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Crystallographic data, vibrational spectra and magnetic properties of the lanthanide digermanates $Ln_2Ge_2O_7$

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Abstract

The vibrational properties of polycrystalline rare earth digermanates of general formula $Ln_2Ge_2O_7$ (Ln ≡ Gd–Lu, Y) have been investigated by means of Raman and IR spectroscopy. Mean amplitudes of vibration for the terminal GeO_3 groups of the $Ge_2O_7^{6-}$ ion and force constants for the $Ge_2O_7^{6-}$ digermanate group have been calculated. The magnetic behaviour of the digermanates has also been studied via magnetic susceptibility measurements in the 4.2–300 K temperature range.

1. Introduction

The $Ln_2Ge_2O_7$ rare earth digermanates exhibit a large variety of structural types and six different typical structures are known up to now [1–3]. Four of them are the so-called "low temperature phases" which belong to the triclinic system, with $P\bar{1}$ or $P1$ space group depending on the ionic radius of the lanthanide (Ln ≡ La, Pr or Nd–Gd respectively) [4, 5]. The remaining rare earth digermanates (Ln ≡ Gd–Lu) show tetragonal symmetry, space group $P4_12_12$, with the $Er_2Ge_2O_7$ structure type [6]. The $Sc_2Ge_2O_7$ phase crystallizes in the monoclinic system with the thortveitite structure [7].

On the other hand, the pyrochlore structure type has been reported for the high temperature ytterbium and scandium digermanates as well as for the high pressure forms with Ln ≡ Ga–Lu [8, 9]. A new high pressure hexagonal

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phase for $Ln_2Ge_2O_7$ (Ln≡Sm, Gd) has also been reported which yields the pyrochlore phase when the pressure is increased [9]. From the structural point of view of these phases the Ge atom is located in octahedral as well as in tetrahedral coordination such as in pyrochlore or in the triclinic phases. In these latter phases, isolated GeO_4^{4-} or condensed $Ge_3O_{10}^{4-}$ groups are observed. However, the monoclinic and tetragonal phases are characterized by $Ge_2O_7^{2-}$ digermanate units in which the lanthanide ion is surrounded by seven O atoms in a distorted pentagonal bipyramid. Unlike the disilicates, polymorphism in the germanates is not so common and only for the gadolinium compound have four phases been reported [4].

In this paper the magnetic and vibrational properties of the tetragonal digermanate series are analysed and discussed and the correlation between the unit cell parameters and the lanthanide ion sizes is reported.

2. Experimental details

The different $Ln_2Ge_2O_7$ compounds were prepared from stoichiometric amounts ($Ln_2O_3+2GeO_2$) of the high purity oxides Ln_2O_3 (99.999%) and GeO_2 (99.99%). The ground powders were heated in air at 1000 °C overnight followed by a thermal treatment at 1250 °C for 24 h with some interruptions to grind the sample to enhance the homogeneity. If the reaction products were heated for longer periods of time, the resulting $Ln_2Ge_2O_7$ digermanates showed the presence of an important amount of unreacted Ln_2O_3 as a consequence of the volatilization of GeO_2 at higher temperatures.

X-ray diffraction data were obtained in a Siemens K810 powder diffractometer using Cu Kα radiation and a D-500 goniometer equipped with a secondary graphite monochromator. The data were analysed by the Rietveld method using the programme FULLPROF [10].

Magnetic susceptibility measurements were performed in the temperature range 4.2–300 K using an apparatus based on the Faraday method. The set-up was calibrated using $Gd_2(SO_4)_3 \cdot 8H_2O$ and $Hg[Co(SCN)_4]$ as standards. The magnetic field was 5.5 kG with $HdH/dz = 17$ kG^2 cm^{-1}.

IR spectra were recorded with a Perkin–Elmer 580B spectrophotometer using the KBr pellet technique. Raman spectra were obtained with a Dilor fully automated spectrometer using the 488 nm line of an argon ion laser for excitation.

3. Results and discussion

3.1. X-ray diffraction study

X-ray diffraction data reveal that all the compounds are single and isostructural phases belonging to the tetragonal system, with space group $P2_12_12$ and $Z=4$, in agreement with the literature [6]. The unit cell of these phases contains eight lanthanum ions in equivalent general positions. The

LnO_7 distorted pentagonal bipyramids form helical chains whose axes coincide with the fourfold axes of the crystal.

On the other hand, condensation of two GeO_4 groups to form $Ge_2O_7^{2-}$ units yields a distorted tetrahedral environment with three shorter Ge–O distances and a Ge–O–Ge bridge angle of about 136°.

As expected, assuming the ionic model, the a and c lattice parameters and the volume of the unit cell, V, show a linear decrease with decreasing lanthanide ionic radius from Gd^{3+} to Yb^{3+}. These relationships are shown in Fig. 1 and are in accordance with the lanthanide contraction.

In addition, when the $Gd_2Ge_2O_7$ oxide is heated above 1250 °C for 12 h, a change in phase is observed and the triclinic form with space group $P1$ is obtained. The lattice parameters agree with those reported earlier [11].

3.2. *Vibrational spectra*

Information on vibrational spectra of germanates and digermanates is very scarce. Tarte investigated the GeO_4 vibration in some oxidic systems

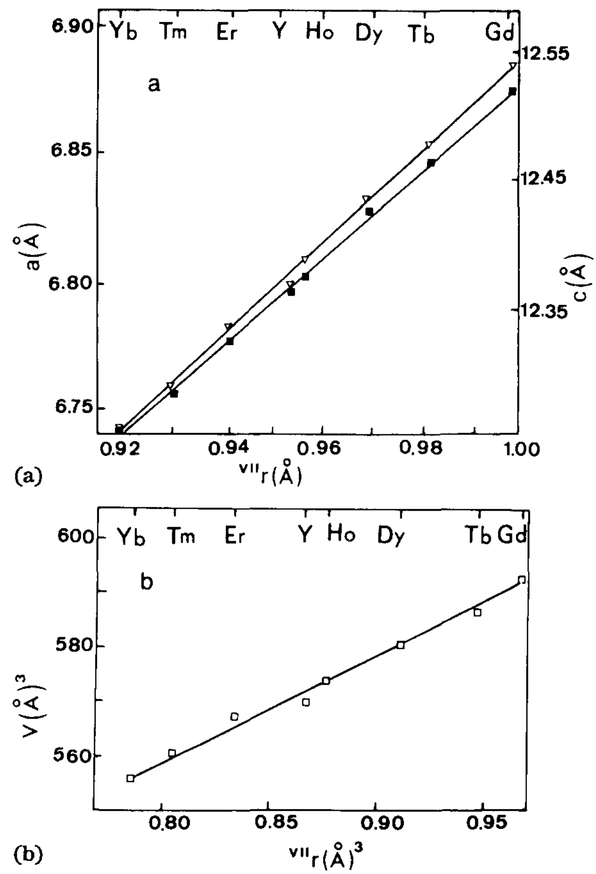

Fig. 1. Variation in (a) lattice parameters a and c and (b) unit cell volume V with Ln^{3+} ionic radius for different $Ln_2Ge_2O_7$ digermanates.

[12, 13], establishing that the stretching vibrations of this tetrahedral group lie between 700 and 800 cm^{-1} while the corresponding deformational modes may be expected around 400 cm^{-1}. A later spectroscopic study of $NaSmGeO_4$ and related materials showed that $\nu_s(GeO_4) > \nu_{as}(GeO_4)$ while most of the deformational modes are located between 450 and 500 cm^{-1} [11]. In the case of digermanates, only some comparisons with related disilicates are occasionally found in the literature [14–16].

The spectroscopic investigation of the present materials therefore provides a good opportunity to obtain a wider insight into the vibrational properties of Ge–O bonds.

The IR and Raman spectra of the different compounds are practically identical, indicating that the change in the Ln^{3+} cations and the related small variations in the unit cell parameters do not much affect the characteristics of the different Ge–O bonds present in these materials. Therefore we have analysed in detail only the IR and Raman spectra of $Y_2Ge_2O_7$, but the results and comments can be extended to all of the members of the investigated series.

Figure 2 shows the IR and Raman spectra of $Y_2Ge_2O_7$. The proposed assignment is given in Table 1. The bridge stretching modes were assigned following the results of Tarte and coworkers based on isotopic data [15,

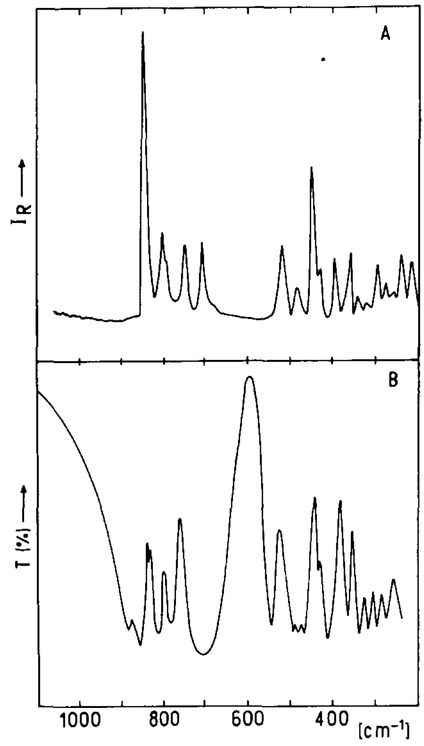

Fig. 2. (A) Raman and (B) IR spectra of $Y_2Ge_2O_7$.

TABLE 1

Assignment of vibrational spectrum of $Y_2Ge_2O_7$ (values in cm^{-1})

Infrared	Raman	Assignment
825 s	–	ν_{as}(Ge–O–Ge)
854 vs	855 vs	$\nu_s(GeO_3)$
832 w	–	$\nu_{as}(GeO_3)$
810 s	801 m	
–	790[a] sh	
778 s	–	
–	766 m	
698 vs	706 m	
535 s	530 m	ν_s(Ge–O–Ge)
487 s	485 w	$\delta_{as}(GeO_3)$
475 s	–	
457 s	460 s	
–	450 w	
426 w	–	$\delta_s(GeO_3)$
406 vs	402 m	
–	372	
357 m	350 w	ν(Y–O) + $\rho(GeO_3)$ + lattice vibrations
328 m	326 vw	
308 m	303 m	
288 m	290 w	
267 m	271 vw	
–	260 m	
	230	
	208	
	196	

Key: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.
[a]Approximate.

16]. The difference between these two frequencies (about 350 cm^{-1}) is in agreement with the value of the bridge angle in the material (about 136°) (see also refs. 14, 17 and 18 and references cited therein). The deformational mode of this bridge probably lies below 200 cm^{-1} [17].

The present results also confirm the fact that the symmetric stretching mode of the terminal GeO_3 lies higher than the asymmetric one. On the other hand, all these frequencies lie slightly higher than in the tetrahedral GeO_4^{4-} ion, as expected from the reinforcement of these terminal Ge–O bonds after condensation.

In the low frequency region the assignment is much more complicated because of the expected strong coupling between internal and external modes. Notwithstanding this, we think that the $\delta_{as}(GeO_3)$ components are relatively "pure" vibrations but that the corresponding symmetric modes are probably mixed with other vibrations, a supposition which is supported by the high intensity of the IR mode assigned to this vibration.

In order to obtain a wider insight into the properties of the $Ge_2O_7^{6-}$ anion, it seemed interesting to calculate the value of some of its fundamental vibrational properties.

The principal force constants of the ion can be obtained using a simplified molecular model originally proposed by Stammreich *et al.* [19] during their study of the dichromate ion and which we have applied with success to other X_2O_7 systems [17, 20–22]. In this model the X_2O_7 species is considered as a pentatomic O_3XO' molecule (O′, bridge oxygen) and the ***G*** and ***F*** matrix elements proposed by Müller *et al.* [23] were used. In this way it is possible to determine six force constants whereas with the original procedure of Stammreich *et al.* only four constants could be calculated.

In the construction of the ***F*** and ***G*** matrix elements the interatomic distances d(Ge–O) = 1.70 Å and d(Ge–O′) = 1.80 Å were used, which were determined by comparison with those of $As_2O_7^{4-}$ [20]. The following frequency values were used in the calculation: ν(Ge–O′) = 677, $\nu_s(GeO_3) = 855$, $\delta_s(GeO_3) = 406$, $\nu_{as}(GeO_3) = 762$, $\rho = 200$ and $\delta_{as}(GeO_3) = 473$ cm^{-1}. The ν(Ge–O′) value was obtained by averaging the two observed bridge frequencies and the ρ value was estimated according to Tarte *et al.* [15].

Table 2 shows the computed values for the force constants; in this table R and r are related to Ge–O′ and GeO_3 bonds respectively, α to the O–Ge–O angle, rr and $\alpha\alpha$ to bond–bond and angle–angle interactions respectively and ρ to the O–Ge–O′ angle. The calculated values reproduce the observed frequencies exactly.

Finally, we have estimated the mean amplitudes of vibration for the Ge–O bonds of the terminal GeO_3 groups in the anion using the method of characteristic vibrations developed by Müller *et al.* [24, 25] (see also ref. 26). The results in the temperature range between 0 and 1000 K are shown in Table 3. These results point to very strong Ge–O bonds.

3.3. *Magnetic properties*

The temperature dependence of the reciprocal magnetic susceptibility for the different $Ln_2Ge_2O_7$ compounds is plotted in Figs. 3–5. At the higher temperatures in all cases the susceptibility follows a Curie–Weiss behaviour. The values of the effective magnetic moments (μ_e) and the Weiss constant (θ) have been obtained by least-squares fits from the linear part of the reciprocal susceptibility curves at higher temperatures. The calculated magnetic moments given in Table 4 agree fairly well with those expected for the different Ln^{3+} free ions. The negative values obtained for the Weiss

TABLE 2

Force constants (mdyn Å^{-1}) for $Ge_2O_7^{6-}$ anion

f_R	f_r	f_α	f_{rr}	$f_{\alpha\alpha}$	f_ρ
3.14	4.77	0.93	0.68	0.20	0.14

TABLE 3

Mean amplitudes of vibration (Å) for terminal GeO_3 groups in $Ge_2O_7^{6-}$

T (K)	$u_{Ge–O}$	$u_{O\cdot\cdot O}$
0	0.0400	0.058
100	0.0400	0.059
200	0.0401	0.060
298.16	0.0408	0.063
300	0.0409	0.063
400	0.0423	0.068
500	0.0442	0.073
600	0.0464	0.077
700	0.0487	0.082
800	0.0509	0.087
900	0.0532	0.091
1000	0.0555	0.096

TABLE 4

Theoretical (μ_c) and experimental (μ_e) magnetic moments and Weiss constant (θ) for different $Ln_2Ge_2O_7$ digermanates

Compound	μ_c (μ_B)	μ_e (μ_B)	θ (K)
$Ge_2Ge_2O_7$	7.94	8.30	0.4
$Tb_2Ge_2O_7$	9.72	9.72	−4.5
$Dy_2Ge_2O_7$	10.65	10.61	−6.9
$Ho_2Ge_2O_7$	10.61	10.54	−4.7
$Er_2Ge_2O_7$	9.58	9.44	−4.3
$Tm_2Ge_2O_7$	7.56	7.58	−7.4
$Yb_2Ge_2O_7$	4.54	4.54	−43.9

constant in all cases do not necessarily mean that low temperature antiferromagnetic interactions are operative; these values are probably due to crystal field effects, as will be examined in the remainder of this paper.

In Fig. 3 it can be observed that the susceptibility of $Gd_2Ge_2O_7$ appears to follow a quasi-Curie-law behaviour over the entire temperature range of measurements and the θ constant takes a value as small as 0.4 K. Similar behaviour found for Gd^{3+} in different compounds has been explained by taking into account that the ground state $^8S_{7/2}$ of Gd^{3+} under the influence of the crystal field is split, giving rise to a maximum of four crystal field levels separated by only a few tenths of a reciprocal centimetre, which justifies neglecting the crystal field effect for Gd^{3+}.

Since Dy^{3+}, Er^{3+} and Yb^{3+} have odd numbers of f electrons, the J value of the free-ion term is a half-integral number and from Kramers' theorem the lowest crystal field level will be at least doubly-degenerate for these ions. The experimental susceptibilities for $Dy_2Ge_2O_7$, $Er_2Ge_2O_7$ and $Yb_2Ge_2O_7$ follow a similar behaviour and the bending downwards from linearity in the χ^{-1}

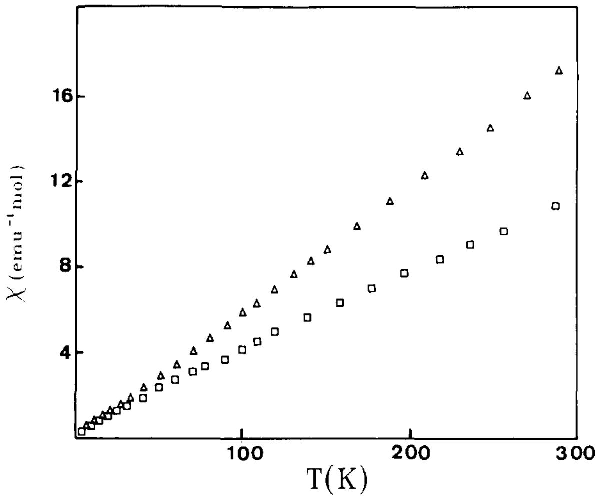

Fig. 3. Temperature dependence of reciprocal molar magnetic susceptibility of $Gd_2Ge_2O_7$ (△) and $Tb_2Ge_2O_7$ (□).

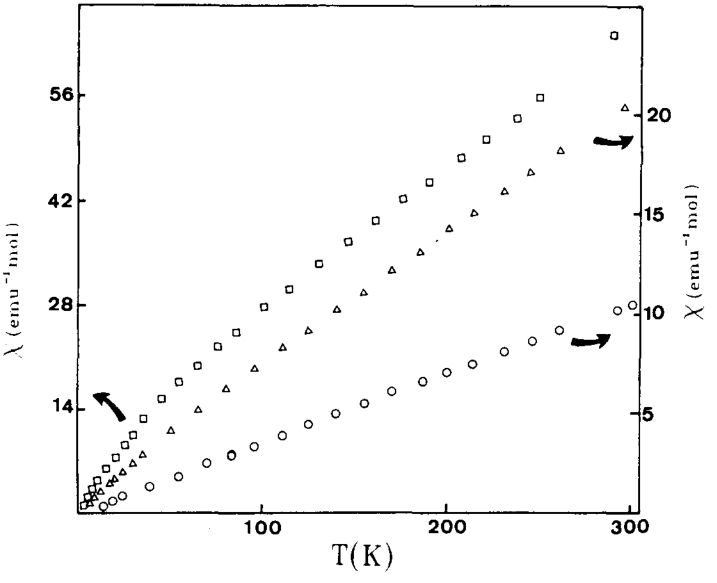

Fig. 4. Temperature dependence of reciprocal molar magnetic susceptibility of $Dy_2Ge_2O_7$ (O), $Tm_2Ge_2O_7$ (△) and $Yb_2Ge_2O_7$ (□).

vs. T plots can be attributed to crystal field effects (Figs. 4 and 5). We note that this deviation is most significant in the case of $Yb_2Ge_2O_7$, which is indicative that the energy levels will be more separated in the case of Yb^{3+} when compared with Dy^{3+} and Er^{3+}. Analogous results have previously been reported for other compounds of these trivalent lanthanide cations [27, 28].

On the other hand, Tb^{3+}, Ho^{3+} and Tm^{3+} have even numbers of f electrons and the lowest crystal field states can be singlet. However, the

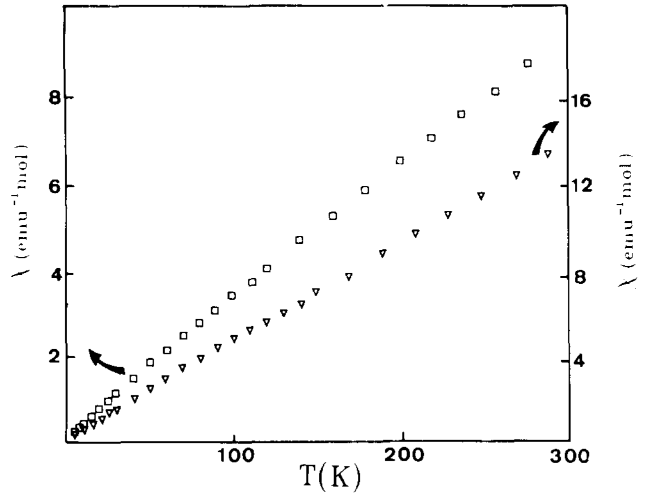

Fig. 5. Temperature dependence of molar magnetic susceptibility of $Ho_2Ge_2O_7$ (□) and $Er_2Ge_2O_7$ (▽).

observed deviations downwards in the Curie–Weiss behaviour in all cases (Figs. 3–5), which are more significant and start at 100 K in the case of $Tb_2Ge_2O_7$, are indicative that for these germanates the ground state crystal field level will be at least doubly degenerate.

For different compounds of these lanthanide cations with a singlet ground state, deviations upwards from linearity have been reported earlier [29, 30]. Although the existence of antiferromagnetic ordering has been reported for these compounds [31], the Néel temperatures are too small (2.15–1.15 K) to explain the deviations from linearity in χ^{-1} *vs. T*, which are too strong to be due only to antiferromagnetic interactions and thus are mostly due to crystal field effects.

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References

1 M. Leskela and L. Niinisto, in K. A. Gschneidner and L. Eyring (eds.), *Handbook on the Physics and Chemistry of the Rare Earths*, Vol. 8, Elsevier, Amsterdam, 1986, Chap. 56.
2 G. Souhet-Vetter and F. Queyroux, *Mater. Res. Bull.*, *10* (1975) 1201.
3 G. Bocquillon, C. Cahteau and J. Loriers, *Rare Earths Mod. Sci. Technol.*, *2* (1980) 209.
4 Y. Smolin, Y. F. Shepelev and T. V. Upatova, *Dokl. Akad. Nauk. SSR*, *187* (1969) 322.
5 Y. Smolin, Y. F. Shepelev and T. V. Upatova, *Kristallografiya*, *16* (1971) 911.
6 Y. Smolin, *Kristallografiya*, *15* (1970) 47.

7 R. D. Shannon and C. T. Prewitt, *J. Solid State Chem.*, *2* (1970) 199.

8 L. N. Demianets, A. N. Lobachev and G. A. Emelchenko, in M. C. Feyhardt (ed.), *Crystals Growth Properties and Applications*, Vol. 4, Springer, Berlin/Heidelberg, 1980, p. 104.

9 R. D. Shannon and A. W. Sleight, *Inorg. Chim.*, *7*(8) (1968) 1649.

10 J. Rodrigue-Carvajal, FULLPROF: a progam for Rietveld refinement and pattern matching analysis, *Satellite Meeting of XVth Congr. of International Union Of Crystallography, Toulouse, 1990,* Abstract d-127.

11 Y. I. Smolin, Y. F. Shepelev and I. K. Butikov, *Sov. Phys.-Crystallogr.*, *16*(5) (1972) 790.

12 P. Tarte, *Spectrochim. Acta, 18* (1962) 467.

13 P. Tarte, *Spectrochim. Acta, 19* (1963) 25–49.

14 A. N. Lazarev, *Vibration Spectra and Structure Of Silicates,* Consultant Bureau, New York, 1972.

15 P. Tarte, M. J. Pottier and A. M. Proces, *Spectrochim. Acta A, 35* (1979) 649.

16 M. Gabelica-Robert and P. Tarte, *Spectrochim. Acta A, 35* (1979) 649.

17 E. J. Baran, I. L. Botto, J. C. Pedregosa and P. J. Aymonino, *Monatsh. Chem.*, *109* (1978) 41.

18 E. J. Baran, *J. Mol. Struct.*, *48* (1978) 441.

19 H. Stammreich, D. Bassi, O. Sala and H. Siebert, *Spectrochim. Acta, 13* (1958) 192.

20 E. J. Baran, *An. Asoc. Quím. Argent.*, *62* (1974) 65.

21 E. J. Baran, J. C. Pedregosa and P. J. Aymonino, *J. Mol. Struct.*, *22* (1974) 377.

22 E. J. Baran, *Z. Naturf. A*, *42* (1987) 307.

23 A. Muller, B. Krebs and W. Holtje, *Spectrochim. Acta A, 23* (1967) 2753.

24 A. Muller, C. J. Peacock, H. Schulze and U. Heidborn, *J. Mol. Struct.*, *3* (1969) 252.

25 A. Muller, E. J. Baran and H. K. Schmidt, Characteristic mean amplitudes of vibrations, in S. J. Cyvin (ed.), *Molecular Structures and Vibrations,* Elsevier, Amsterdam, 1972, p. 67.

26 E. J. Baran, *An. Asoc. Quím. Argent.*, *61* (1973) 141.

27 E. Antic-Fidancev, C. Cascales, M. Lemaitre-Blaise, P. Porcher, R. Saez-Puche and I. Rasines, *Eur. J. Solid State Inorg. Chem.*, *28* (1991) 77.

28 Y. Laureiro, M. L. Veiga, F. Fernandez, R. Saez-Puche, A. Jerez and C. Pico, *J. Less-Common Met.*, *157* (1990) 335.

29 I. Bueno, C. Parada, R. Saez-Puche, I. L. Botto and E. J. Baran, *J. Phys. Chem. Solids, 41*(9) (1990) 1117.

30 M. D. Guo, A. T. Aldred and S. K. Chan, *J. Phys. Chem. Solids, 48*(3) (1987) 229.

31 B. M. Wanklyn, *J. Mater. Sci.*, *8* (1973) 649.