CCA-285

546.195:546.16:538.24
Preliminary Communication

Magnetic Measurements on XeF_4

S. Maričić and Z. Veksli

Institute »Ruđer Bošković«, Zagreb, Croatia

J. Slivnik and B. Volavšek

»Jožef Stefan« Institute for Nuclear Research, Ljubljana, Slovenia, Yugoslavia

Received March 22, 1963

A few weeks after the measurements reported in our previous communications[1,2] were performed the sample of XeF_4 showed signs of decomposition. It was therefore resublimed together with a new batch of XeF_4. The results to be reported here were consistent within past few months and are regarded as characteristic of pure XeF_4.

Special care was taken in measuring the magnetic susceptibility down to 77°K. In order to avoid any spurious effects two different kinds of glass were used for the container in the Gouy method. The results in Fig. 1. are fairly conclusive: XeF_4 is purely diamagnetic between 77° and 293°K. Any sign of a temperature dependence of the magnetic susceptibility as indicated in Fig. 1. is attributed to experimental uncertainties. The presented results were obtained on samples of very fine crystallites. However, temperature cycling of another sample showed crystal-growth and hysteresis effects with apparent increase of diamagnetic susceptibility on lowering the temperature. This may be due to molecular (and crystal structure) anisotropy of the diamagnetic susceptibility in XeF_4-crystals with preferential orientation during their growth. Single crystal measurements are desirable.

We repeated the fluorine magnetic resonance measurements (at 29 Mc/s). The results differ from those previously reported in that the spectra are of the same asymmetric shape in the whole temperature range (see Fig. 2.). Total second moment values of these lines were calculated and corrected for modulation broadening. Their temperature dependence is shown in Fig. 3. A molecular reorientation mechanism is evident.

Most likely the asymmetry of these spectra is due to the anisotropy of the fluorine chemical shift. (A low-field shift of the total line has been measured by Blinc *et al.*[3]). In trying to work out the degree of the anisotropy we applied Lebedev's[4] calculations. (Originally, these are for the case of an isotropic, motionless distribution of the anisotropic g-factors in electron paramagnetic resonance.) As the matching of the line shapes is more elaborate, we presently made use only of Lebedev's nomograms. This restricts the information obtained to the difference between the fields corresponding to the parallel and perpendicular component line ($\Delta H_{anis} = |H_{\parallel} - H_{\perp}|$). In addition, the ratio (δ) of this difference to the width of individual line components is also available. The latter linewidth was supposed to be due to nuclear dipole-dipole interaction in the present (n.m.r.) case. The temperature dependence of ΔH_{anis} calculated from our spectra is shown in Fig. 4. A fairly sharp drop (within some 20 degrees) in ΔH_{anis} is centered around 250°K. The data above this temperature correspond to »effective« ΔH_{anis}. The fact that a non-zero value is attained at higher temperatures is evidence for a restricted molecular motion which is insufficient to average out completely the chemical shift anisotropy. The measurements below 225°K give $\Delta H_{anis} = 5.7 \pm 0.2$ G, and those from 263° to 293°K result in $\Delta H_{anis} = 1.4_7 \pm 0.1$ G.

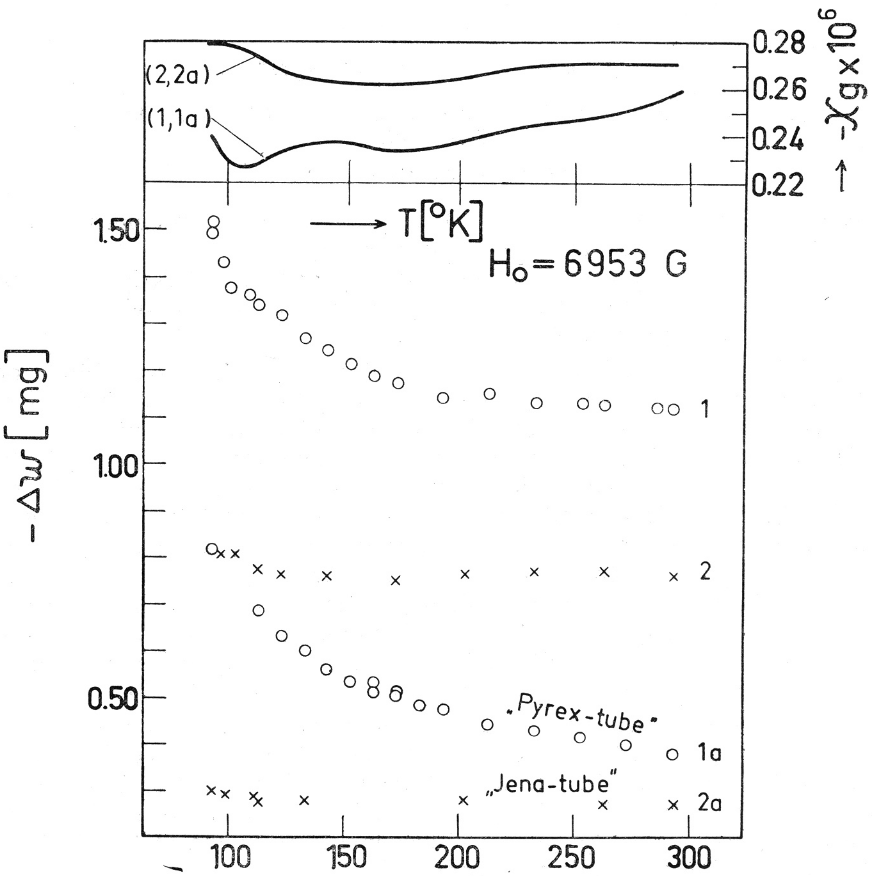


Fig. 1. Magnetic susceptibility measurements on XeF_4

Owing to the contribution from chemical shift anisotropy the low temperature second moment value (Fig. 3, 5.7 G^2) cannot be used in discussing Van Vleck's sum. However, by knowing ΔH_{anis} and δ we estimated the width of individual ($\parallel$ and $\perp$) component-lines to be 3.8 ± 0.2 G, which for a gaussian shape means a (corrected) second moment of 3.2 G^2.

The last value is to be related to the presently available Xe-F bond length from crystal structure determinations of XeF_4:

1.92 Å[5] and 1.93 Å[6] by x-rays, and
1.95 Å[7] by neutron diffraction.

Using the data given in ref. 6 we calculate an intermolecular second moment of 1.78 G^2. The intramolecular second moment for the square planar molecule with Xe-F bond length of 1.95 Å is 1.62 G^2 (Xe^{129} and Xe^{131} contribution included). The total second moment thus obtained, 3.40 G^2, is within the experimental error of the above derived value from our measurements.

Lebedev's method[4] should greatly facilitate the application of fluorine chemical shift anisotropy in single crystal studies. Its exactness has to be verified through direct measurements of the field dependence of second moments.

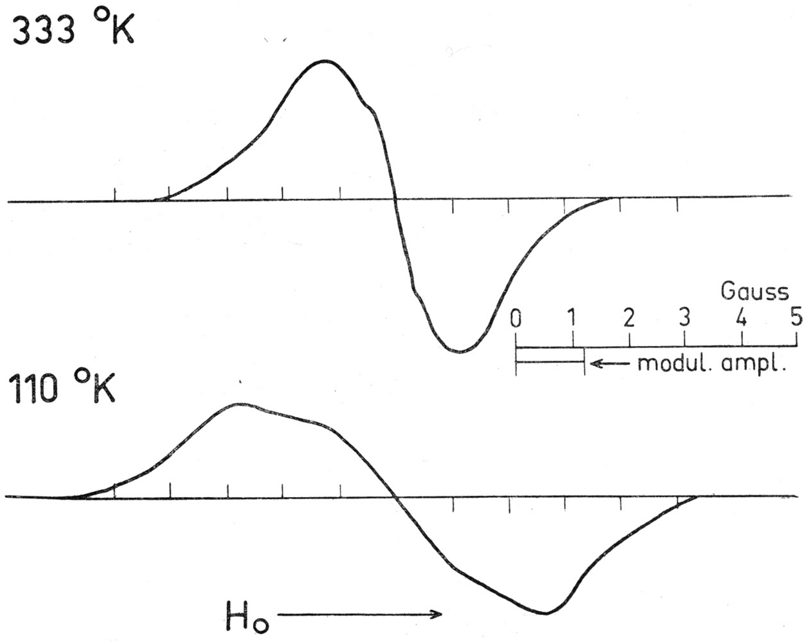
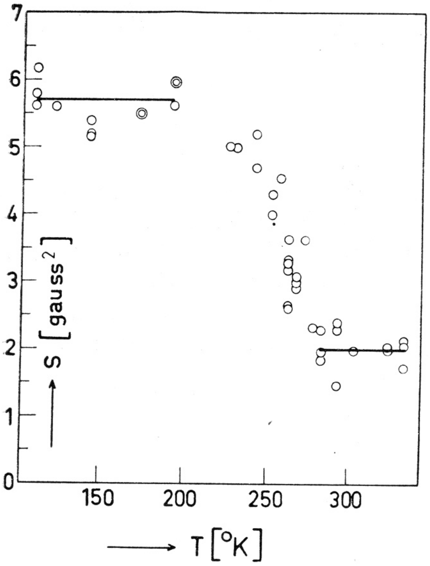


Fig 2. The line shapes of fluorine magnetic resonance in XeF_4 at 29 Mc/s.

Acknowledgment. The authors are indebted to D. Gudlin for skillfull technical assistance. Thanks are due to Dr. R. Blinc for keeping us informed on the progress of the n.m.r. study of XeF_4 in the »Jožef Stefan« Institute for Nuclear Research. We are obliged to the referees for helpful critical remarks.

REFERENCES

1. J. Slivnik, B. Brčić, B. Volavšek, A. Šmalc, B. Frlec, A. Zemljič, A. Anžur, and Z. Veksli, *Croat. Chem. Acta* 34 (1962) 187.
2. S. Maričić and Z. Veksli, *Croat. Chem. Acta* **34** (1962) 189.
3. R. Blinc, P. Podnar, J. Slivnik, and B. Volavšek, *Physics Letters* **4** (1963) 124.



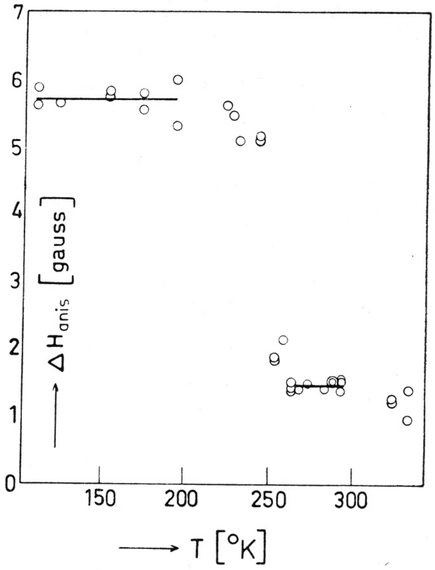


Fig. 3. Second moment values of fluorine magnetic resonance spectra in XeF_4 *vs.* temperature at 29 Mc/s.

Fig. 4. The anisotropy of fluorine (n.m.r.) chemical shift in XeF_4 at 29 Mc/s *vs.* temperature.

4. J. S. Lebedev, *Zhur. Strukt. him.* **4** (1963) 22.
5. J. A. Ibers and W. C. Hamilton, *Science* **139** (1963) 106.
6. D. H. Templeton, A. Zalkin, J. D. Forrester and S. M. Williamson, *J. Am. Chem. Soc.* **85** (1963) 242.
7. P. A. Agron, G. M. Begun, H. A. Levy, A. A. Mason, C. G. Jones, and D. F. Smith, *Science* **139** (1963) 842.

IZVOD

Magnetska mjerenja na XeF_4

S. Maričić, Z. Veksli, J. Slivnik i B. Volavšek

Utvrđeno je da je XeF_4 dijamagnetičan između 77° i 293° K. U spektrima fluorove magnetske rezonancije dobivenim kod 29 Mc/s ustanovljena je anizotropija kemijskog pomaka. Ona se mijenja oko 250°K od vrijednosti $5{,}7 \pm 0{,}2$ gausa na $1{,}4_7 \pm 0{,}1$ gausa iznad ove temperature, što ukazuje na ograničeno molekularno gibanje u kristalu. Drugi moment za čistu nuklearnu interakciju na niskim temperaturama slaže se s onim izračunanim iz podataka o kristalnoj strukturi XeF_4.

INSTITUT »RUĐER BOŠKOVIĆ«
ZAGREB
I
NUKLEARNI INSTITUT »JOŽEF STEFAN«
LJUBLJANA

Primljeno 22. ožujka 1963.