ■ (Ref. 21).

errors in some of the earlier experimental density data, and data were therefore selected to be used in the correlation which yielded what was considered to be a more reasonable molar polarizability curve based on our knowledge of other similar fluids. Admittedly, this procedure is somewhat arbitrary, but considering the difficulties encountered in measuring densities close to
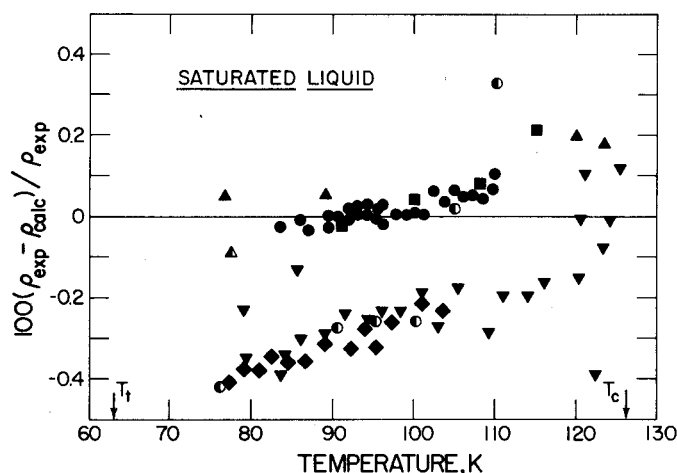
TABLE IV. Expansion coefficients a_n appearing in Eqs. (3) and (4).

n	298.5 K[a]	273.2 K	223.2 K	158.2 K
1	−4.4762169−03	−9.5955125−03	−2.4702641−02	−6.3683926−02
2	1.2689547−03	1.1470737−03	1.4295737−03	2.4818952−03
3	2.1865302−05	7.1458178−05	5.1447984−05	2.2286296−05
4	1.7441939−06	−3.5181450−06	−2.9779351−06	7.6899665−06
5		1.7485265−07	1.7644540−07	−9.5342428−07
6				4.9159163−08
7				−7.3599346−10

n	143.1 K	110.0 K	92.0 K	saturation
1	−8.1772829−02	1.0784920−01	2.7032665−01	3.0483364−01
2	4.7156962−03	2.0922013−02	9.8875773−02	5.8135734−01
3	−5.7797969−04	9.7922257−04	−1.5656782−02	−2.7351345−01
4	9.5209509−05			1.3456586−00
5	−8.6418884−06			−1.6517934−00
6	4.2055809−07			8.2057726−01
7	−1.0125749−08			
8	9.4818173−11			

[a]The notation m−n means that the number m should be multiplied by a factor of 10 to the −n.

FIG. 4. Deviations between all experimental saturation densities and those calculated using Eq. (4). ◐ (Ref. 23), ▲ (Ref. 24), △ (Ref. 25), ■ (Ref. 26), ● (Ref. 27), ▼ (Ref. 28), and ◆ (Ref. 29). As is discussed in Sec. IV of the text, the data base for the correlation does not include any data from Ref. 23 and 29 and includes only selected data in the temperature range 110–125 K from Ref. 28.

the critical point, it was felt that this approach was justified.

The sources from which data were selected for use in the analysis are as follows: Haynes and Stewart, [25] Weber, [24] Miller, [26] and Brauns, [27] 78 to 110 K; Goldman and Scrase, [28] 110 to 125 K. It should be emphasized that the data of Goldman and Scrase in the temperature range 78 to 110 K were not used in the data base. A function of the form

$$\rho = \sum_{n=1} a_n x^{n-1}, \tag{4}$$

where $x^3 = (1 - T/T_c)$, $T_c =$ critical temperature, 126.20 K, and ρ is the density in g/cm^3 was fitted in a least squares sense to the selected data. The coefficients obtained from the fit are listed in Table IV and the results of the fit are shown graphically in Fig. 4. It shows systematic differences of about 0.3 percent in the low temperature data of Goldman and Scrase, [28] Street and Staveley, [23] and Terry et al. [29] We offer no explanation for this discrepancy, but as mentioned earlier, justify the choice of data and resulting correlation on the reasonability of the derived molar polarizability curve and its relative position with respect to the higher temperature, more precisely determined isotherms.

At low densities, the primary source of uncertainty in the polarizabilities is due to the possibility of small errors in the capacitance measurements. This arises from the fact that when $\epsilon - 1$ approaches zero, it is necessary to measure the capacitance extremely accurately. For example at 223.2 K with $\rho = 1.495$ mol/ℓ and $\epsilon = 1.01982$, an uncertainty of ± 0.003 percent in the measured capacitance gives rise to an uncertainty of ± 0.15 percent in the calculated molar polarizability. For this reason, it is difficult to assess the accuracy of the dielectric virial coefficients listed in Table III. An examination of Table III shows, however, that our values of A_D agree well with those values reported by Cole

et al. [2,3] which were determined by a more precise, low density method. Also, it is seen that the temperature dependence of the B_D is proportional to $1/T$, in agreement with theory[7,8] and other experimental results. With these considerations in mind, a rough estimate of the accuracy of these coefficients is: A_D, ± 0.13 percent; B_D, ± 60 percent; and C_D, ± 90 percent.

V. SUMMARY

Wide range measurements of the dielectric constant of nitrogen have been performed and accurate values of the molar polarizability have been calculated. In the process of deriving the molar polarizabilities, the available saturation density data for liquid nitrogen have been re-analyzed and a correlation which, on the basis of the molar polarizability is probably the most accurate currently available, has been presented. Also, dielectric virial coefficients which appear to have the proper temperature dependence and which are consistent with other investigations, have been derived from the calculated molar polarizabilities. In general, we feel that these data will be extremely valuable for improving future correlations of compressibility and thermodynamic properties data for nitrogen.

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