# Vibrational Spectra and Magnetic Properties of $Eu_3[BN_2]_2$ and $LiEu_4[BN_2]_3$

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**Abstract.** $Eu_3[BN_2]_2$ and $LiEu_4[BN_2]_3$ were synthesized from a stoichiometric mixture of EuN, BN, europium metal and $Li_3N$, EuN and BN (ratio: 1:4:3) in sealed niobium ampoules at 1475 and 1275 K, respectively. Temperature dependent susceptibility measurements of $Eu_3[BN_2]_2$ and $LiEu_4[BN_2]_3$ show Curie-Weiss behavior with experimental magnetic moments of 8.03(5) and 8.5(1) $\mu_B$/Eu atom, respectively, compatible with divalent europium. Both nitridoborates order ferromagnetically at $T_C$ = 32.0(5) K ($Eu_3[BN_2]_2$) and 22.0(5) K ($LiEu_4[BN_2]_3$). The saturation magnetizations of 5.73(5) $\mu_B$/Eu atom at 5 K and 7 T for $Eu_3[BN_2]_2$ and 4.2 $\mu_B$/Eu atom at 5 K and 2 T for $LiEu_4(BN_2)_3$ are smaller than the maximum value of 7 $\mu_B$. $^{151}$Eu Mössbauer data of $Eu_3[BN_2]_2$ at 4.2 K show an isomer shift of −11.4(1) mm/s and an experimental line width of 3.1(2) mm/s. Full magnetic hyperfine field splitting with 26.2(3) T at the europium nuclei is detected. Vibrational spectra of $Eu_3[BN_2]_2$ are interpreted on the basis of discrete $[BN_2]^{3-}$ units with symmetry $D_{\infty h}$ by taking into account the existence of two crystallographically independent $[BN_2]^{3-}$ anions and their dynamic coupling in the unit cell (factor group splitting).

**Keywords:** Magnetism; Mössbauer spectroscopy; Nitridoborate; Vibrational spectroscopy

# Schwingungsspektren und Magnetische Eigenschaften von $Eu_3[BN_2]_2$ and $LiEu_4[BN_2]_3$

**Inhaltsübersicht.** $Eu_3[BN_2]_2$ and $LiEu_4[BN_2]_3$ wurden ausgehend von einem stöchiometrischen Gemenge von EuN, BN und Europiummetall bzw. $Li_3N$, EuN und BN (Molverhältnis 1:4:3) in verschweißten Nb-Ampullen bei 1475 bzw. 1275 K synthetisiert. Temperaturabhängige Suszeptibilitätsmessungen an $Eu_3[BN_2]_2$ und $LiEu_4[BN_2]_3$ zeigen Curie-Weiss Verhalten mit experimentellen magnetischen Momenten von 8,03(5) und 8,5(1) $\mu_B$/Eu-Atom, was in Einklang mit zweiwertigem Europium steht. Beide Nitridoborate ordnen ferromagnetisch bei $T_C$ = 32,0(5) K ($Eu_3[BN_2]_2$) und 22,0(5) K ($LiEu_4[BN_2]_3$). Die Sättigungsmagnetisierungen von 5,73(5) $\mu_B$/Eu-Atom bei 5 K und 7 T für $Eu_3[BN_2]_2$ und 4,2 $\mu_B$/Eu-Atom bei 5 K und 2 T für $LiEu_4[BN_2]_3$ sind kleiner als der maximal mögliche Wert von 7 $\mu_B$. $^{151}$Eu Mössbauer-Daten von $Eu_3[BN_2]_2$ bei 4,2 K zeigen eine Isomerieverschiebung von −11,4(1) mm/s und eine experimentelle Linienbreite von 3.1(2) mm/s. Volle magnetische Hyperfeinfeldaufspaltung mit 26,2(3) T an den Europiumkernen wird beobachtet. Die Interpretation der Schwingungsspektren von $Eu_3[BN_2]_2$ erfolgte auf der Basis isolierter $[BN_2]^{3-}$−Gruppen mit $D_{\infty h}$-Symmetrie unter Berücksichtigung der Existenz zweier kristallographisch unanhängiger $[BN_2]^{3-}$−Baueinheiten und deren dynamischer Kopplung in der Elementarzelle (Faktorgruppenaufspaltung).

## Introduction

The crystal structure of $Eu_3[BN_2]_2$ was recently published as a short communication [1]. This nitridoborate is the first member of the cubic $M^{II}{}_3[BN_2]_2$ series ($M^{II}$ = Ca, Sr, Ba; space group: $Im\bar{3}m$) [2−6] crystallizing with the primitive space group $Pm\bar{3}m$. An interesting detail in this report is the magnetic moment of $\mu_{exp}$ = 7.4 $\mu_B$/Eu atom, giving rise to the assumption that the sample might contain to some extend $Eu^{3+}$, intrinsically or simply as an impurity. Therefore, a new $Eu_3[BN_2]_2$ sample was synthesized and reinvestigated by magnetic susceptibility measurements, $^{151}$Eu Mössbauer and vibrational spectroscopy. The first two methods are of special interest as very sensitive probes for the determination of the valence state of europium. The data will be discussed and compared with those of $LiEu_4[BN_2]_3$ [4, 6] in which europium is definitely divalent. We also report on the consequences of the structural change from $Im\bar{3}m$ to $Pm\bar{3}m$ on the vibrational behavior of the $[BN_2]^{3-}$ units. These results are discussed with respect to the vibrational spectra of $Sr_3[BN_2]_2$ [7].

## Experimental

### Synthesis

$Eu_3[BN_2]_2$ can be synthesized both from the binaries EuN (distilled Eu metal, nitridation at $T_{max}$ = 1073 K, 10 h) and

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BN (ratio 3 : 2, according to $3EuN + 2BN \rightarrow Eu_3[BN_2]_2 + 1/2N_2\uparrow$) or from a stoichiometric mixture of EuN, BN and europium metal in niobium ampoules. After sealing, the samples were heated to 1475 K, followed by annealing at 1375 K for 12 h and rapid cooling to room temperature. $Eu_3[BN_2]_2$ was obtained as a dark red to black crystalline product, very sensitive to air and moisture. Therefore, reopening of the ampoules as well as all handling operations were carried out under inert conditions (i.e. glove box, $N_2$; $O_2$ < 1 ppm; $H_2O$ < 1 ppm). $LiEu_4[BN_2]_3$ was prepared from a mixture of $Li_3N$, EuN and BN (ratio: 1:4:3) in sealed niobium ampoules at 1275 K. The details of the synthesis have been reported elsewhere [6]. The purity of the samples was checked by X-ray powder diffraction.

### *Magnetic measurements and $^{151}$Eu Mössbauer spectroscopy*

The magnetic susceptibilities of polycrystalline pieces of $Eu_3[BN_2]_2$ and $LiEu_4[BN_2]_3$ were determined with a MPMS SQUID magnetometer (Quantum Design, Inc.) between 4.2 and 300 K with magnetic flux densities of up to 7 T. The 21.53 keV transition of $^{151}$Eu with an activity of 130 MBq (2% of the total activity of a $^{151}$Sm:$EuF_3$ source) was used for the Mössbauer spectroscopic experiments. The measurements were performed with a commercial helium bath cryostat. The temperature of the absorber could be varied from 4.2 to 300 K and was measured with a metallic resistance thermometer with an accuracy better than ±0.5 K. The source was kept at room temperature. The sample was placed within a thin-walled PVC container with a thickness corresponding to about 10 mg Eu/cm$^2$.

### *Vibrational spectroscopy*

FT-Raman spectra were recorded from powdered samples sealed in silica tubes (d = 4 mm) with a module FRA 106 (Nd YAG-Laser, 1064 nm, 200 mW). The FT-IR spectra were obtained from PE/KBr pellets with a Bruker IFS 113v spectrometer.

## Results and Discussion

### *Magnetic measurements and $^{151}$Eu Mössbauer spectroscopy*

The temperature dependence of the inverse magnetic susceptibilities of $Eu_3[BN_2]_2$ measured at a flux density of 1 T is presented in Figure 1. Above 80 K the susceptibilities of $Eu_3[BN_2]_2$ obey the Curie-Weiss law. The experimental effective magnetic moment of $\mu_{exp} = 8.03(5)\ \mu_B$/Eu obtained from the linear part of the $1/\chi$ vs T plot according to $\mu_{exp} = 2.83[\chi/n(T-\Theta)]^{1/2}\mu_B$ [8] compares well with the theoretical effective moment $\mu_{eff} = 7.94\ \mu_B$ for a free $Eu^{2+}$ ion calculated from $\mu_{eff} = g[J(J+1)]^{1/2}\mu_B$. The paramagnetic Curie temperature (Weiss constant) $\Theta = 40(1)$ K was determined by extrapolation of the linear high-temperature part of the $1/\chi$ vs T plot to $1/\chi = 0$. Susceptibility measurements at much lower flux densities (not shown) revealed a small anomaly at 70 K, which we attribute to a small ferromagnetic ($T_C$ = 70 K) EuO impurity [9−11].

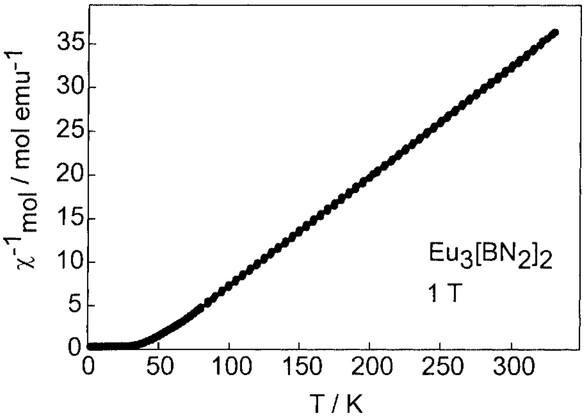

**Figure 1** Temperature dependence of the reciprocal magnetic susceptibilities of $Eu_3[BN_2]_2$ determined at a magnetic flux density of 1 T.

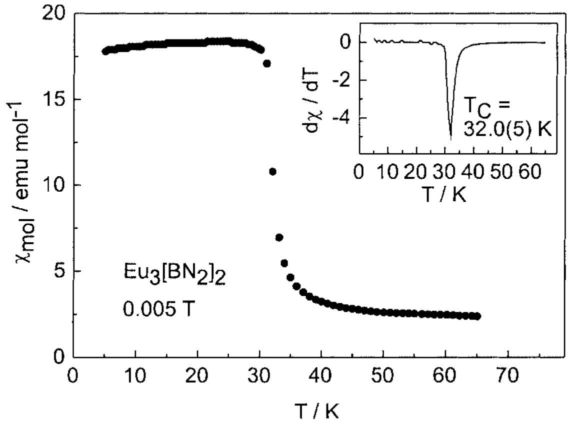

**Figure 2** Low-temperature susceptibilities (field-cooling mode) of $Eu_3[BN_2]_2$ as a function of temperature determined at a magnetic flux density of 0.005 T. The derivative of the data is shown in the inset.

From the divergence of $\chi$ i.e. $1/\chi \rightarrow 0$ at temperatures below $T_C$ (Figure 1) a ferromagnetic ordering of $Eu_3[BN_2]_2$ can be concluded. More detailed data for the low-temperature behavior are shown in Figure 2. The Curie temperature of 32.0(5) K was determined from the inflection point of the susceptibilities (Figure 2) measured at 0.005 T in a field-cooling cycle. The magnetization vs external magnetic field dependence at 5 K is presented in Figure 3. At the highest obtainable magnetic field of 7 T the magnetization has reached a value of 180 emu/g which corresponds to a saturation magnetisation (sm) of $\mu_{exp(sm)} = 5.73(5)\ \mu_B$/Eu, somewhat lower than the maximum saturation moment of $\mu_{calc(sm)} = 7.0\ \mu_B$/Eu calculated from $\mu_{calc(sm)} = g{\cdot}S$. A similar magnetization behavior was observed for a variety of intermetallic europium compounds [12].

$LiEu_4[BN_2]_3$ shows Curie-Weiss behaviour above 70 K (Figure 4) with an experimental effective magnetic moment of $\mu_{exp} = 8.5(1)\ \mu_B$/Eu and a Weiss constant of $\Theta = 45(1)$

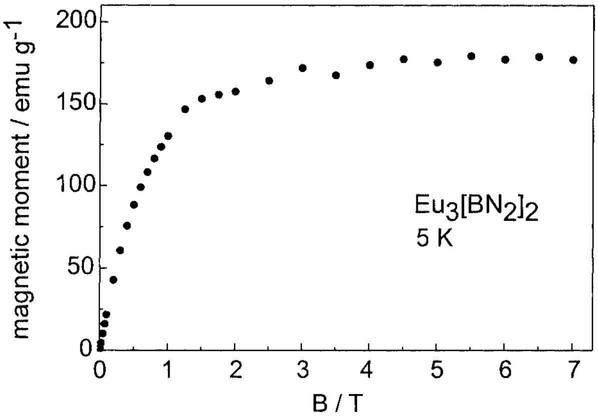

**Figure 3** Magnetization *vs* external magnetic flux density of $Eu_3[BN_2]_2$ measured at 5 K.

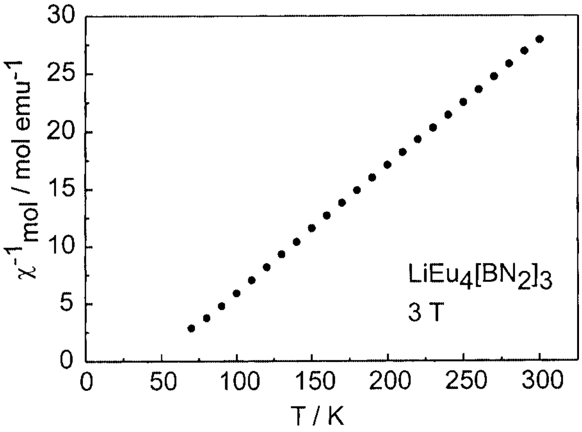

**Figure 4** Temperature dependence of the reciprocal magnetic susceptibilities of $LiEu_4[BN_2]_3$ determined at a magnetic flux density of 3 T.

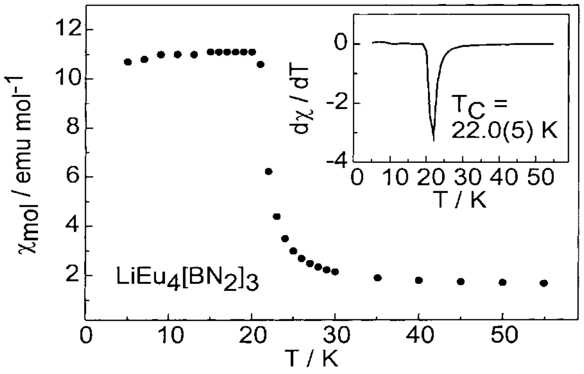

**Figure 5** Low-temperature susceptibilities of $LiEu_4[BN_2]_3$ as a function of temperature determined at a magnetic flux density of 0.01 T. The derivative of the data is shown in the inset.

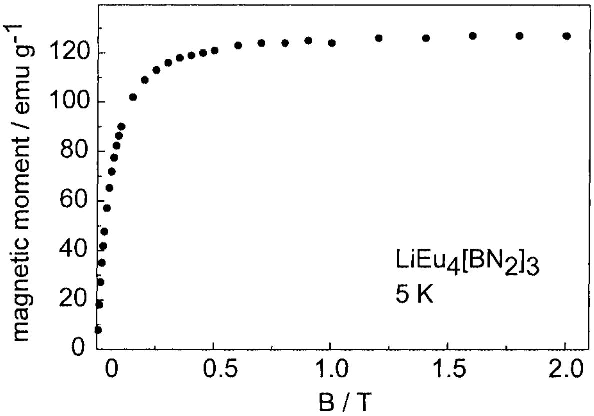

**Figure 6** Magnetization *vs* external magnetic flux density of $LiEu_4[BN_2]_3$ measured at 5 K.

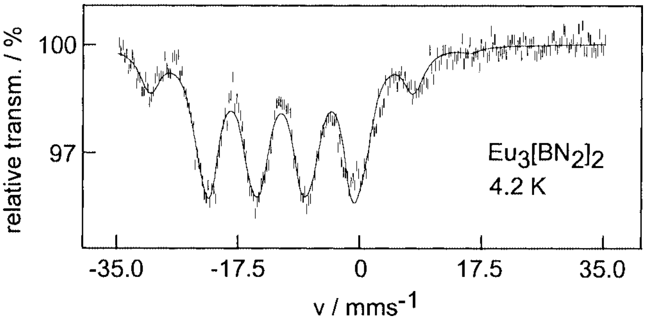

**Figure 7** $^{151}$Eu Mössbauer spectrum of $Eu_3[BN_2]_2$ at 4.2 K.

K. The slightly enhanced magnetic moment may be attributed to impurity effects. The low temperature magnetic properties determined at a field strength of 0.01 T (field-cooling data) are displayed in Figure 5. The Curie temperature of 22.0(5) K was deduced from the inflection point of the susceptibilities (Figure 5). Like for $Eu_3[BN_2]_2$ also the $LiEu_4[BN_2]_3$ sample showed a small feature in the susceptibilities around 70 K in the measurements at very low external fields. We attribute the anomaly to a small ferromagnetic impurity of EuO. This impurity, however, was not evident in the X-ray powder pattern. The field dependence of the magnetic moment is plotted in Figure 6. $LiEu_4[BN_2]_3$ shows saturation already at a magnetic flux density of 1 T with $\mu_{exp(sm)}$ = 4.2(1) $\mu_B$/Eu. The nature of the reduced moments of $Eu_3[BN_2]_2$ and $LiEu_4[BN_2]_3$ in the magnetically ordered state is yet unknown. Neutron diffraction experiments might help to determine the magnetic structures of both compounds.

Since $Eu_3[BN_2]_2$ was obtained in larger quantities, we could also record the $^{151}$Eu Mössbauer data. Above the magnetic ordering temperature of 32 K the $^{151}$Eu Mössbauer spectrum consists of a single signal, whereas full magnetic hyperfine field splitting is observed at low temperatures. As an example we present the spectrum at 4.2 K in Figure 7 together with a transmission integral fit. The fitting parameters are $\delta = -11.4(1)$ mm/s, $\Gamma = 3.1(2)$ mm/s, and B = 26.2(3) T. The isomer shift of −11.4 mm/s is negative as is usually observed for highly ionic compounds with pure divalent europium, e.g. −12.44 mm/s for β-$Eu_2GeS_4$ [13] and −11.82 mm/s for $Eu_2Si_5N_8$ [14]. According to the cubic site symmetry, no quadrupole splitting is detected. The high magnetic hyperfine field of 26.2 T is compatible with full magnetic splitting. Similar hyperfine fields occur in various intermetallic europium compounds in the magnetically ordered state.

### *Vibrational spectra*

The spectroscopic relevant unit in $Eu_3[BN_2]_2$ is the discrete linear anion $[BN_2]^{3-}$ with the symmetry $D_{\infty h}$ for which the following fundamentals are expected:

$$\Gamma_{vib} = \Sigma_g(\nu_1, R) + \Sigma_u(\nu_2, IR) + \Pi_u(\nu_3, IR)$$

Only modes with parity g are Raman active and those with the parity u exclusively IR active. In crystalline $Eu_3[BN_2]_2$ the nitridoborate anions center the sites $D_{4h}$-4/*mmm*. Thus the selection rules for the free $[BN_2]^{3-}$ anion will also be preserved in the solid state compound. There are two sets of crystallographically distinct nitridoborate groups each expected to give rise to two independent sets of fundamentals with significantly different wave numbers. The primitive unit cell contains Z = 3 formula units − i.e. six $[BN_2]^{3-}$ units- which may undergo a dynamic coupling (factor group splitting). In this case (factor group: $O_h^1$) all modes should split into sextets, half of them being Raman and IR active, respectively. In addition, the IR active modes are expected to exhibit the characteristic $^{10}B/^{11}B$ isotope splitting, each u-mode giving rise to doublets with $\nu(^{11}B)/\nu(^{10}B) \approx 0.95$ and $I(^{11}B)/I(^{10}B) \approx 4$ (I = intensity).

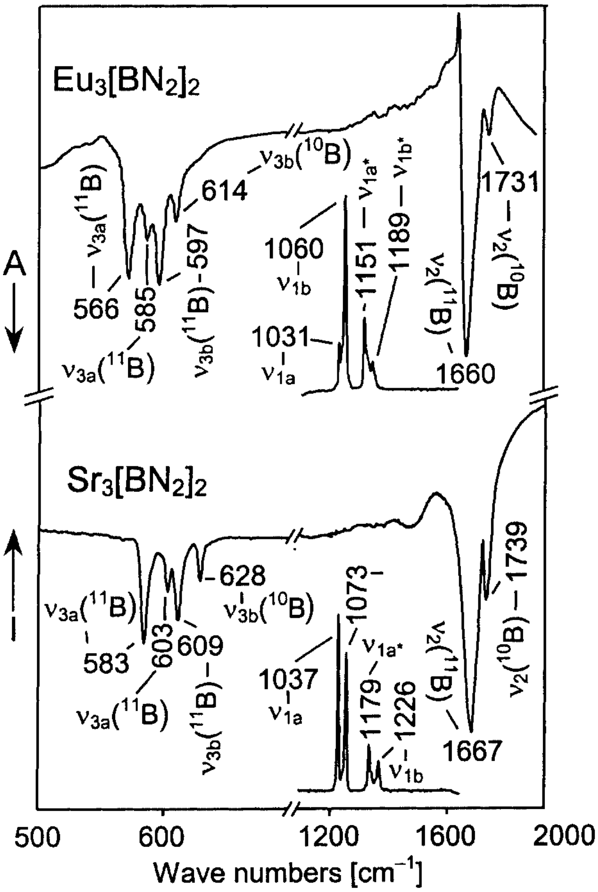

**Figure 8** Comparison of the IR (A = absorption, arbitrary units) and Raman Spectra (I = Intensity, arbitrary units) of $Eu_3[BN_2]_2$ and $Sr_3[BN_2]_2$ [7].

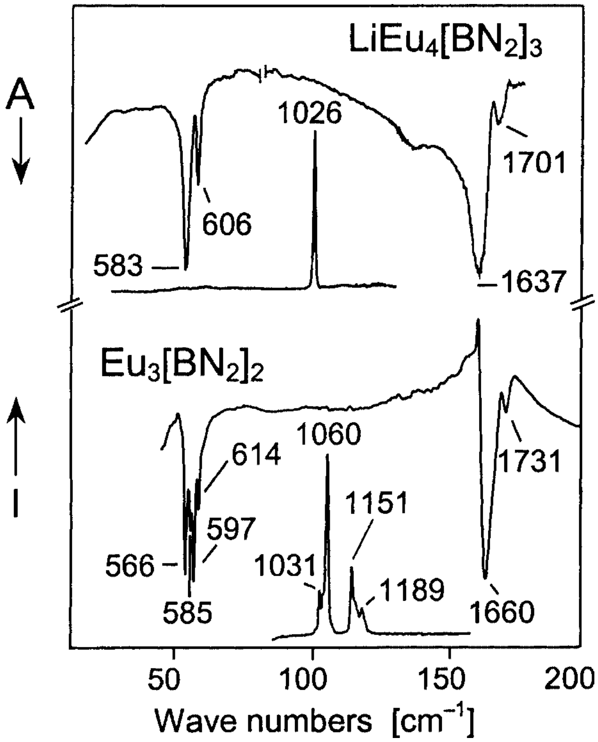

**Figure 9** Comparison of the characteristic splitting patterns in the vibrational spectra of $LiEu_4[BN_2]_3$ (*space group*: *Im*$\bar{3}$*m*) and $Eu_3[BN_2]_2$ (*Pm*$\bar{3}$*m*). A = Absorption and I = Intensity, both in arbitrary units.

In accordance with these predictions the vibrational spectra of $Eu_3[BN_2]_2$ illustrated in Figures 8 and 9 are quite complex and characterized by patterns of bands localized at three well-separated wavenumber regions:

- a pair of doublets in the Raman spectrum around 1000 $cm^{-1}$ ($\nu_{1a}/\nu_{1b}$ = 1031/1060 $cm^{-1}$) and 1100 $cm^{-1}$ ($\nu_{1a^*}/\nu_{1b^*}$ = 1151/1189 $cm^{-1}$), representing the symmetric stretching vibration and
- a quartet in the IR spectrum around 590 $cm^{-1}$ ($\nu_{3a}(^{11}B/^{10}B)$ = 566 $cm^{-1}$/585 $cm^{-1}$; $\nu_{3b}(^{11}B/^{10}B)$ = 597 $cm^{-1}$/614 $cm^{-1}$) and a doublet at $\nu_2(^{11}B/^{10}B)$ = 1660 $cm^{-1}$/1731 $cm^{-1}$, arising from the bending mode $\Pi_u$ and the antisymmetric stretching $\Sigma_u$ of the $[BN_2]^{3-}$ units, respectively.

The splitting in the Raman spectrum originates from both the presence of two sets of crystallographically independent $[BN_2]^{3-}$ groups ($\nu_{1a}/\nu_{1b}$) and the factor group splitting ($\nu_{1a*}/\nu_{1b*}$). The latter pair is assigned to the "out of phase" coupling of the totally symmetric modes of vibration of the different $[BN_2]^{3-}$ anions in the unit cell. As a result of the dynamic coupling the modes $\nu_{1a*}/\nu_{1b*}$ are shifted and appear at a rather high frequency region. The band splitting in the IR spectra arises only partially from the $^{10}B/^{11}B$ isotope splitting. The presence of the pair of doublets $\nu_{3a}/\nu_{3b}$ is clearly attributed to the existence of the crystallographically independent $[BN_2]^{3-}$ groups. In contrast to the Raman spectrum, no factor group splitting for the IR active modes could be registered, probably due to the overlap with the splitting caused by the solid state and isotope effects. The differences in the splitting pattern for $\nu_1$ ($\Sigma_g$) and ($\Pi_u$) in $Eu_3[BN_2]_2$ and the cubic body centered compounds $M^{II}{}_3[BN_2]_2$ and $M^I$ $M^{II}{}_4[BN_2]_3$ [4] represented by the spectroscopically well characterized nitridoborate $LiEu_4[BN_2]_3$ [4] in Figure 9 are very significant and can be used for identification. For this purpose, a single infrared spectrum in the wave region of $\nu_3$ (500−700 cm$^{-1}$) will be sufficient to decide whether the given cubic structure is centered ($Im\bar{3}m$) ($\nu_3$ splits into a doublet) or primitive ($Pm\bar{3}m$) (quartet). This can be verified by comparison of the spectra of $Eu_3[BN_2]_2$ and $Sr_3[BN_2]_2$, the latter originally reported as cubic body centered [3] (a reinvestigation led to space group $Pm\bar{3}m$ [7]). The most striking feature of the vibrational spectra in Figure 8 is their similarity both in the wave numbers and the splitting patterns of the fundamentals − including the factor group splitting for $\nu_1$ − underlining that space group $Pm\bar{3}m$ for $Sr_3[BN_2]_2$ is correct.

Utilizing $\nu_2$ ($\Sigma_u$) the averaged frequencies for $\nu_1$ ($\Sigma_g$) and $\nu_3$ ($\Pi_u$), the (B−N) stretch, bending and interaction force constants f, $f_D$ and f' for the $[BN_2]^{3-}$ group in $Eu_3[BN_2]_2$ and $Sr_3[BN_2]_2$ have been calculated according to [Ncm$^{-1}$]: 8.04, 1.09, 0.45 (Eu); 8.09, 1.09, 0.43 (Sr). The values for the (B−N) force constants are directly comparable and fit well with those of the other binary and ternary nitrodoborates [4].

In summary, the results of the magnetic measurements, as well as the $^{151}$Eu Mössbauer and the vibrational spectroscopic investigations confirm divalent europium and linear $[BN_2]^{3-}$ anions in the $Eu_3[BN_2]_2$ structure.

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