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Magnetic anisotropy of the smectic A phases of lanthanide complexes derived from Schiff's bases and DOS, NO_3 anions†

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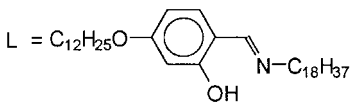
The magnetic anisotropy, $\Delta\chi$, of the smectic A phases of two series of lanthanide complexes derived from Schiff's bases and $C_{12}H_{25}OSO_3$ or NO_3 anions is measured. The $\Delta\chi$ values of some of the lanthanide (Tb, Dy, Ho) complexes are about two orders of magnitude greater than those of usual liquid crystals. Experimental data are interpreted within the framework of Bleaney's theory of the anisotropic paramagnetic susceptibility. It is shown that the sequence of $\Delta\chi$ signs and the tendency to variation of their magnitudes through the lanthanide series are in accordance with theoretical predictions for isostructural series of lanthanides.

1. Introduction

Anisotropy of the electric and magnetic susceptibility is one of the most important physical properties of liquid crystals. The director reorientation under the action of an external electric or magnetic field is responsible for the vast majority of electro-optical and magneto-optical effects in liquid crystals. The electric and magnetic anisotropy of such a medium is the prime cause of its reorientation [1]. Amplification of the magnetic anisotropy will result in an enhancement of the sensitivity of liquid crystals to the action of a magnetic field and, as a consequence, in the detection of new magneto-optical and cross electro-magneto-optical effects.

Most liquid crystals found in the last two decades are composed of diamagnetic molecules and, hence, their magnetic anisotropy $\Delta\chi$ is not large (it does not usually exceed $50 \times 10^{-6}\,\mathrm{cm^3\,mol^{-1}}$ [2]). Incorporating a transition metal atom into a mesogenic molecule (to give a metallomesogen) has paved the way for a radical modification of the electric, magnetic, non-linear optical and other properties of liquid crystals [3]. The first synthesized calamitic metallomesogens with paramagnetic properties contained 3d atoms [4]. As shown in previous work on non-mesogenic complexes of transition metals, maximum values of the magnetic anisotropy are exhibited by lanthanide complexes, many of which are used as shift reagents in NMR spectroscopy [5]. Magnetic anisotropy is due to the orbital part of the motion of electrons which have a rigid binding with the molecular frame. The orbital contribution is much larger for f-electron complexes than for d-electron complexes, owing to the small crystal-field splitting of internal (screened) f-electrons and to the strong spin-orbital coupling. This is not the case for d-electrons, for their orbital motion is essentially quenched. After the successful synthesis of calamitic lanthanide mesogens [6], very high $\Delta\chi$ values were found for the liquid crystalline phases of some (Tb, Dy) lanthanide compounds [7]. However, we have not yet succeeded in obtaining accurate data on mesogenic lanthanide structures because of difficulties in preparing single crystal samples for X-ray measurements.

Some results of more systematic measurements of the magnetic susceptibility anisotropy for two series of lanthanide compounds with the general formula $L_3\mathrm{Ln}X_3$ are reported in this work. Here Ln = La, Nd, Eu, Gd, Tb, Dy, Ho, Er, Yb; $X = C_{12}H_{25}OSO_3$ (DOS), NO_3; and the structure of L is shown below.



DOS-containing mesogens differ from NO_3-containing mesogens in their greater molecular volumes and lower phase transition temperatures. It is shown that a characteristic feature of lanthanide-based liquid crystals is a

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large anisotropy of their magnetic susceptibility. Signs and magnitudes of the magnetic anisotropy change in a predictable manner through the series.

2. Experimental and results

The compounds were synthesized as described previously [6, 8] and characterized using NMR and IR spectroscopy and elemental analysis. When studying their mesogenic properties, we employed differential scanning calorimetry, hot-stage polarizing optical microscopy and, in some cases, X-ray diffraction [7]. All the complexes show smectic A mesomorphism.

The magnetic susceptibility and its anisotropy were studied using an original home-made magnetometer. This is a moving-sample instrument combining the approaches used in the Foner construction and in the SQUID-magnetometer. Its operation is based on measurement of the charge that passes through the pick-up coils as the sample (contained in an ampoule of 2 mm inner diameter) moves between two fixed points located in the gaps of the magnetic system with a permanent induction of 1.2 T. The instrument was calibrated using $CoHg(CSN)_4$, $CuSO_4\ 5H_2O$, $NiSO_4\ 7H_2O$ and distilled water, all substances with known magnetic properties [9].

The diamagnetic susceptibility and anisotropy of MBBA were measured as $\chi = -160 \times 10^{-6}\,\mathrm{cm^3\,mol^{-1}}$ and $\Delta\chi = 30 \times 10^{-6}\,\mathrm{cm^3\,mol^{-1}}$. A detailed description of the magnetometer may be found elsewhere [10].

The magnetic susceptibility χ of the sample was determined by heating it to a temperature several degrees above $T_{\text{Sm-I}}$ (smectic to isotropic phase transition temperature) and then using slow (at a rate of 0.3°C min^{-1}) cooling in the permanent magnetic field of 1.2 T (see figure 1 as an example). The difference $\chi_{\text{or}} - \chi_{\text{iso}}$ is due to the orientation of the director **n** in the magnetic field. The polydomain (i.e. macroscopically isotropic) sample orients itself near $T_{\text{Sm-I}}$ to minimize the energy

$$W = -\frac{1}{2}\Delta\chi(\mathbf{nH})^2 \qquad (1)$$

of the system in the magnetic field **H**. The indices $\|$ and $\perp$ in $\Delta\chi = \chi_\| - \chi_\perp$ correspond to the parallel and perpendicular directions of the director **n** with respect to **H**.

Further slowing of the cooling rate (to 0.03°C min^{-1}) does not, within the error of measurement, change the results.

During the first heating, the magnetic susceptibility of all the samples varied according to the Curie law:

$$\chi = \chi_{\text{dia}} + \frac{\mu^2}{8T} \qquad (2)$$

where χ is the molar magnetic susceptibility ($\mathrm{cm^3\,mol^{-1}}$), μ is the effective magnetic moment (measured in Bohr magnetons), T is the temperature (K); $\chi_{\text{dia}} = -1440\,\mathrm{cm^3\,mol^{-1}}$ for the NO_3 series and $-2110\,\mathrm{cm^3\,mol^{-1}}$ for the DOS series (experimental values for La complexes). This orientation occurs only during cooling of the sample and not during heating, because of the high viscosity of the mesophase. This is typical behaviour for smectic phases. With further decrease in temperature, the magnetic susceptibility also behaves closely to the Curie pattern, but with a different (higher) value of χ.

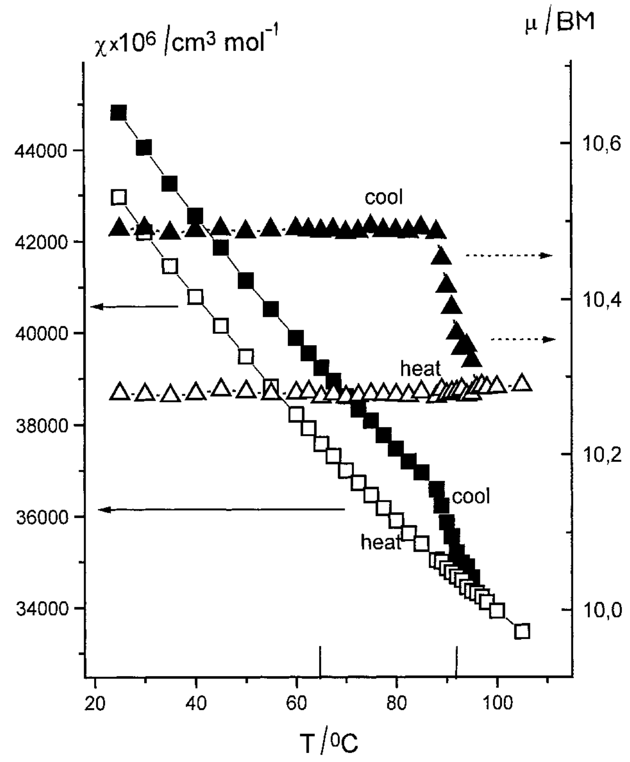

Figure 1. Temperature dependences of χ_{mol} (□, ■) and μ (△, ▲) values for the $L_3Tb(DOS)_3$ complex during the initial heating (□, △) and cooling (■, ▲) of the sample.

During subsequent heating and cooling cycles, the results obtained for the first cooling are completely reproduced. During heating, the magnetic susceptibility follows the Curie law with higher χ values which decrease in the vicinity of $T_{\text{Sm-I}}$ to reach their initial values corresponding to the lower curves in figure 1. During cooling, the χ and μ values increase again near $T_{\text{Sm-I}}$ and then follow the upper curves.

The results of the measurements for all the samples are presented in the table. The fact that the measured values of the magnetic moments of the lanthanide ions (given in the table) somewhat exceed the theoretical values is probably associated with the presence of small (2–3%) amounts of the salts of the ions used as precursor materials.

It is also possible to perform a direct measurement of the magnetic susceptibility anisotropy of samples which

Table. Phase transition temperatures and magnetic properties of the mesogenic $L_3\mathrm{Ln}X_3$ complexes. All susceptibilities are in units of $10^{-6}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ at the temperature $T_{\mathrm{Cr\text{-}Sm}}$.

Ln	X	$T_{\mathrm{Cr\text{-}Sm}}$/°C	$T_{\mathrm{Sm\text{-}I}}$/°C	μ_{iso}/BM	χ_{iso}	χ_{or}	$(\chi_{\mathrm{or}} - \chi_{\mathrm{iso}})$	$\Delta\chi_{\mathrm{min}}$
La	NO_3	112	160	—	− 1440	− 1380	60	90
Nd	NO_3	100	161	3.75	3270	3530	260	− 780
Eu	NO_3	112	156	3.70	3010	3140	130	195
Gd	NO_3	112	150	8.10	20280	20330	50	75
Tb	NO_3	96	149	9.95	32010	33860	1850	− 5500
Dy	NO_3	130	147	10.80	34670	35790	1120	− 3360
Ho	NO_3	129	146	10.90	35440	36400	960	− 2880
Er	NO_3	127	146	9.95	29540	29930	390	585
La	DOS	63	89	—	− 2110	− 2030	80	120
Nd	DOS	61	98	3.75	3200	3420	220	− 660
Gd	DOS	69	79	8.45	24010	24080	70	105
Tb	DOS	64	92	10.25	37070	39090	2020	− 6060
Dy	DOS	61	89	11.20	44940	46000	1060	− 3180
Ho	DOS	59	81	11.20	44980	46020	1040	− 3120
Er	DOS	60	88	10.20	36860	37350	490	735
Yb	DOS	64	103	4.85	6610	6810	200	300

have previously been oriented by a magnetic field and then cooled with the ampoule. It has been found before [7*e*] that mesogenic lanthanide samples readily form glasses on cooling, with retention of their optical texture.

Figure 2 presents the variation of the magnetic susceptibility of a Dy-containing sample prepared in this way, as a function of the angle α between the axis of maximal magnetic susceptibility and the magnetic field vector. This axis is determined by the magnetic field direction on cooling the sample. The values of $\Delta\chi$ calculated from

$$\Delta\chi^H = \chi(\alpha = 0°) - \chi(\alpha - 90°) \equiv \chi_\parallel^H - \chi_\perp^H$$

for Dy and Er complexes are very close (within experimental error) to the values given by the above-mentioned method.

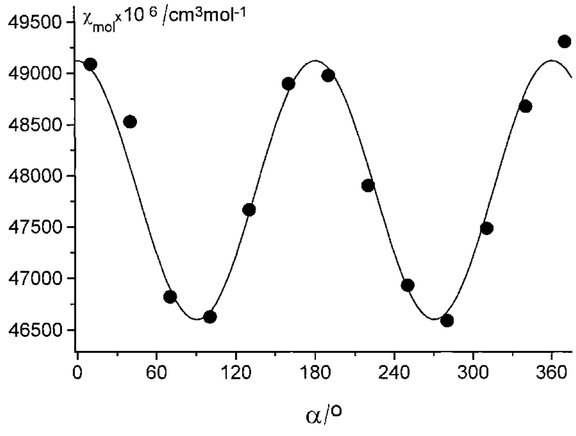

Figure 2. The χ_{mol} value for the $L_3\mathrm{Dy(NO_3)_3}$ complex as a function of the angle α between the direction of the predominant orientation and the magnetic field at 21°C.

3. Discussion

The quantities $\chi_{\mathrm{or}} - \chi_{\mathrm{iso}}$ and $\chi_\parallel^H - \chi_\perp^H$ are related to the magnetic anisotropy $\Delta\chi$ of uniaxial liquid crystals by simple expressions:

$$\chi_{\mathrm{or}} - \chi_{\mathrm{iso}} = 2Q(H)\Delta\chi/3 \tag{3a}$$

and

$$\chi_\parallel^H - \chi_\perp^H = Q(H)\Delta\chi \tag{3b}$$

where $Q(H) = \langle 3\cos^2\theta - 1\rangle/2$, and θ is the angle between the director **n** and the magnetic field. $Q(H)$ is the macroscopic order parameter which is field- and viscosity-dependent [11]. The quantities measured by the two methods described above are interconnected:

$$\chi_\parallel^H - \chi_\perp^H = 3(\chi_{\mathrm{or}} - \chi_{\mathrm{iso}})/2. \tag{4}$$

Our experimental data confirm this relation.

In the absence of a magnetic field, a macroscopic sample consists of domains with different orientations of the director **n**, and therefore $Q(H) = 0$. In a completely oriented (monodomain) system $Q(H) = 1$ for $\Delta\chi > 0$, and $Q(H) = -1/2$ for $\Delta\chi < 0$. The magnetic anisotropy ($\Delta\chi$) of a monodomain sample is related to its molecular magnetic anisotropy $\Delta\chi^{\mathrm{m}}$ by the expression

$$\Delta\chi = NS\Delta\chi^{\mathrm{m}} \tag{5}$$

where N is the number density and S is the microscopic (Maier–Saupe) order parameter. It has a weak dependence on the magnetic field [12], almost solely due to intermolecular interactions.

To determine $\Delta\chi$ from equations (3*a*) and (3*b*), it is necessary to know the value and the sign of $Q(H)$; or the sign only, provided that the field strength corresponds to the perfect-orientation regime. We were able to change the sample cooling (heating) rate, but not the **H** value (1.2 T). The dependence of $\chi_{or} - \chi_{iso}$, typical for all investigated paramagnetic lanthanide samples, on the cooling rate is presented in figure 3. The rather large value of $\Delta\chi$ for the diamagnetic La complex may also be said to be evidence of the appropriateness of the 0.3°C min^{-1} cooling rate to obtain values of $Q(H)$ close to the maximum.

The sign of $\Delta\chi$ for diamagnetic La complexes is definitely positive. The magnetic anisotropy $\Delta\chi^L = \chi^L_{\parallel} - \chi^L_{\perp}$ (where indices $\parallel$ and $\perp$ correspond to the molecular long and short axes) of the ligands (L), calculated using the increment system [13], is $\Delta\chi^L = 34 \times 10^{-6}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$. The magnetic anisotropy of the phenyl ring, as follows from experimental data [2] and from calculations, gives the main contribution ($30 \times 10^{-6}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$) to the anisotropy of the ligand. Contributions from other parts of the molecule constitute 10–15% only and may be neglected, since they are comparable to measurement errors for $\Delta\chi$ for diamagnetic complexes.

The experimental values of $\Delta\chi = 90 \times 10^{-6}$ and $120 \times 10^{-6}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ obtained for La complexes (containing 3 phenyl rings) with NO_3 and DOS, respectively, probably indicate a high value of the order parameter for the phenyl rings. Gd complexes have a high magnetic moment, but still with a purely spin magnetic moment of the f^7 electron configuration (S-term). Therefore the Gd sample orientation is defined only by the diamagnetic anisotropy of the ligands, similarly to that of the La complexes.

The signs of $\Delta\chi$ for the other paramagnetic lanthanide samples were defined on the basis of our previous results [7*b*, 14] from magnetic birefringence (Cotton–Mouton effect) measurements for similar lanthanide complexes (with the NO_3 anion) in solution; as well as on the basis of (i) EPR probe results for Tb and Er complexes with the NO_3 anion—with the Gd lanthanide complex of the same composition as a probe—in the mesophase [15], and (ii) EPR measurements at 10 K of previously oriented glass samples of Nd, Tb, Dy and Er complexes with DOS [16]. The resultant signs are: $\Delta\chi < 0$ for Nd, Tb, Dy, Ho; $\Delta\chi > 0$ for La, Eu, Gd, Er, Yb complexes of both series.

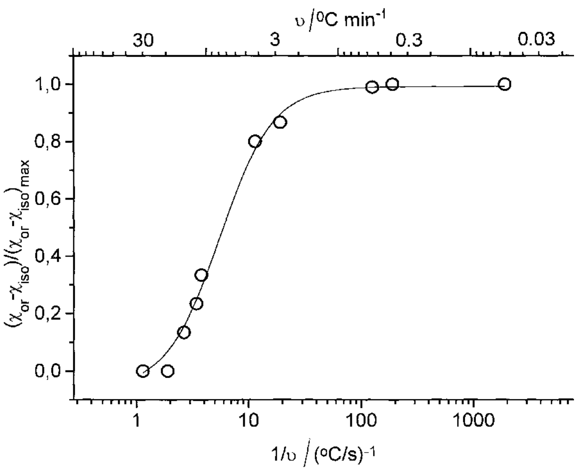

Figure 3. The $(\chi_{or} - \chi_{iso})/(\chi_{or} - \chi_{iso})_{max}$ (○) value for the $L_3Tb(NO_3)_3$ complex as a function of the cooling rate υ.

Values of $\Delta\chi$ listed in the last column of the table are obtained by multiplication of the $\chi_{or} - \chi_{iso}$ values given in the penultimate column of the table by the factor 1.5 or 3, depending on the sign of $\Delta\chi$. The values of $\Delta\chi$ so obtained are minimal values, because the macroscopic order parameter may correspond to an imperfect orientation of the system.

To discuss the sign of $\Delta\chi$ and its tendency to vary within the series of paramagnetic mesogens, as well as to estimate the scale of magnitude of the crystal fields acting upon the metal ion, let us use the single-parameter approximation of Bleaney's theory of anisotropic paramagnetic susceptibility [17].

The ground state of a lanthanide ion in a complex, specified by the quantum number J, is split by the ligand field into sub-levels which are (at room temperature) populated in the usual Boltzmann way. Averaging of the magnetic susceptibility over the ground J-manifold yields, to a first approximation, its isotropic value: $\chi = [Ng^2\beta^2J(J+1)]/3kT$ (the Curie law). In the second approximation (with respect to the Zeeman and crystal-field interactions) anisotropic terms appear, if the symmetry of the local electric field acting upon the ion is lower than cubic [17].

If one of the principal axes of the magnetic susceptibility χ_z coincides with the molecular long axis, and the values of χ_x and χ_y are averaged to give $\chi_{\perp} = (\chi_x + \chi_y)/2$, we can obtain from equation (28) in [17]:

$$\Delta\chi^{\mathrm{theor}} = (\chi_{\parallel} - \chi_{\perp})^{\mathrm{theor}} = \frac{-N\beta^2 A_2^0 \langle r^2 \rangle\, \Phi(J) \left[1 + a\left(\frac{kT}{\Delta W}\right) + \ldots\right]}{10(kT)^2}$$

and

$$\Phi(J) = g^2 \langle J \| \alpha \| J \rangle\, J(J+1)(2J-1)(2J+3) \qquad (6)$$

where g is the Lande g-factor, β is the Bohr magneton, A_2^0 is the crystal field coefficient, $\langle r^2 \rangle$ is the mean power of the electron radius of the 4f electrons, and $\langle J \| \alpha \| J \rangle$ is a numerical coefficient whose values are listed in table 1 of [17] for all lanthanide ions. This coefficient determines the relative signs of $\Delta\chi$ for ions in each lanthanide series.

The terms of the order of $a(kT/\Delta W)$ and the terms of higher orders in $kT/\Delta W$ arise from excited states with $J \pm 1$, $J \pm 2$. Except for the case of the Eu complex, they have energies ΔW greater than $2000\,\text{cm}^{-1}$, which should be compared with $kT \approx 270\,\text{cm}^{-1}$. Following [17], we may omit all these terms, since they result in corrections of less than 1–3% for the case of the lanthanides being discussed. More rigorous consideration [18] shows that corrections to the Bleaney theory may reach 20%.

To compare the signs and the measured values of $\Delta\chi$ given in the table, we should multiply $\Delta\chi^{\text{theor}}$ by the order parameter S and the parameter G. If the principal axis of magnetic susceptibility does not coincide with the molecular long axis, it is necessary to transfer to molecular coordinate systems with $\chi_{\parallel}$ being the molecular long axis:

$$G=\frac{1}{2}(3l_z^2-1)+\frac{1}{2}(l_x^2-l_y^2)\frac{A_2^2}{A_2^0} \qquad (7)$$

where l_z, l_x, l_y are the direction cosines of the principal axes of the molecular magnetic susceptibility with respect to the molecular long axis. In dipivaloyl methanate complexes with picoline Ln(dpm)$_3$(4-picoline)$_2$, for example, the angle between the molecular long axis and the z-magnetic axis may be up to 18° [19]. Unfortunately, the directions of the magnetic axis are unknown for our complexes. Figure 4 shows the result which was obtained by using only one (specific for each lanthanide series) fitting parameter $A_2^0\langle r^2\rangle SG$ equal to $-77.7\,\text{cm}^{-1}$ for the NO$_3$ series and $-79.6\,\text{cm}^{-1}$ for the DOS series; and $Q(H)=1$ for $\Delta\chi>0$ and $Q(H)=-1/2$ for $\Delta\chi<0$. We also neglect the difference in $T_{\text{Cr-Sm}}$ for compounds which belong to one and the same series. The fitting parameter is chosen to minimize the sum $\Sigma_i(\Delta\chi_i^{\text{theor}}S-\Delta\chi^{\text{exp}}+\Delta\chi_{\text{dia}}^{\text{exp}})^2$ over all ions studied for each series. It follows from figure 4 that the signs of the experimental and theoretical values of $\Delta\chi$ coincide, and that the relative quantities correlate even in this rough approximation. The absolute magnitudes of the parameter $A_2^0\langle r^2\rangle SG$ are comparable with the average $A_2^0\langle r^2\rangle$ for the ions under investigation: $-70\,\text{cm}^{-1}$ for double nitrates, $108\,\text{cm}^{-1}$ for the rare-earth ethyl sulphate series, or $97\,\text{cm}^{-1}$ for the anhydrous rare-earth chlorides [20]. For a more rigorous discussion of the correlation between the $\Delta\chi^{\text{theor}}$ and $\Delta\chi^{\text{exp}}$ values, one has to know a complete set of crystal-field parameters for each individual lanthanide ion, and perform numerical calculations similar to those made in [18] which involve all the excited states.

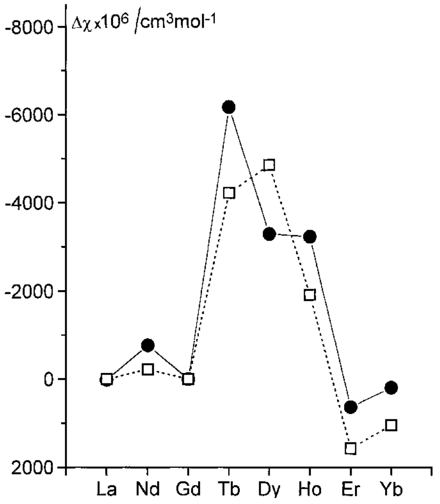

Figure 4. $\Delta\chi_{\text{exp}}$ (●) and $\Delta\chi_{\text{theor}}$ (□) calculated from equation (7) for the series L_3Ln(DOS)$_3$. The correlation coefficient $R_1=0.918$.

Not only the value of the parameter $A_2^0\langle r^2\rangle$, but also even the sign of the crystal-field parameter may, in principle, change depending on the structure of the first coordination sphere of the ion. The angle of non-coincidence between the magnetic axis and the molecular long axis may also change from one ion to another. The fact that, in spite of these circumstances, we obtain correct relative signs and a rough correlation between the experimental and theoretical values of $\Delta\chi$ when using a single realistic value of the parameter $A_2^0\langle r^2\rangle$ suggests that the compounds studied are close to isostructural.

4. Conclusions

1. The sequence of $\Delta\chi$ signs, and roughly of the magnitudes through the series of lanthanide mesogens, is in accordance with theoretical predictions for isostructural series of lanthanides.
2. The characteristic feature of the smectic A phases of lanthanide liquid crystals is the large anisotropy of their magnetic susceptibility $\Delta\chi$. It may be about two orders of magnitude larger than the anisotropy of usual liquid crystals.
3. The size difference between NO$_3$ and DOS anions does not essentially influence the values and the signs of the magnetic anisotropy of corresponding lanthanide complexes of the two series investigated.

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References

[1] (*a*) De Gennes, P. G., 1974, *The Physics of Liquid Crystals* (Oxford: Clarendon Press); (*b*) Blinov, L. M., 1983, *Electro-Optical and Magneto-Optical Properties of Liquid Crystals* (Chichester: Wiley).

[2] Stannarius, R., 1998, in *Handbook of Liquid Crystals*, Vol. 2A, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill (Wiley-VCH), p. 113.

[3] (*a*) Maitlis, P. M., and Giroud-Godquin, A. M., 1991, *Angew. Chem. int. Ed. Engl.*, **30,** 402; (*b*) Hudson, S. A., and Maitlis, P. M., 1993, *Chem. Rev.*, **93,** 861;

(*c*) Bruce, D. W., 1992, in *Inorganic Materials*, edited by D. W. Bruce and D. O'Hare (Chichester: Wiley), p. 405; (*d*) Serrano, J. L. (editor), 1996, *Metallomesogens: Synthesis, Properties and Applications* (Weinheim: VCH).

[4] (*a*) Ovchinnikov, I., Galyametdinov, Yu., Ivanova, G., and Yagfarova, L., 1984, *Dokl. Akad. Nauk SSSR*, **276,** 126 [1984, *Doklady Chemistry*, **276,** 164 (English)]; (*b*) Galyametdinov, Yu., Ivanova, G., and Ovchinnikov, I., 1984, *Zh. obshch. Khim.*, **54,** 2796; (*c*) Galyametdinov, Yu., Ivanova, G., and Ovchinnikov, I., 1988, *Zh. obshch. Khim.*, **58,** 1326; (*d*) Galyametdinov, Yu., Zakieva, D., and Ovchinnikov, I., 1986, *Izv. Akad. Nauk SSSR ser. Khim*, **2,** 491; (*e*) Chandrasekhar, S., Sadashiva, B. K., Rameshe, S., and Skiranta, B. S., 1986, *Pramana, J. Phys.*, **27,** 4713.

[5] Reuben, J., and Elgavish, G. A., 1979, *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 4, edited by K. A. Gschneidner Jr and L. Eyring (Amsterdam: North-Holland), p. 483.

[6] Galyametdinov, Yu., Ivanova, G., and Ovchinnikov, I., 1991, *Izv. Akad. Nauk SSSR ser. Khim*, 1232 [1991, *Bull. Acad. Sci. USSR, Div. chem. Sci.*, **40,** 1109 (English)].

[7] (*a*) Galyametdinov, Yu., Atanassopoulo, M., Khaase, V., and Ovchinnikov, I., 1995, *Koordinats. Khim.*, **21,** 751 [1995, *Russ. coord. Chem.*, **21,** p. 633 (English)]; (*b*) Galyametdinov, Yu., Ivanova, G., Ovchinnikov, I., Prosvirin, A., Guillon, D., Heinrich, B., and Bruce, D. W., 1996, *Liq. Cryst.*, **20,** 831; (*c*) Bikchantaev, I., Galyametdinov, Yu., Kharitonova, O., Ovchinnikov, I., Bruce, D. W., Dunmur, D. A., Guillon, D., and Heinrich, B., 1996, *Liq. Cryst.*, **20,** 489; (*d*) Kharitonova, O., Prosvirin, A., Galyametdinov, Yu., and Ovchinnikov, I., 1996, *Izv. Akad. Nauk ser. Khim*, 2331 [1996, *Russ. chem. Bull.*, **45,** 2213 (English)]; (*e*) Galyametdinov, Yu., Athanassopoulou, M., Griesar, K., Kharitonova, O., Soto-Bustamante, E., Tinchurina, L., Ovchinnikov, I., and Haase, W., 1996, *Chem. Mat.*, **8,** 922; (*f*) Turanov, A., Ovchinnikov, I., Galyametdinov, Yu., Ivanova, G., and Goncharov, V., 1999, *Izv. Akad. Nauk ser. Khim*, 694 [1999, *Russ. chem. Bull.*, **48,** 690 (English)].

[8] (*a*) Binnemans, K., Galyametdinov, Yu., Collinson, S., and Bruce, D. W., 1998, *J. mat. Chem.*, **8,** 1551; (*b*) Galyametdinov, Yu., Ivanova, G., Ovchinnikov, I., Binnemans, K., and Bruce, D. W., 1999, *Izv. Akad. Nauk ser. Khim*, **2,** 387 [1999, *Russ. chem. Bull.*, (English)].

[9] Vulfson, S. G., 1998, *Molecular Magnetochemistry* (Australia: Gordon and Breach).

[10] Goncharov, V., and Turanov, A., 1998, *Pribory i Tekhnika Experimenta*, **41,** 145 [1998, *Instrum. Exp. Tech.*, **41,** 579 (English)].

[11] Dunmur, D. A., and Palffy-Muhoray, P., 1988, *J. phys. Chem.*, **92,** 1406.

[12] Hama, H., 1985, *J. phys. Soc. Jpn.*, **54,** 2204.

[13] Flygare, W. H., 1974, *Chem. Rev.*, **74,** 653.

[14] Prosvirin, A., 1998, PhD thesis, Kazan, Physico-Technical Institute, Russia.

[15] Bikchantaev, I., and Galyametdinov, Yu., 1999, in Abstracts of the 6th International Symposium on Metallomesogens, Rotenburg, Darmstadt University of Technology, Abstract 73.

[16] Ovchinnikov, I., Petrashen', V., Ivanova, T., Galyametdinov, Yu., and Turanov, A., *Fizika Tverdogo Tela* (in preparation).

[17] Bleaney, B., 1972, *J. magn. Reson.*, **8,** 91.

[18] Golding, R. M., and Pyykko, P., 1973, *Mol. Phys.*, **26,** 1389.

[19] Dew-Horrocks, W. Jr. and Sipe, J. P. III, 1972, *Science*, **177,** 994.

[20] Abragam, A., and Bleaney, B., 1970, *Electron Paramagnetic Resonance of Transition Ions* (Oxford: Clarendon Press).