CHAPTER - IV

STUDY OF REFRACTIVE INDICES AND ORDER PARAMETER IN SOME LIQUID CRYSTALS

Optical birefringence is one of the important physical propertiies of liquid crystals. This property forms one of the basis of several applications like the display devices. The strong optical birefringence arises from the alignment of molecules with large molecular anisotrophy[1]. This molecular anisotropy causes the ordinary light travel with vibrations in all directions, to split up into two constituent polarized components having planes of vibrations at right angles to each other, and hence travel with different speeds. The molecular anisotropy reflects the geometric shape of the molecules and the anisotropy of their electronic orbitals. With increasing molecular alignment the optical birefringence increases accordingly and therefore it can be used as a measure of the order parameter. Because the degree of orientational order in a liquid crystal varies with temprature, the indices of refraction for light polarized parallel and perpendicular to the director also changes with temperature. At higher temperatures, when the order parameter is smaller, the indices are closer to each other in value. The opposite is true at lower temperatures in the liquid crystalline phase where the order parameter is large.

As the temperature increases, the ordinary refractive index n_o increases while the extraordinary refractive index n_e decreases, therefore the birefringences $\triangle n=n_e - n_o$ decreases with the increase in temprature. At the nematic - isotropic transition temperature (T_{NI}) a step- like change of both coefficients takes place and they reach the value n_{ISO} charactaristic for isotropic liquids consequently the value of birefringence On falls stepwise to zero. The order parameter of liquid crystals is one of the most important parameters which governs nearly all its physical properties. Macroscopically the bulk tensorial properties such as refractive index, dielectric constant, magnetic susceptibility ect can in principle be used to determine the order parameters which is refered to as the macroscopic order parameter Q [2-4]. The tensor order parameter Q is given by

$$Q = G(\epsilon_{<,B} - 1/3\ S_{<,B}\ G) \ldots\ldots\ldots\ldots\ldots\ (1)$$

where $\epsilon_{<,B}$ may be taken as the electric polarizability, dielectric constant, refractive index or susceptibility, G is the normalization constant. Because of the local field effects on the tensorial properties, the macroscopic order parameter Q differ from the microscopic order parameter S[5,6].

Assuming the validity of a given local field model, it is possible to have a simplified connection between the macroscopic tensors and the microscopic quantities in which the molecules are assumed to be approximately rigid, and the molecules to be uniaxial rods. Saupe [7.8] suggested the relation

$$S = <_e - <_o / <_{\parallel} - <_{\perp} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (2)$$

Where $\prec_e$ and $\prec_o$ are the principal polarizabilities of the liquid crystalline phase, $\prec_{\parallel}$ and $\prec_{\perp}$ are the longitudinal and transverse component of the perfect molecular polarizability tensor on the microscopic level. Liquid crystalline phase being more ordered than the high temperature isotropic liquid " an order parameter" S is defined such that it is non zero in the nematic phase and vanishes due to symmetry reasons in the isotropic phase. The thermal motion present makes the molecules in the liquid crystalline phase not all exactly parallel and the extent of parallelelism can be measured by the order parameter. Therefore on the microscopic level, where the molecules are assumed to be simple rod - like in shape, the measure of the alignment a long the director n is given by

$$S = 1/2\ (3\ \mathrm{Cos}^2\theta - 1) \ \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where θ is the angle between the long axis of the molecules and the axis of preferred orientation which coincides with the symmetry axis in uniformly oriented liquid crystal [1,5-7]. For perfectly parallel orientation of molecules, S=1 and for the isotropic liquid S=0.

The knowledge of polarization field is required for the determination of the order parameter from optical anisotropy. The calculation of the polarization and orientational order parameter from the refractive index data involves the knowledge of the nature of local electric field inside the medium. The problem of the local electric field has been treated mainly from the famous two different approaches.

1) Vuks' approach [8.9], in which he assumes isotropic local field.

2) Neugebauer's approach [10-12], obtained from the point dipole approximation and involves anisotropic local field. If we assume that the local field is isotropic as assumed in Vuks' relation [8.9], we have

$$<_{e,o} = 3/4\pi N(n_{e,o}-1/n^2+2) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where $n^2 = 1/3\ (n_e^2 + 2n_o^2)$,

$N = N_o S/M$

Where N is the number of molecules per cm^3; N_o, the Avogadro's number; S the density and M, the molecular wieght. If however, the local field is anisotropic, as is indeed the case, one can use Neugebanauer's relation [10,11]

$$n^2_{e,o} - 1 = 4\pi N<_{e,o} /1-N<_{e,o}\ r_{e,o} \quad \ldots\ldots\ldots\ldots (5)$$

where r_e and r_o are the internal field factors with

$$r_e + 2r_o = 4\pi \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

It can be seen that $<_{e,o}$, can be determined from $n_{e,o}$ only if r_e and r_o are known. For a single crystal with known crystal structure, it is possible to determine, the internal field factors. Because of the change in the order parameter with temperature in liquid crystals the internal field factors are themselves temperature dependent. But since $r_e + 2r_o = 4\pi$ equation 3 can be written as

$$1/<_e+2/<_o= 4\pi N\{(n^2_e+2/n^2_e-1)+2(n^2_o+2)/n^2_o-1)\} \quad \ldots\ldots (7)$$

In the isotropic phase,

$$r_e = r_o = 4\pi/3,$$

$$n_e = n_o = n,$$

$$\alpha_e = \alpha_o = \bar{\alpha}$$

Assuming that the mean polarizability (α) remains the same in all the phases, we have

$$\alpha_e + 2\alpha_o = \alpha_{\parallel} + 2\alpha_{\perp} = 3\alpha = 9/4\pi N \quad (n^2-1/n^2+2) \quad \ldots\ldots(8)$$

where N is the number of molecules per cm^3 in the isotropic phase Using the above equations, α_e , α_o can be determined by Vuks' and Neugebaur's approaches.

The order parameter S can be expressed as

$$S= \alpha_e - \alpha_o / \alpha_{\parallel} - \alpha_{\perp} \quad \ldots\ldots\ldots\ldots\ldots\ldots(9)$$

Where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the principal molecular polarizabilities parallel and perpendacular to the long axis of the molecules in the crystalline state. The values of $\alpha_{\parallel}$ and $\alpha_{\perp}$ are obtained by the method of Haller et al [13]. Graphs are plotted for log α_e/α_o vs log $(T_{NI}-T)$ where T_{NI} is the nematic- isotropic transition temperature. These plots are straight lines at lower temperature and intersect the log α_e/α_o axis at 0°K, assumed to correspond to log $\alpha_{\parallel}/\alpha_{\perp}$ value in the crystaline state. The order parameter S is then calculated by using equation 9.

LITERATURE SURVEY :

Derzhanski and Petrov [13], de Jeu and Bordewijk [14] have suggested another model in which the molecules are assumed to occupy a spheroidal cavity whose volume is equal to the volume available to the molecule and that the spheroid shaped molecule is uniformly polarizable and the medium surrounding the Spheroidal Cavity is a homogeneous anisotropic dielectric. The basic approximations involved in both point dipole and spheroidal molecule models do simplify in nature.

Practically the molecules are of finite size and their shapes are irregular and some times consists of groups which are polarizable to different extents. Moreover, the immediate visinity of a molecule can not be approximated by a continuous medium. Therefore, the calculations of the cavity field determined by electrostatic theory with the application of boundary conditions, for spheroidal cavity, are not likely to lead to the true value. Further, it is found that the orientational order parameter evaluated through Vuks' and Neugebauer's approaches are consistent with the values obtained from other sutdies on diamagnetic anisotropy, NMR, EPR, magnetic susceptibility & X-rays. Moreover Madhusudana [15] has drawn some theoretical conclusions about the validity of the density and refractive index measurements used for evaluating the order parameter. Chatelain [16, 17], Brunet Germain [18] have employed the prism refractometer for the measurements. Bata et al [19] and Balzarini [20] have employed the lazer light for the determination of the birefringence. The refractive indices in the nematic and isotropic phases of p-n-butoxy and p-n-amyloxy benzoic acids were reported by Yakhmi et al [21]. They reported higher values of the order parameter by using Vuks' approach and attributed that to the dimer formation and to the existence of a dimer-monometer equilibrium. Refractive index and dielectric permittivity of some liquid crystals and their related applications were reported by de Jue [22]. Employing the Wedge method Sarana et al [23] have studied the refractive indices of the Polymesomorphic HBT and OBT. The order parameter values determined using Vuks' and Neugebauer's models agree well in the nematic phase but differ considerably in the Smectic phase. O'Shea and Kuster [24] have measured the refractive indices in oriented Cholesteryl dodecyl carbon and a smectic liquid crystal p-n-octyloxy-benzylidene-p-n butylaniline have been measured as a function of temperature. They have calculated the order parameter also. Mada and Kobayashi [25] have reported the dependance of refractive indices on voltage and wavelength employing the interferrogram technique. The agreement between the theoretical and experimental results were good. Shashidhara et al [26] have reported the refractive indices in nematic, re-entrant isotropic and isotropic phases. Alongwith these results the sequence of the phases were confirmed with DSC measurements.

Rao et al [27] have computed the molecular paralizabilities and molecular polarizabilities and it's anisotropics at different wavelengths by using different internal fields. Kali Krishnakoli etal [28] and Sen etal [29] have reported the refractive index and diellectric constants data for alkyl/alkoxyphenyl cyclohexane carboxylate and phenyl cylohexane nematic liquid crystals. They found that the replacement of a phenyl ring with a cyclohexyl ring reduces the order parameter appreciably. Mitra and Paul [30] have reported the measurements of refractive indices and densities of p-ethoxyphenyl trans-4-butyl cyclohexane carboxylate at different temperatures. They have computed the molecular polarizabilities from the refractive indices data using Vuks' fromula and determined the order parameter from the polarizability values. They compered the order parameter results with those obtained from Maier-Saupe theory. Employing Fabry-Perot interferometer the ordinary and extraordinary refractive indices of a ferroelectric S_c have been studied as a function of wavelength and temperature by Masahiro Kawaida et al [31]. They observed that the refractive indices have a normal wavelength dispersion similar to a nematic liquid crystal. Recently Mitra et al [32] have reported the ordinary and extraordinary refractive indices and density of the homologous series, cyanophenyl alkyl ether. They have computed the orientational order from the polarizability data and interpreted their results on the basis of McMillan theory.

The orientational order parameter S of a liquid crystal is an important physical parameter as it decides it's use in a particular purpose. Dielectric permittivity, diamagnetic susceptibility, X-ray scattering, UV, IR dichroism are all usefull methods used to measure the ordeer parameter. However, optical anisotropy measurements offer a simple method for obtaining the order parameter. Therefore several workers have shown considerable interest in studying the refractive indices of liquid crystals as can be seen from the above survey. However, comparatively less work has been done systematically on homologous serieses and the evaluation of the validity of Vuks' and Neugebauer's theories. In this context, to test the validity of these two theories the author has measured the refractive indices in a homologous series, and in the same series but with different terminal group. The order parameter was also estimated using both the theories.

RESULTS :

The author has studied the liquid crystals described in chapeter III, viz.

(1) p-(p'-n pentyloxybenzoyloxy) nitrophenol (PBNP)
(2) p-(p'-n hexyloxybenzoyloxy) nitrophenol (H6BNP)
(3) p-(p'-n heptyloxybenzoyloxy) nitrophenone (H7BNP)
(4) p-(p'-n heptyloxybenzoyloxy) benzaldehyde (HBB)
(5) p-(p'-n Octyloxybenzoyloxy) benzaldehyde (OBB)

The refractive indices measurements were carried out by a modified spectrometer, the details of which are given in chapter II. All the measurements were carried out while cooling.

The actual measured values of ordinary and extraordinary refractive indices n_o, n_e at different tempeatures for the five liquid crystals are presented in Table 4.1 through 4.5. The results are plotted in Figure 4.1 through 4.5. The values of the refractive indices for the isotropic phase n_{ISO} are also included. The density values are included from chapter III. Some of the densities presented in the table at temperatures where the refractive indices are not measured are the interpolated values read from the temperature-density graph. The birefringence values are also included.

The principal polarizabilities α_e, α_o are computed using Vuks' and Neugebauer's approaches are presented in Table 4.~~5~~ through 4.6 4.10. The values $\alpha_{\parallel}$, $\alpha_{\perp}$ obtained from Haller extrapolation are indicated below the Tables of order parameter for Vuks' and Neugebauer's values. The same results α_e , α_o are plotted in Figuer 4.5 through 4.10. The order parameter was also estimated using both the theories and the results are presented in Table 4.11 through 4.15. The same results are presented in Figure 4.11 through 4.15. All the results are presented for the liquid crystal PBNP, H6BNP, H7BNP, HBB & OBB are in respective sequence.

TEMPERATURE VARIATION OF REFRACTIVE INDICES (n_o, n_e AND n) AND BIREFRINGES ($\triangle$N):

The variation of n_o, n_e, n with temperature is shown in Figure 4.1 through 4.5 for the liquid crystals PBNP,H6BNP, H7BNP, HBB & OBB respectively. From the Figures it can be seen that the behaviour of the ordinary refractive index n_o and extraordinary refractive index, n_e is common for all the Liquid crystals studied. The extraordinary refractive index n_e increases with the decrease in temperatures while the ordinary refractive index n_o decreases with decrease in temperature in the nematic or the smectic phase. The refractive index n_{Iso} decreases with an increase in temperature as in normal organic liquids. The figures indicate that the birefringence ($\triangle$n) decreases rapidly with increase in the temperature.

It is observed that n_e is higher than n_o and birefringence for all the liquid crystals studied. It is also observed that n_e,n_o and $\triangle$n decreases as the alkyl chain increases, in other words as we proceed to higher members of the homologous sereis, the value of $\triangle$n decreases.

TEMPERATURE VARIATION OF PRINCIPAL POLARIZABILITIES $<_e$, $<_o$ & THE VARIATIONS OF THE ORDER PARAMETER BY VUKS' AND NEUGEBAUER'S APPROACHES:

The principal polarizabilities $<_e$, $<_o$ and the order parameter S are estimated using Vuks' and Neugebaur's approaches. The values are presented in Table 4.6 through 4.10 for PBNP, H6BNP, H7BNP, HBB & OBB respectively. The same has been represented graphically in Figure 4.6 through 4.10. The temperature variations of the order parameter S computed from both approaches are presented in Table 4.11 through 4.15. The order parameter using both approaches is represented in Figures 4.11 through 4.15.

To compare the order parameter results, a uniform reduced temperature $T=T_{NI}/T$ has been introduced. It results from theory [1] that, the temperature variation of order paameter of Liquid crystals. When expressed against the reduced temperature, should exhibit common features. An examination of these Figures indicate that the order parameter S, estimated using both the theories increases with decrease in temperature in the nematic phase. Moreover it can be observed that the order parameter is sensitive to the temperature variation. The Figure indicate also that the order parameter S for all the liquid crystals studied are comparable, for both Vuks' and Neugebaure's approaches. The reason for that the anisotropy of the principal polarizabilities increase, in same proportions in Vuks' as well as Neugebauer's theories. Subramanyan et al [32] have observed that the polarizability values obtained from the Neugebauer's relation agree well with isotropic polarizabilities estimated from the bond polarizability data. Moreover/ the minor differences in the values of the order parameter S may be related to the values of $(\alpha_{\parallel},\alpha_{\perp}$ which is not determined directly, but evaluated from an extrapolation technique, which has a limitation of 10 % [4, 33]. Further Vuks' had assumed an isotropic internal field in the Liquid crystalline phase, but practically it is difficult to visualize how in a medium of anisotropic molecular distribution as in liquid crystals the local field would be isotropic. In an anisotropic molecular distribution as in the liquid crystals the internal field parameters can not be the same along the molecular axis and perpendicular to it, though the determination of the order parameters of Liquid crystals by Neugebauer's and Vuks' approaches give nearly the same values. As liquid crystals are systems with molecular anisotropy, the Neugebauer's approach is to be preferred as a more theoretically sound model than the Vuks', since it assumes that the internal field constants are different along and perpendicular to the molecular axis. Further other workers confirmed that the principal polarizabilities obtained from Neugebauer's approach agree well with the values obtained from bond polarizabilities [32]. In the homologous series which is the subject of our investigations, the order parameter is nearly equal and slightly increases as the alklyl chain increases. Other workers have observed the same in their investigations on other homologous series [34].

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TABLE 4.1				
TEMPERATURE VARIATION OF n_o, n_e AND Δn in PBNP				
Temperature T°C	**Density S gm/cm^3**	**Refractive Indices n_o**	**n_e**	**Birefringence Δn**
52	1.1763	1.5276	1.6611	0.1335
53	1.1752	1.5281	1.6607	0 1326
54	1.1741	1.5284	1.6599	0.1315
55	1.1730	1.5290	1.6590	0 1300
56	1.1719	1.5300	1.6586	0.1286
57	1 1707	1.5303	1.6568	0 1265
57.5	1 1701	1.5318	1.6562	0.1244
58	1.1695	1.5319	1.6540	0.1221
58.5	1.1689	1.5341	1.6536	0.1195
59	1.1684	1.5345	1.6510	0.1140
59.5	1.1678	1.5366	1.6480	0.1114
60	1.1673	1.5380	1.6442	0.1062
60.5	1.1666	1.5391	1.6408	0.1017
61	1.1660	1.5420	1.6310	0.0920
61.5	1.1652	1.5446	1.6211	0.0765
62	1.1645	1.5883		
63	1.1626	1.5838		

TABLE 4.2

TEMPERATURE VARIATION OF n_o ,n_e AND Δn in H6BNP

Temperature T°C	Density S gm/cm^3	Refractive Indices n_o	n_e	Birefringence Δn
58	1.1480	1.5240	1.6445	0.1198
59	1.1469	1.5246	1.6441	0.1195
59.5	1.1463	1.5257	1.6437	0.1180
60	1.1457	1.5267	1.6436	0.1169
60.5	1.1451	1.5277	1.6416	0.1139
61	1.1445	1.5288	1.6413	0.1125
61.5	1.1439	1.5299	1.6406	0.1107
62	1.1433	1.5307	1.6370	0.1085
62.5	1.1426	1.5316	1.6336	0.1030
63	1.1421	1.5324	1.6300	0.0986
63.5	1.1415	1.5342	1.6254	0.0925
64	1.1410	1.5359	1.6219	0.0870
64.5	1.1404	1.5384	1.6164	0.0780
65	1.1395	1.5741		
66	1.1380	1.5709		

TABLE 4.3

TEMPERATURE VARIATION OF n_o, n_e AND Δn in H7BNP

Temperature T°C	Density S gm/cm³	Refractive Indices		Birefringence Δn
		n_o	n_e	
48	1.1442	1.5096	1.6230	0.1134
49	1.1430	1.5097	1.6227	0.1130
50	1.1416	1.5099	1.6222	0.1123
50.5	1.1409	1.5102	1.6218	0.1116
51	1.1403	1.5104	1.6241	0.1110
51.5	1.1397	1.5107	1.6208	0.1101
52	1.1390	1.5110	1.6201	0.1091
52.5	1.1384	1.5115	1.6194	0.1079
53	1.1377	1.5125	1.6163	0.1038
53.5	1.1370	1.5151	1.6142	0.0991
54	1.1364	1.5179	1.6101	0.0931
54.5	1.1360	1.5193	1.6052	0.0863
55	1.1355	1.5222	1.5979	0.0752
55.5	1.1350	1.5275	1.5944	0.0669
56	1.1341	1.5310		
57	1.1324	1.5612		
58	1.1312	1.5597		

TABLE 4.4

TEMPERATURE VARIATION OF n_o ,n_e AND Δn in HBB

Temperature T°C	Density S gm/cm³	Refractive Indices n_o	n_e	Birefringence Δn
52	1.0356	1.4805	1.6096	0.1291
53	1.0355	1.4814	1.6094	0.1280
54	1.0344	1.4823	1.6093	0.1270
55	1.0322	1.4832	1.6093	0.1261
56	1.0321	1.4840	1.6085	0.1245
57	1.0310	1.4849	1.6067	0.1218
58	1.0299	1.4858	1.6054	0.1196
59	1.0285	1.4868	1.6032	0.1164
60	1.0273	1.4880	1.6005	0.1125
61	1.0257	1.4920	1.5928	0.1008
61.5	1.0244	1.4952	1.5892	0.0940
62	1.0234	1.5350		
62.5	1.0221	1.5338		

TABLE 4.5

TEMPERATURE VARIATION OF n_o, n_e AND Δn in OBB

Temperature T°C	Density S gm/cm³	Refractive Indices n_o	n_e	Birefringence Δn
60	1.0127	1.4671	1.6022	0.1351
61	1.0117	1.4682	1.6003	0.1321
62	1.0180	1.4695	1.5982	0.1287
63	1.0099	1.4709	1.5962	0.1253
64	1.0090	1.4718	1.5945	0.1227
65	1.0081	1.4730	1.5922	0.1192
66	1.0072	1.4741	1.5896	0.1155
67	1.0063	1.4753	1.5875	0.1122
68	1.0055	1.4761	1.5852	0.1085
69	1.0044	1.4802	1.5830	0.1028
69.5	1.0039	1.4847	1.5808	0.0961
70	1.0020	1.5300		
70.5	1.0008			

TABLE 4.6

TEMPERATURE VARIATION OF α_o, α_e in PBNP

Temperature T°C	Vuks' Approach $\alpha_o (A°)^3$	$\alpha_e (A°)^3$	Neugebauer's Approach $\alpha_o (A°)^3$	$\alpha_e (A°)^3$
52	33.4375	44.1112	34.2845	42.221
53	33.5209	44.1144	34.3155	42.219
54	33.5597	44.0912	34.3995	42.221
55	33.6359	44.0056	34.4660	42.198
56	33.731	44.0046	34.4580	41.192
57	33.8005	43.9563	34.5970	42.186
57.5	33.9149	43.9045	34.6967	42.177
58	33.9569	43.7653	34.7364	42.037
58.5	34.1143	43.6157	34.8838	42.013
59	34.1964	43.4561	34.9285	41.743
59.5	34.3479	43.3331	35.0653	41.882
60	34.4763	43.0093	35.1585	41.513
60.5	34.6127	43.7902	35.3041	41.351
61	34.7979	41.8532	35.4932	40.2186

TABLE 4.7

TEMPERATURE VARIATION OF α_o, α_e in PBNP

Temperatu T°C	Vuks' Approach		Neugebauer's Approach	
	$\alpha_o (A^\circ)^3$	$\alpha_e (A^\circ)^3$	$\alpha_o (A^\circ)^5$	$\alpha_e (A^\circ)^3$
58	36.5406	45 7231	36 4006	44.0038
59	35.6886	45.8923	36.4921	44.1058
59.5	35.7843	45.8637	36.5829	44.2758
60	35.8693	45.8583	36.6426	44 1543
60.5	35.9724	45.7075	36.7368	44.1026
61	36.0658	45.6845	36.8251	44.1598
61.5	36.1644	45,6324	36.8577	43.9746
62	36.2439	45.5305	36.9699	43.9502
62.5	36.3794	45.2066	37.0643	43.6114
63	36.4720	44.9096	37.1268	43.4864
63.5	36.5730	44.4887	37.2024	43.1252
64	36.7534	44.1978	37.3445	42.9210
64 5	37.0579	43.7254	37.5833	42.5934

TABLE 4.8				
TEMPERATURE VARIATION OF α_o, α_e in H7BNP				
Temperature T°C	Vuks' Approach		Neugebauer's Approach	
	$\alpha_o(A°)^3$	$\alpha_e(A°)^3$	$\alpha_o(A°)^3$	$\alpha_e(A°)^3$
48	36.3727	46.4760	37.1415	44.7770
49	36.4203	46 5012	37.1886	44 8028
50	36.4851	46.5125	37.2015	44.8070
50.5	36.5306	46.5006	37.2145	44.8120
51	36.5515	46.4901	37.2357	44.8386
51 5	36.6147	46.4601	37.2506	44.7888
52	36.6626	46.4232	37.3223	44.8254
52.5	36 7234	46.3807	37.4541	44.7718
53	36.8440	46.1368	37.5666	44.5408
53.5	37.0674	45.9293	37.7564	44.4272
54	37.2843	45.5198	37.9557	44.1236
54 5	37.4033	45.1451	38.0501	44.7925
55	37.7608	44.5303	38.3027	43 4648
55.5	38.1787	44.1594	38.6464	43 1672

TABLE 4.9

TEMPERATURE VARIATION OF α_o, α_e in HBB

Temperature T°C	Vuks' Approach $\alpha_o(A°)^3$	$\alpha_e(A°)^3$	Neugebauer's Approach $\alpha_o(A°)^3$	$\alpha_e(A°)^3$
52	36.2866	48.432	37.1829	46.4042
53	36.3592	48.401	37.2285	46.4430
54	36.4663	48.4256	37.3558	46.4084
55	36.6092	48.3972	37.4891	46.4218
56	36.6797	48.3562	37.5489	46.4722
57	36.8016	48.3027	37.6534	46.3932
58	36.9188	48.2215	37.7510	46.3579
59	37.0636	48.0756	37.8863	46.2394
60	37.2214	47.8733	38.0122	46.1057
61	37.6407	47.1951	38.3673	45.6055
61.5	37.9645	46.8725	38.6376	45.3947

TABLE 4.10

TEMPERATURE VARIATION OF α_o, α_e in OBB

Temperature T°C	Vuks' Approach $\alpha_o (A°)^3$	Vuks' Approach $\alpha_e (A°)^3$	Neugebauer's Approach $\alpha_o (A°)^3$	Neugebauer's Approach $\alpha_e (A°)^3$
60	37.6376	51.1808	38.6220	48.9261
61	37.7777	51.0288	38.6548	49.0000
62	37.9356	50.8535	38.8654	48 8739
63	38.0985	50.6821	38.9958	48.6584
64	38.2190	50.5491	39.1088	48.5424
65	38.3673	50.3516	39.2401	48.3798
66	38.5154	50.1346	39.3617	48.2366
67	38.6640	49.9574	39.4784	48.1432
68	38.8292	49.7552	39.6147	48 0106
69	39.1694	49.5257	39.9201	47.8698
69.5	39.5715	49.2514	40.2928	47.6544

TABLE 4.11

TEMPERATURE VARIATION OF ORDER PARAMETER S IN PBNP

Temperature T°C	ORDER PARAMETER (S)	
	Neugebauer's Approach	Vuks' Approach
0.8387	0.6152	0.6493
0.8548	0.6127	0.6444
0.8709	0.6055	0.6406
0.8871	0.5994	0.6308
0.9032	0.5995	0.6249
0.9194	0.5883	0.6177
0.9274	0.5799	0.6076
0.9354	0.5659	0.5965
0.9435	0.5527	0.5779
0.9516	0.5283	0.5632
0.9597	0.5284	0.5465
0.9677	0.4926	0.5190
0.9758	0.3663	0.5582
	$\alpha_{\parallel}=5214(A^{\circ})$ $\alpha_{\perp}=39.24(A^{\circ})$	$\alpha_{\parallel}=5214(A^{\circ})$ $\alpha_{\perp}=39.24(A^{\circ})$

TABLE 4.12

TEMPERATURE VARIATION OF ORDER PARAMETER S IN H6BNP

Temperature T°C	ORDER PARAMETER (S)	
	Neugebauer's Approach	Vuks' Approach
0.8923	0.5804	0.6074
0.9076	0.5812	0.6074
0.9154	0.5872	0.6000
0.9231	0.5872	0.5946
0.9308	0.5623	0.5795
0.9385	0.5599	0.5725
0.9462	0.5639	0.5636
0.9538	0.5328	0.5528
0.9615	0.4998	0.5254
0.9692	0 4845	0.5022
0.9769	0.4521	0.4712
0.9846	0.4257	0.4431
0.9923	0.3824	0.3969
	$\alpha_{\parallel}$=52.02(A°) $\alpha_{\perp}$=38.92(A°)	$\alpha_{\parallel}$=55.64(A°) $\alpha_{\perp}$=38.84(A°)

TABLE 4.13

TEMPERATURE VARIATION OF ORDER PARAMETER S IN H7BNP

Temperature T°C	ORDER PARAMETER (S)	
	Neugebauer's Approach	Vuks' Approach
0.8571	0.6411	0.6561
0.8750	0.6393	0.6546
0.8929	0.6389	0.6511
0.9018	0.6379	0.6474
0 9107	0.6316	0.6454
0.9196	0.6329	0.6393
0.9286	0.6299	0.6338
0.9375	0.6144	0.6271
0.9464	0.5860	0.6034
0.9554	0.5601	0.5754
0.9643	0.5183	0.5348
0.9732	0.4826	0.5027
0.9821	0.4334	0.4396
0.9912	0.3800	0.3883
	$\alpha_{\parallel}=52.04$(A°) $\alpha_{\perp}=40.13$(A°)	$\alpha_{\parallel}=55.91$(A°) $\alpha_{\perp}=40.51$(A°)

TABLE 4.14 TEMPERATURE VARIATION OF ORDER PARAMETER S IN HBB		
Temperature T°C	ORDER PARAMETER (S)	
	Neugebauer's Approach	Vuks' Approach
0.8387	0.7104	0.7361
0.8548	0.7098	0.7298
0.8710	0.6974	0.7248
0.8871	0.6882	0.7144
0.9032	0.6875	0.7077
0.9194	0.6733	0.6970
0.9355	0.6631	0.6851
0.9516	0.6434	0.6674
0.9677	0.6235	0.6456
0.9839	0.5576	0.5609
0.9919	0.5206	0.5399
	$\alpha_{\parallel}=54.32(A^{\circ})$ $\alpha_{\perp}=41.34(A^{\circ})$	$\alpha_{\parallel}=56.91(A^{\circ})$ $\alpha_{\perp}=40.41(A^{\circ})$

TABLE 4.15

TEMPERATURE VARIATION OF ORDER PARAMETER S IN OBB

Temperature T°C	ORDER PARAMETER (S)	
	Neugebauer's Approach	Vuks' Approach
0.8571	0.7467	0.7566
0.8714	0 7497	0.7403
0.8857	0.7253	0.7217
0.9000	0.7001	0.7030
0.9143	0.6836	0.6888
0.9286	0.6623	0.6695
0.9429	0.6431	0.6491
0.9571	0.6279	0.6309
0.9714	0.6084	0.6104
0.9857	0.5761	0.5227
0.9929	0.5334	0.5407
	$\alpha_{\parallel}$=54.62(A°) $\alpha_{\perp}$=40.82(A°)	$\alpha_{\parallel}$=56.72(A°) $\alpha_{\perp}$=38.82(A°)

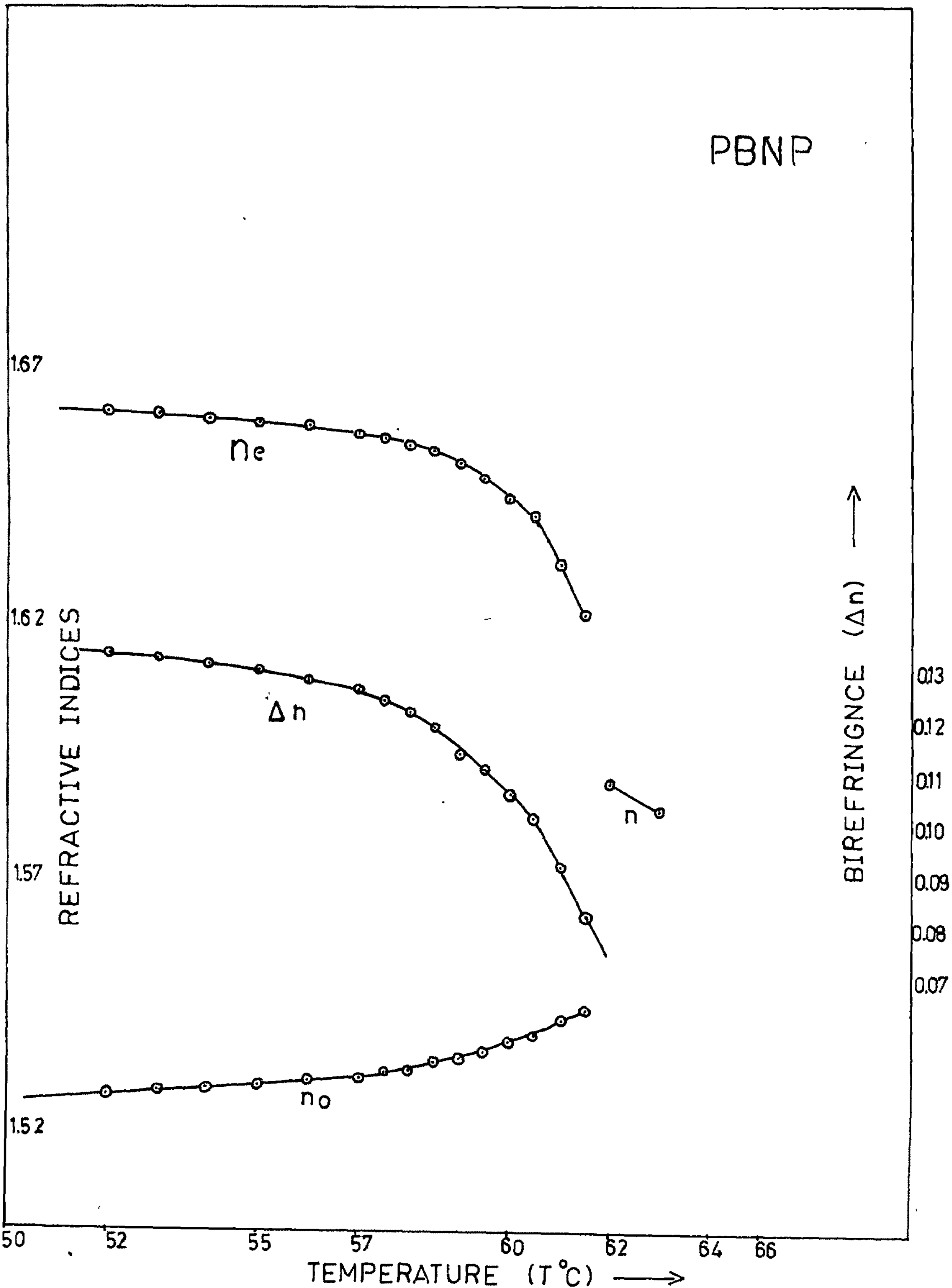
PBNP
1.67
1.62
1.57
1.52
REFRACTIVE INDICES
ne
Δn
no
n
BIREFRINGNCE (Δn) →
0.13
0.12
0.11
0.10
0.09
0.08
0.07
50
52
55
57
60
62
64
66
TEMPERATURE (T °C) →

Figure 4.1

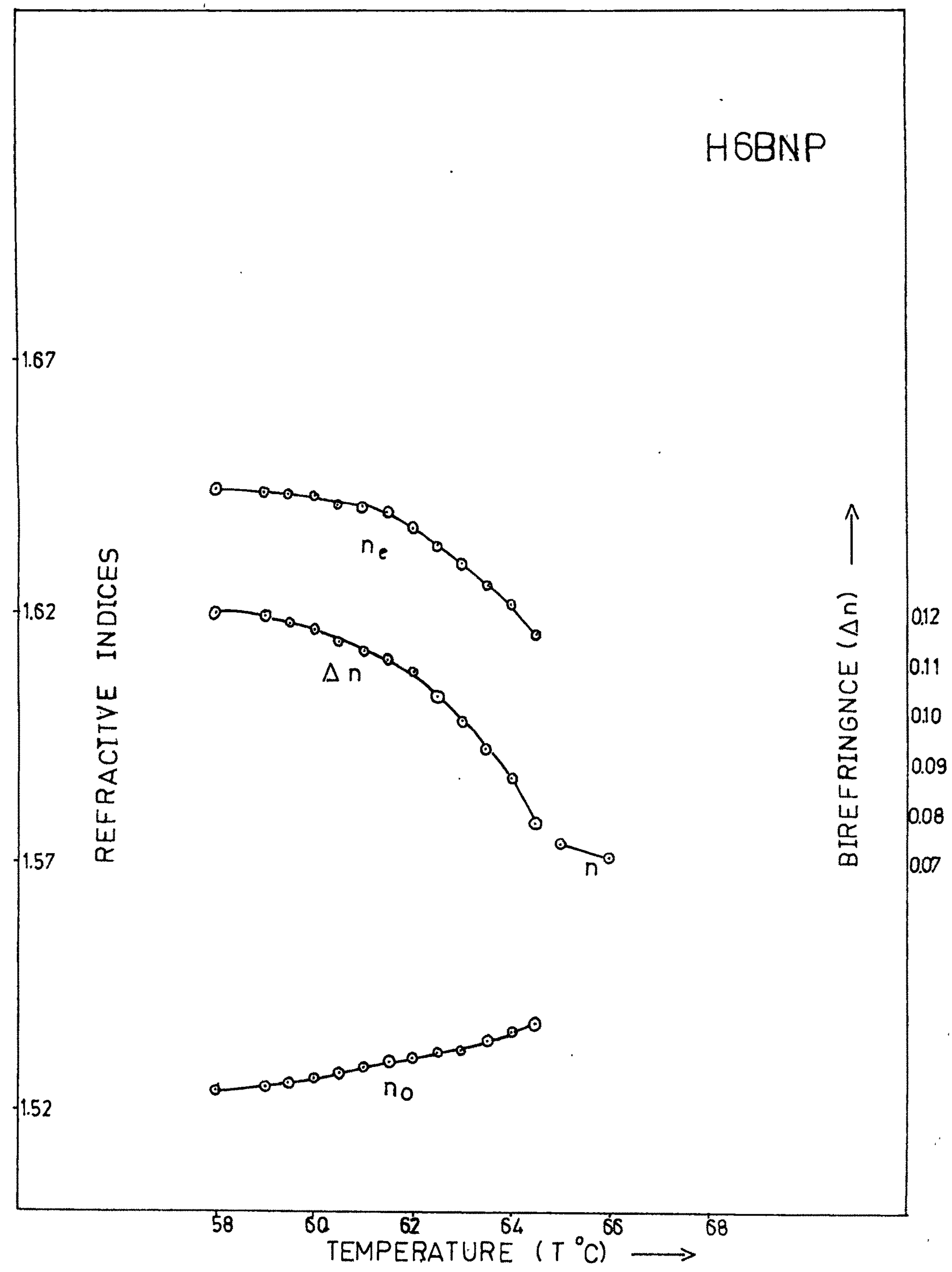
H6BNP
REFRACTIVE INDICES
1.67
1.62
1.57
1.52
BIREFRINGNCE (Δn)
0.12
0.11
0.10
0.09
0.08
0.07
n_e
Δ n
n
n_o
58
60
62
64
66
68
TEMPERATURE (T °C)

Figure 4 2

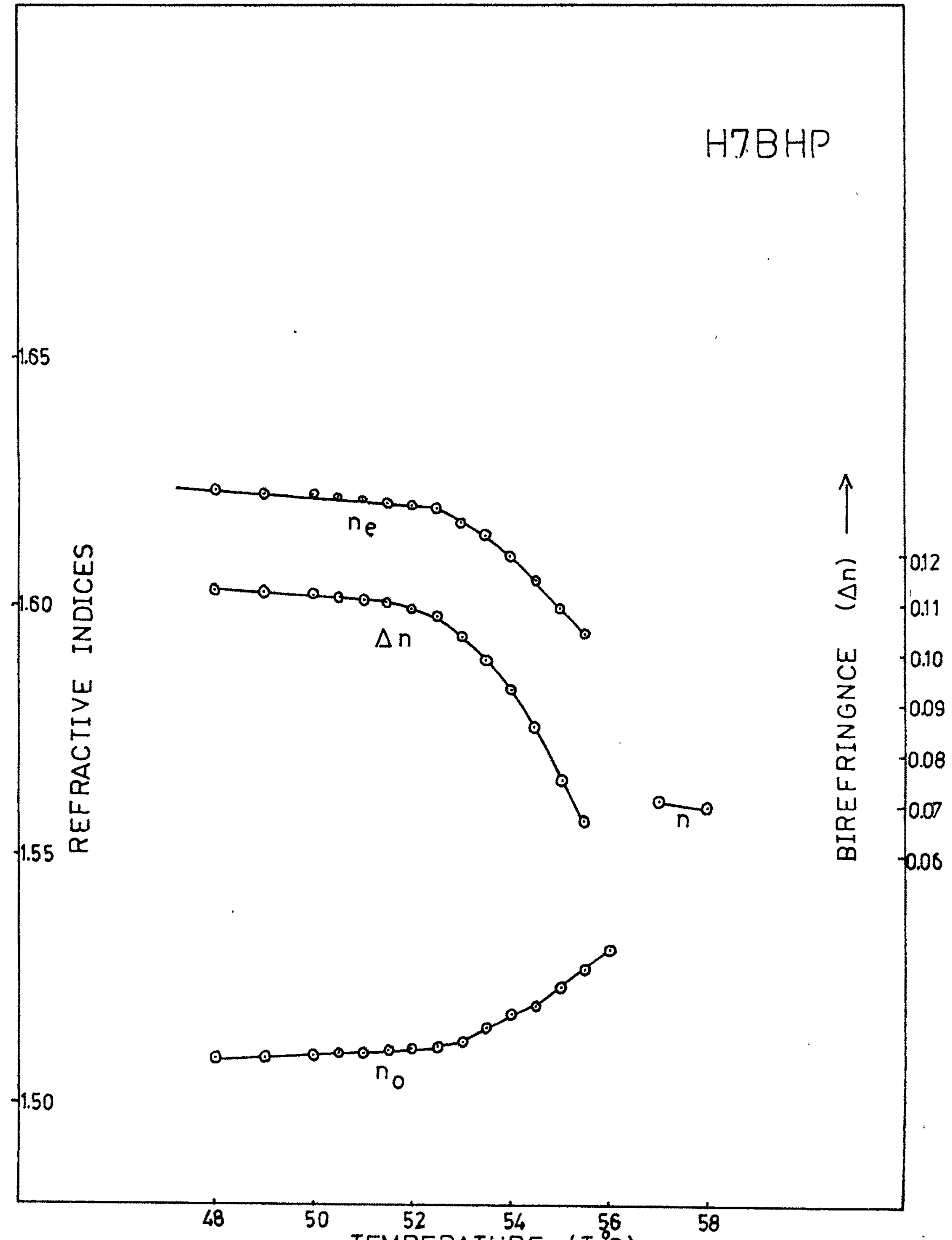
H7BHP
REFRACTIVE INDICES
1.65
1.60
1.55
1.50
BIREFRINGNCE (Δn) →
0.12
0.11
0.10
0.09
0.08
0.07
0.06
n_e
Δn
n
n_o
48
50
52
54
56
58
TEMPERATURE (T °C) →

Figure 4.3

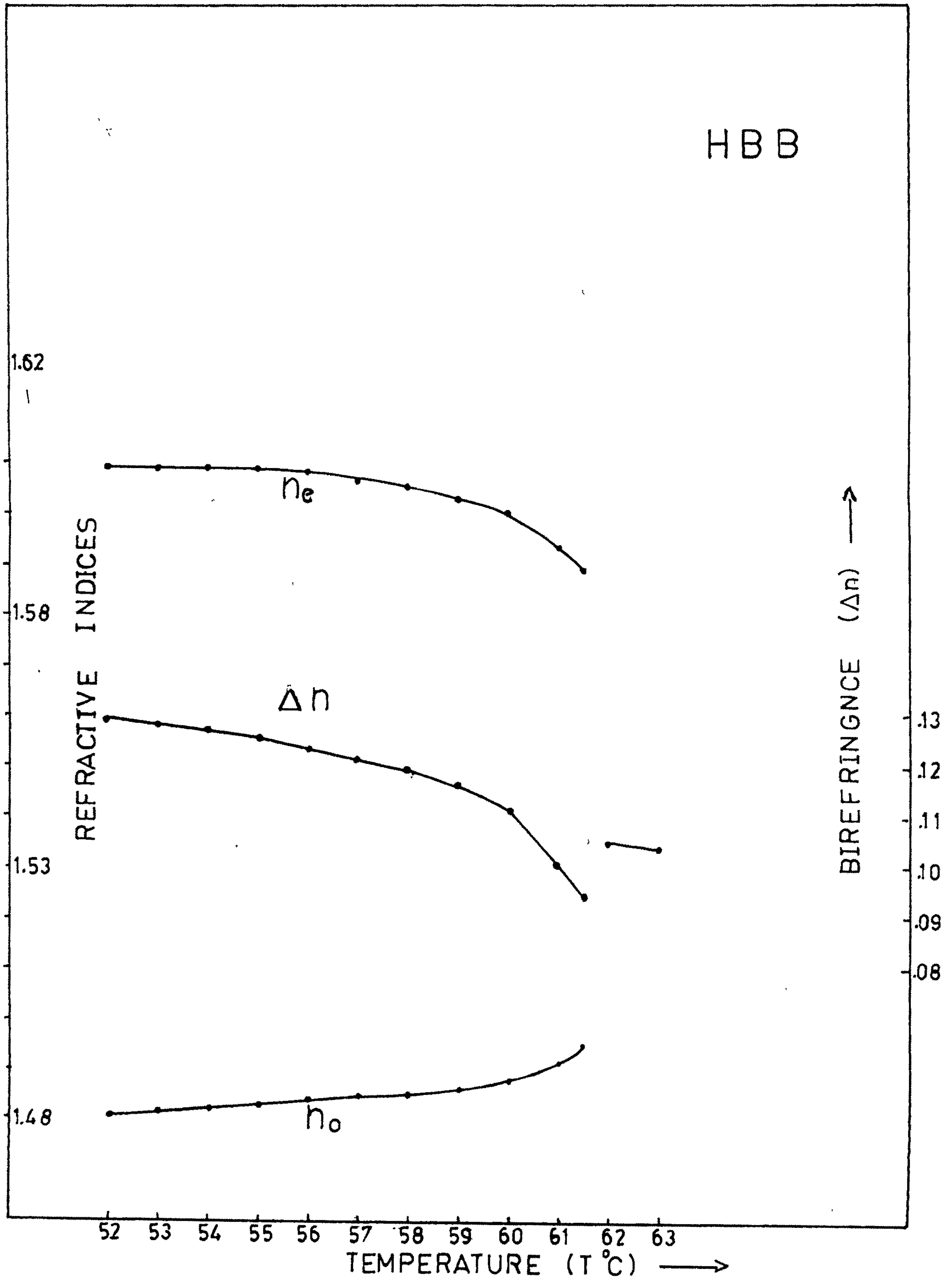
HBB
REFRACTIVE INDICES
1.62
1.58
1.53
1.48
n_e
Δn
n_o
BIREFRINGNCE (Δn) →
.13
.12
.11
.10
.09
.08
52
53
54
55
56
57
58
59
60
61
62
63
TEMPERATURE (T °C) →

Figure 4.4

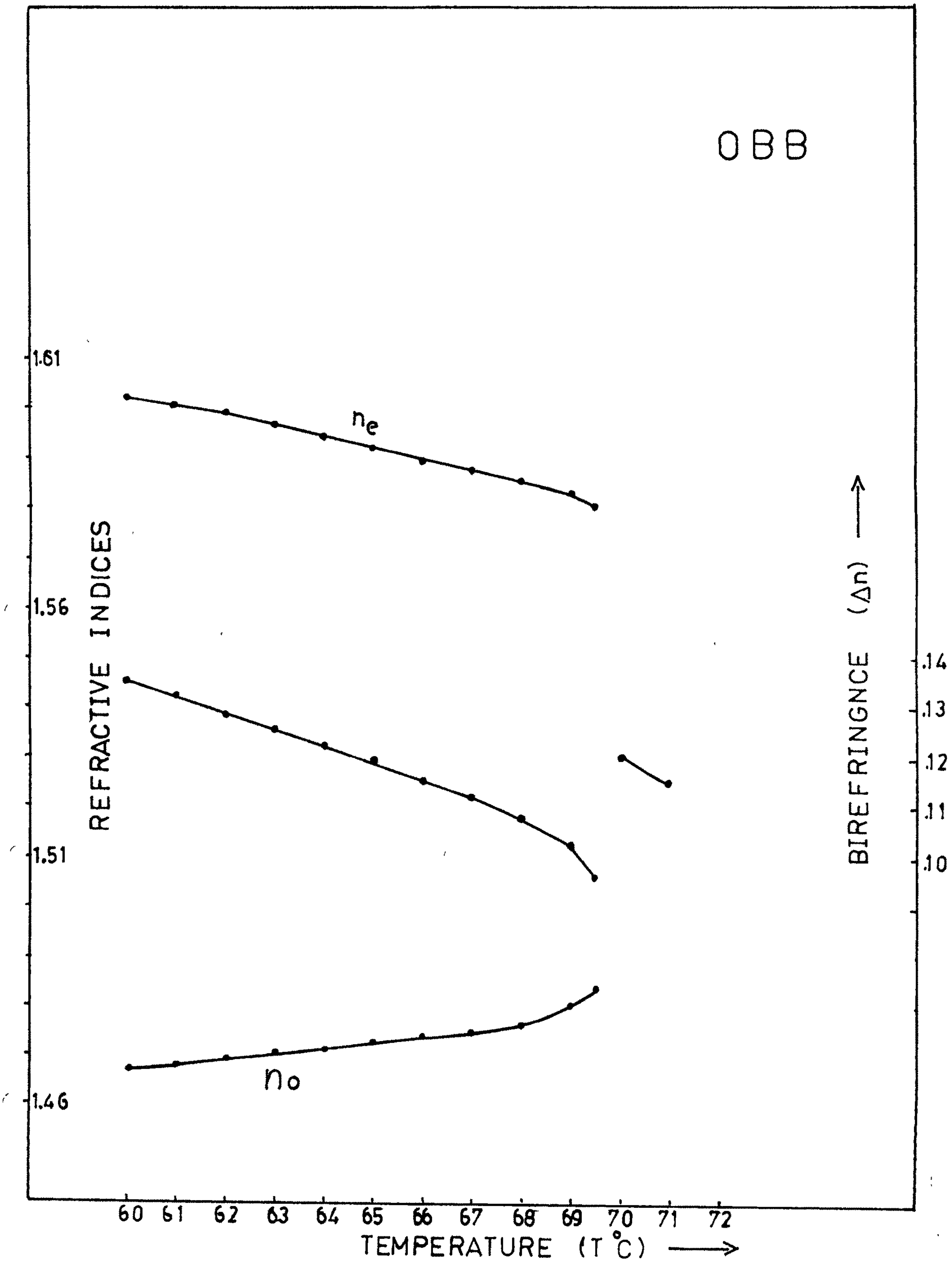
OBB
REFRACTIVE INDICES
BIREFRINGNCE (Δn) →
n_e
n_o
1.61
1.56
1.51
1.46
.14
.13
.12
.11
.10
60
61
62
63
64
65
66
67
68
69
70
71
72
TEMPERATURE (T °C) →

Figure 4.5

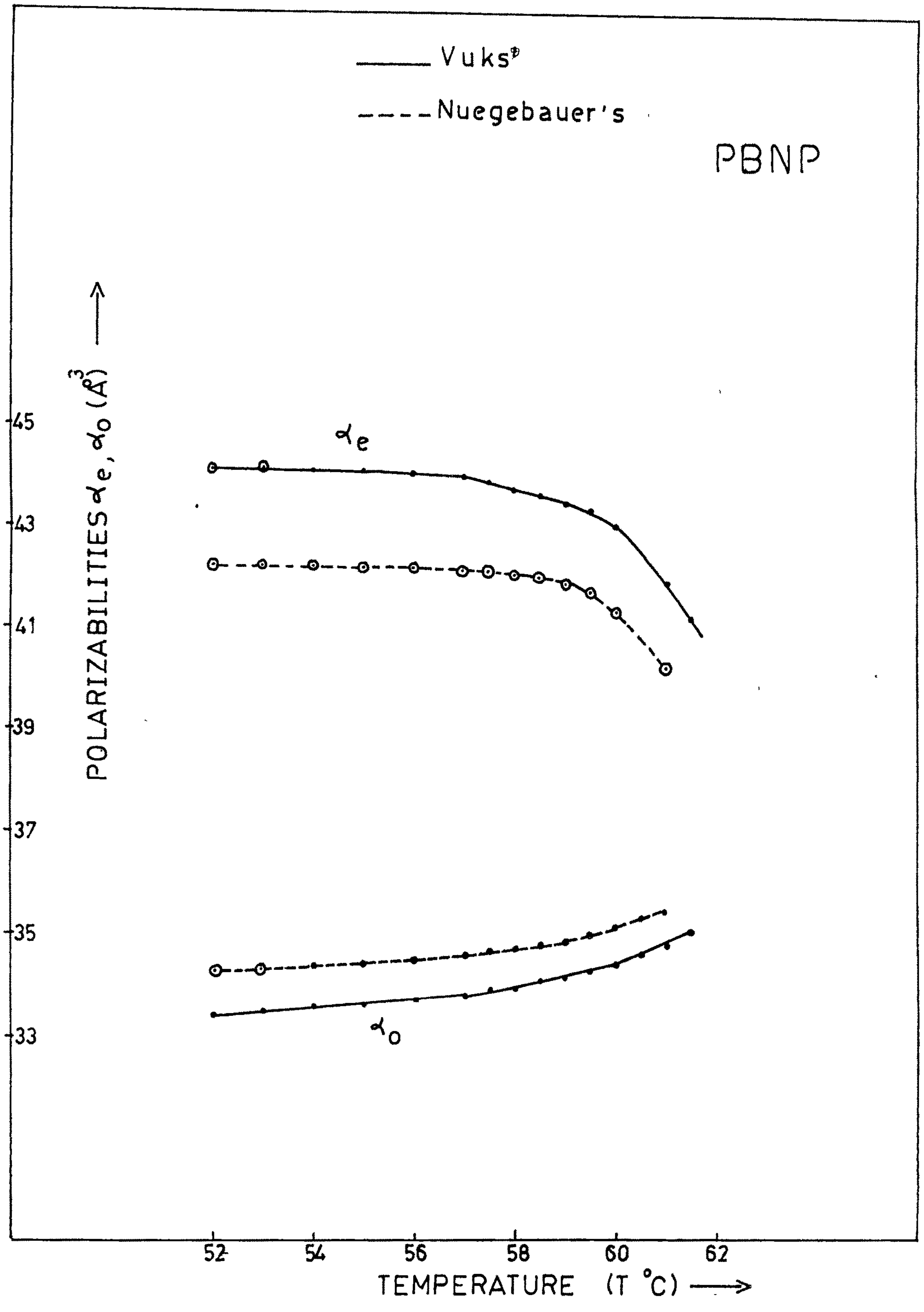Vuks'
Nuegebauer's
PBNP
POLARIZABILITIES α_e, α_o ($\AA^3$)
α_e
α_o
45
43
41
39
37
35
33
52
54
56
58
60
62
TEMPERATURE (T °C)

Figure 4.6

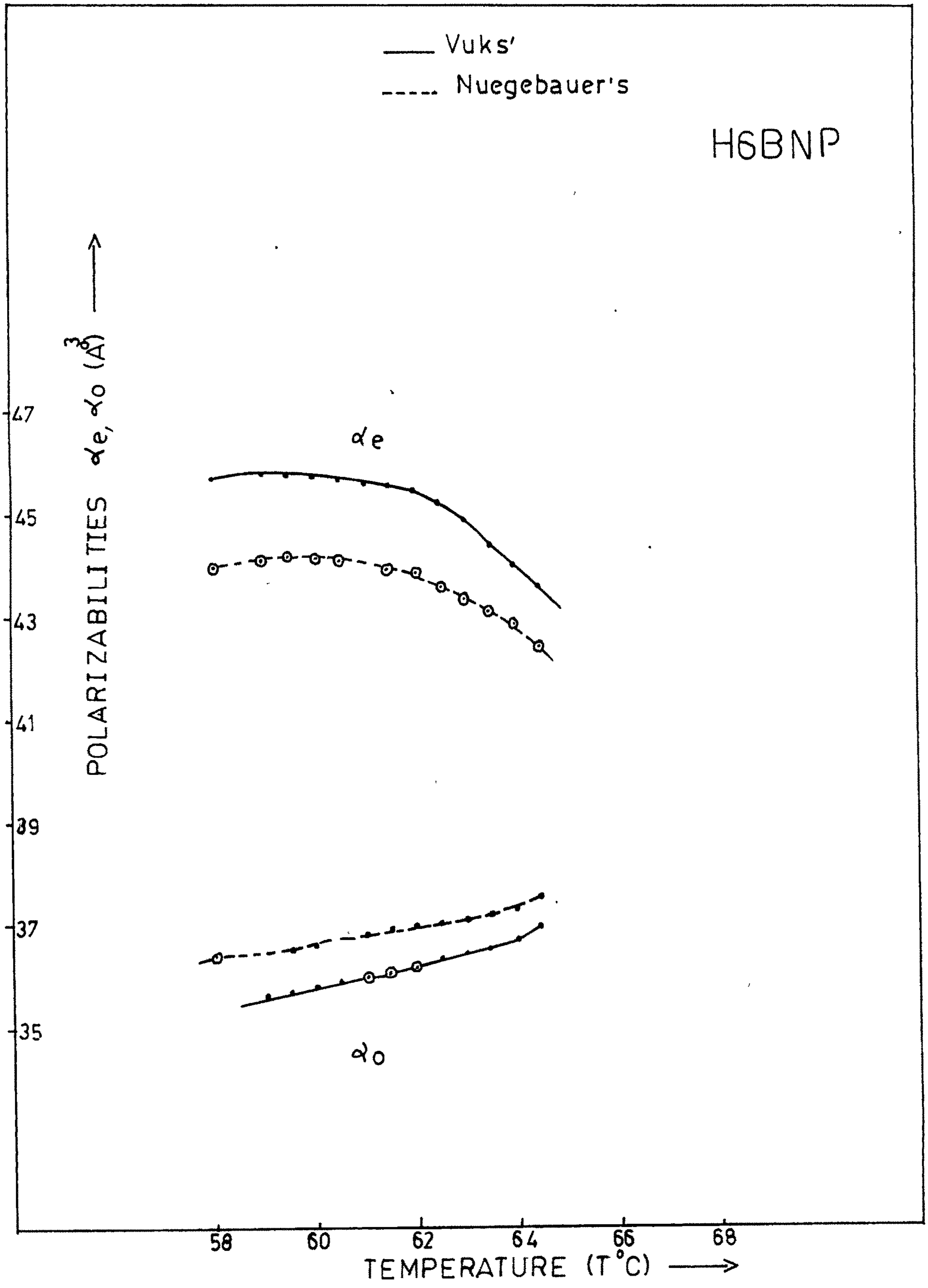
Vuks'
Nuegebauer's
H6BNP
POLARIZABILITIES αe, αo (Å³) →
47
45
43
41
39
37
35
αe
αo
58
60
62
64
66
68
TEMPERATURE (T°C) →

Figure 4.7

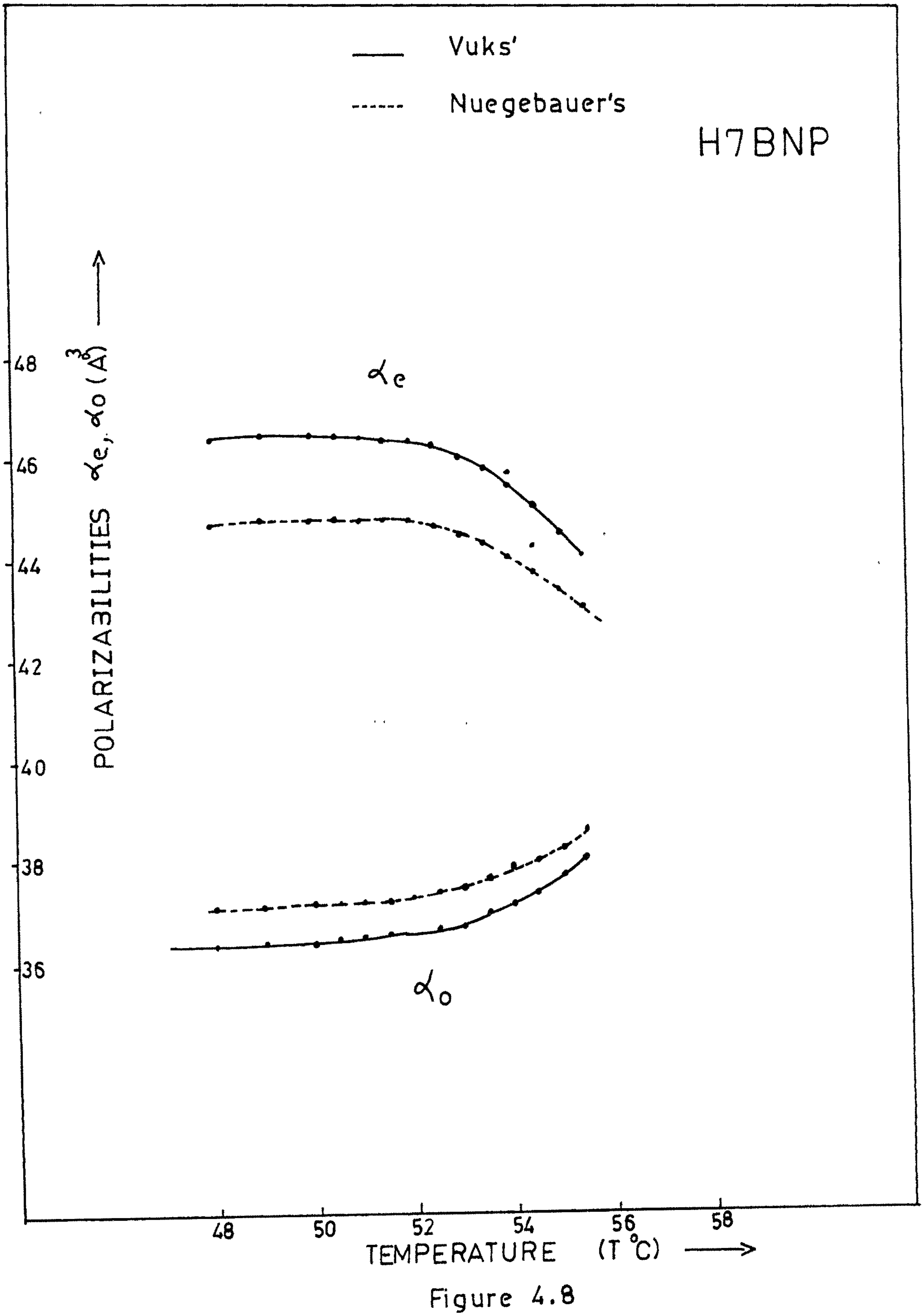
Vuks'
Nuegebauer's
H7BNP
POLARIZABILITIES α_e, α_o ($\AA^3$) →
α_e
α_o
48
46
44
42
40
38
36
48
50
52
54
56
58
TEMPERATURE (T °C) →

Figure 4.8

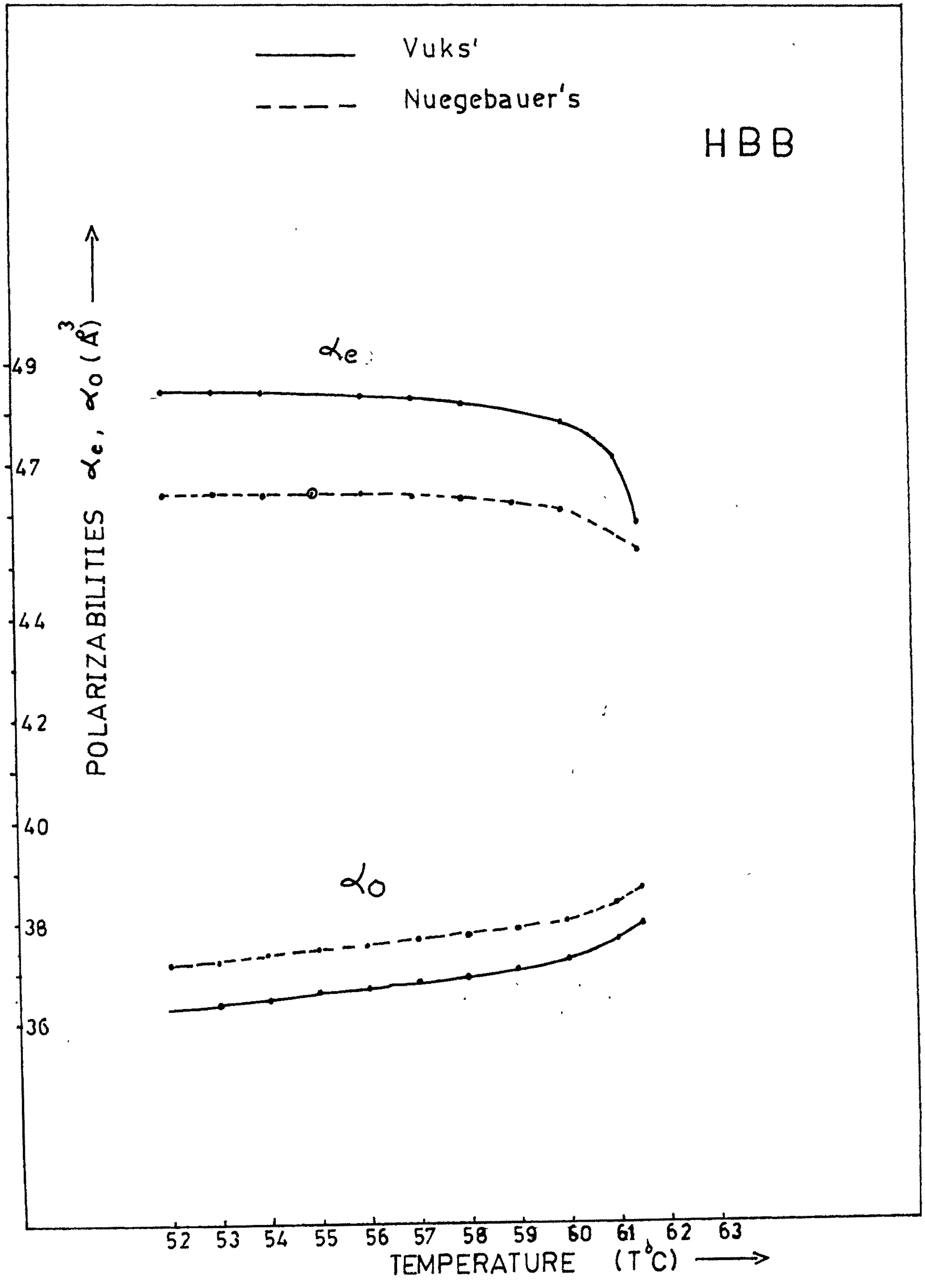Vuks'
Nuegebauer's
HBB
α_e
α_o
POLARIZABILITIES α_e, α_o ($\AA^3$)
49
47
44
42
40
38
36
52
53
54
55
56
57
58
59
60
61
62
63
TEMPERATURE (T°C)

Figure 4.9

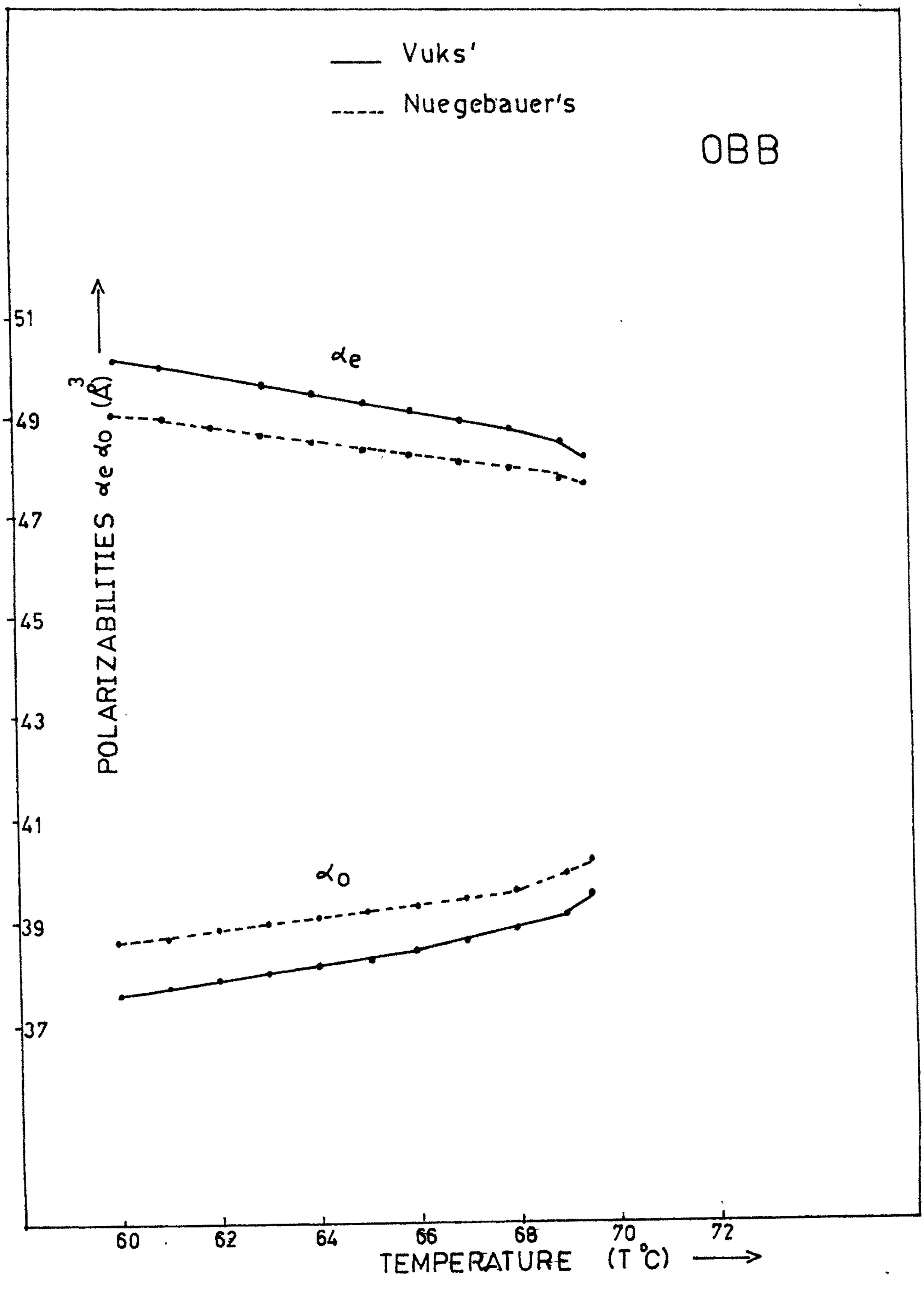
Vuks'
Nuegebauer's
OBB
α_e
α_o
POLARIZABILITIES α_e α_o $(\AA^3)$
51
49
47
45
43
41
39
37
60
62
64
66
68
70
72
TEMPERATURE (T °C)

Figure 4.10

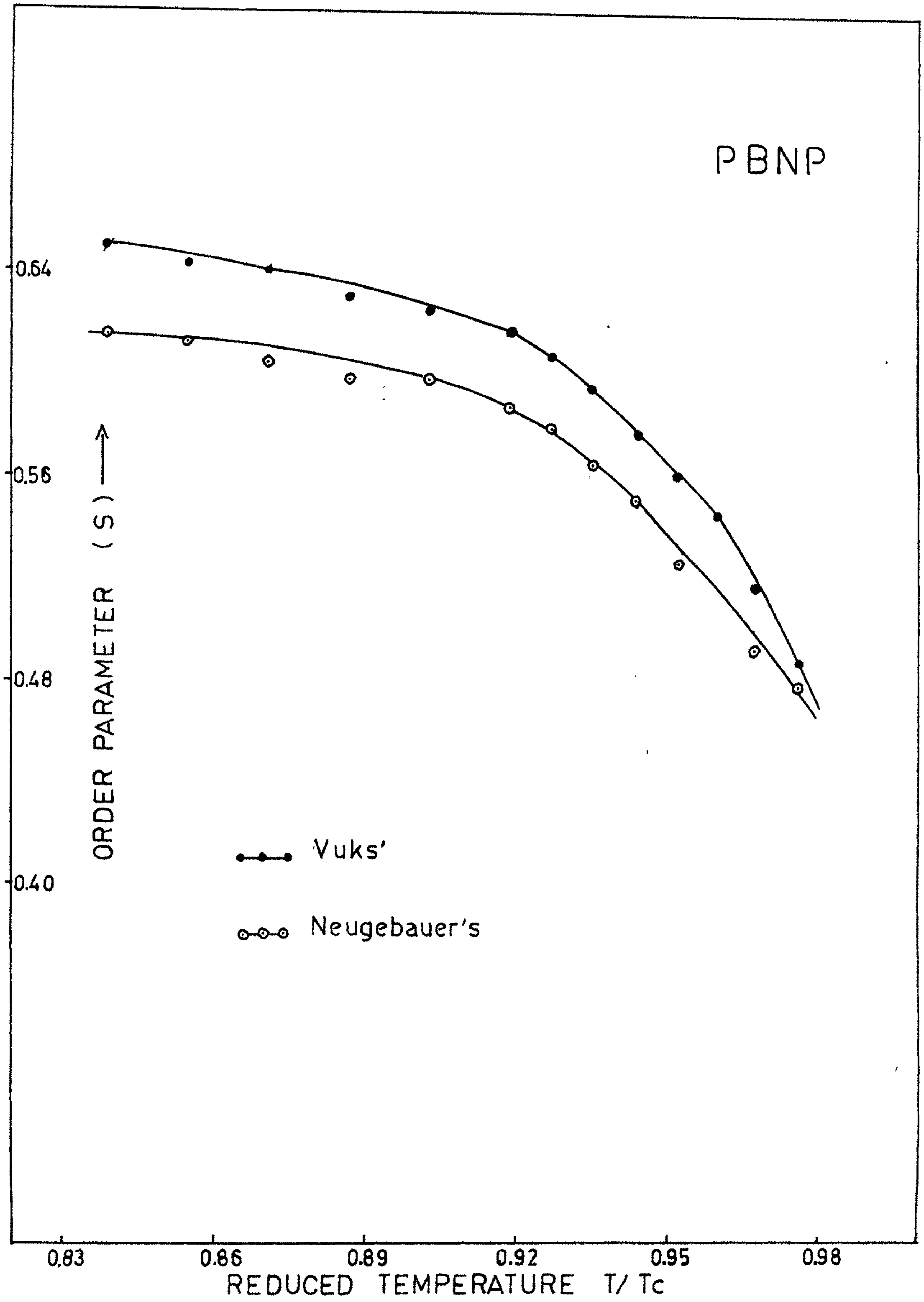
PBNP
ORDER PARAMETER (S) →
0.64
0.56
0.48
0.40
Vuks'
Neugebauer's
0.83
0.86
0.89
0.92
0.95
0.98
REDUCED TEMPERATURE T/ Tc

Figure 4.11

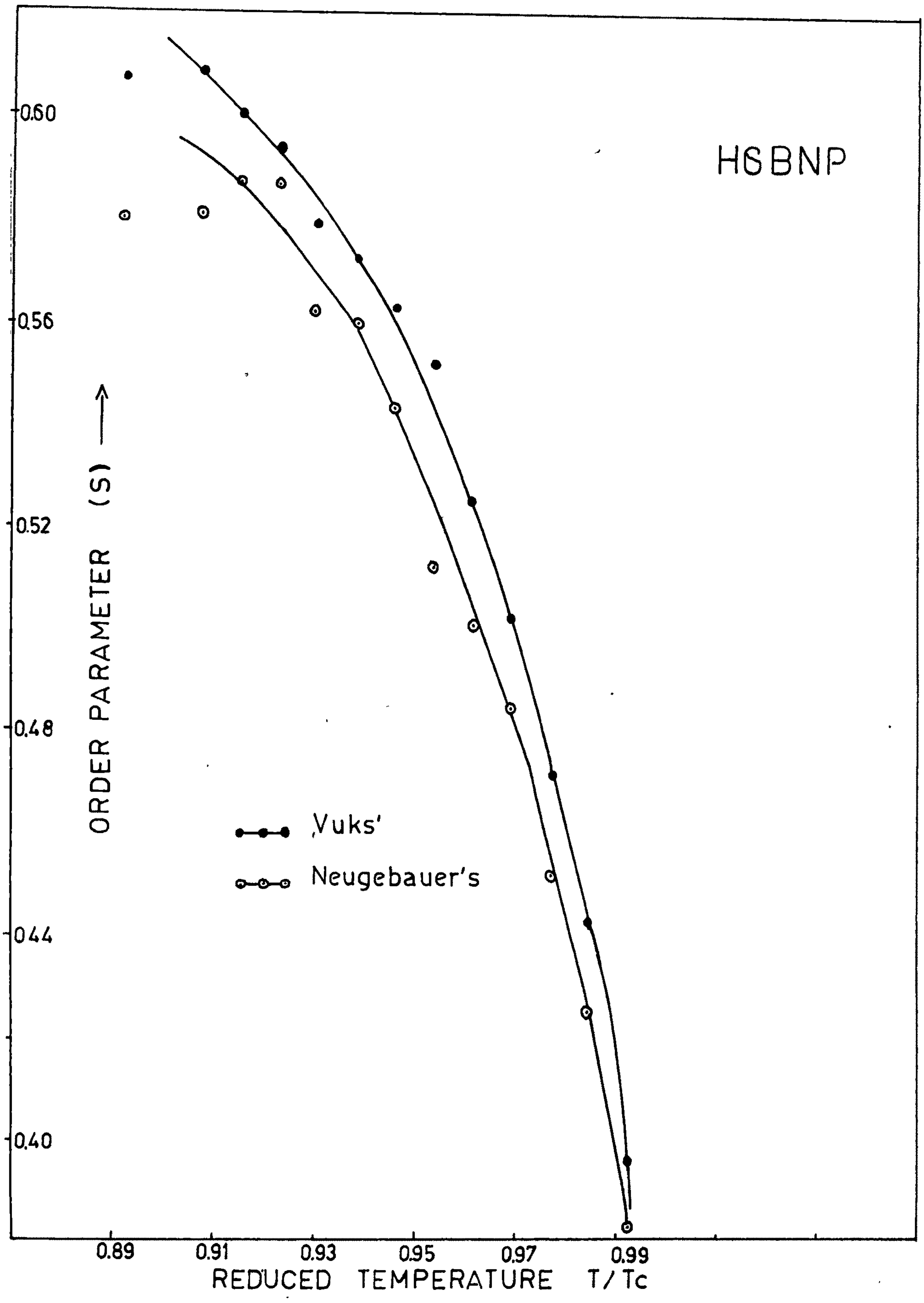
HGBNP
ORDER PARAMETER (S) →
0.60
0.56
0.52
0.48
0.44
0.40
0.89
0.91
0.93
0.95
0.97
0.99
REDUCED TEMPERATURE T/Tc
Vuks'
Neugebauer's

Figure 4.12

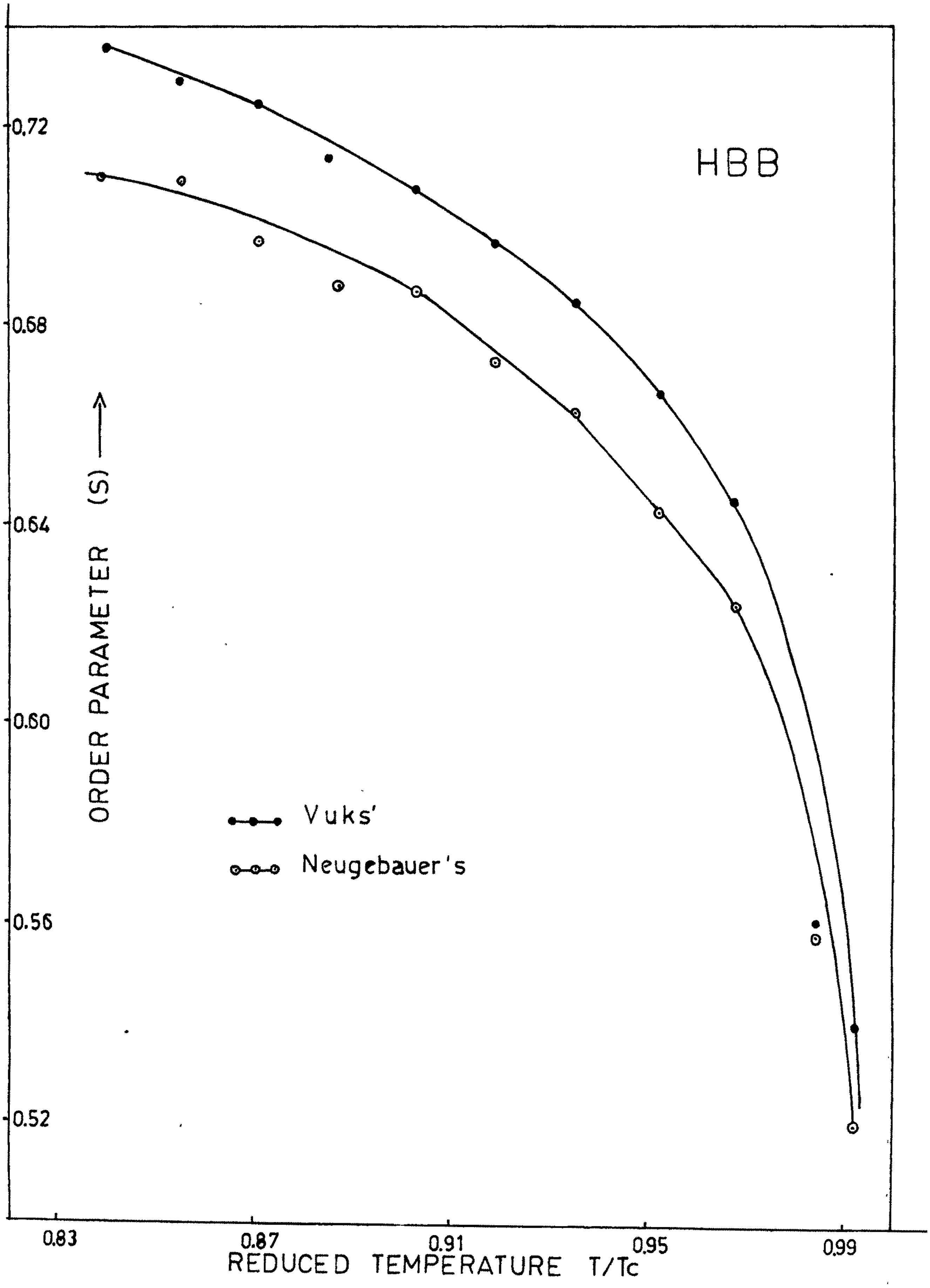
HBB
ORDER PARAMETER (S) ⟶
0.72
0.68
0.64
0.60
0.56
0.52
Vuks'
Neugebauer's
0.83
0.87
0.91
0.95
0.99
REDUCED TEMPERATURE T/Tc

Figure 4.14

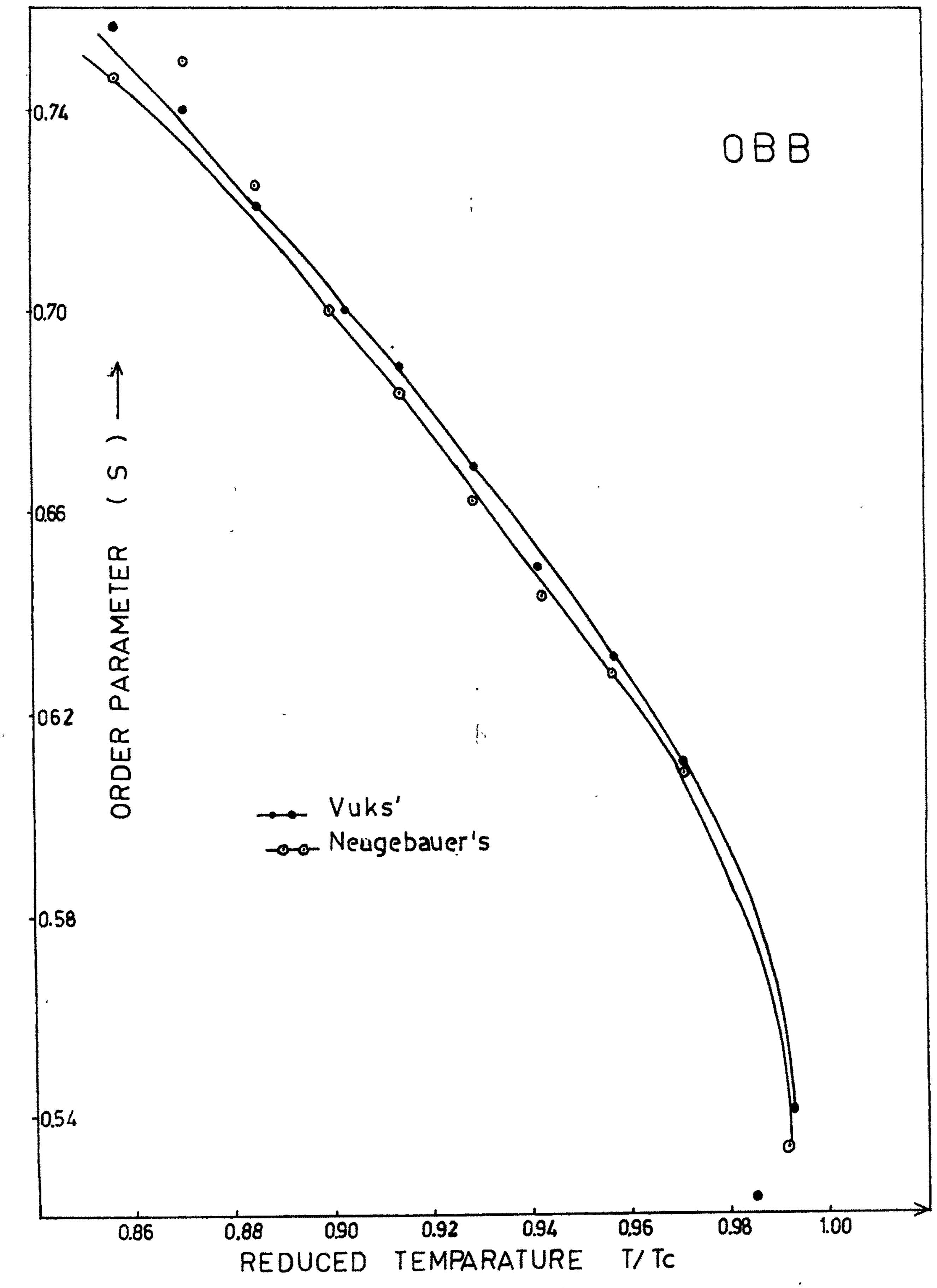
OBB
ORDER PARAMETER (S) →
0.74
0.70
0.66
0.62
0.58
0.54
0.86
0.88
0.90
0.92
0.94
0.96
0.98
1.00
REDUCED TEMPARATURE T/ Tc
Vuks'
Neugebauer's

Figure 4.15