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Synthesis and Structures of the Quaternary Chalcogenides of the Type $KLnMQ_4$ (Ln = La, Nd, Gd, Y; M = Si, Ge; Q = S, Se)

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Some new quaternary compounds of the type $KLnMQ_4$ (Ln = La, Nd, Gd, Y; M = Si, Ge; Q = S, Se) have been synthesized by the reaction of K_2S_5 or K_2Se_5 with lanthanide sulfides or selenides and elemental Ge or Si at 1000°C. The crystal structures of two of these compounds have been determined by X-ray diffraction techniques and are isostructural. Crystal data: $KLaGeS_4$—space group $P2_1$, M = 378.84, Z = 2, a = 6.653(1), b = 6.679(2), c = 8.643(2) Å, β = 107.57(1)° (T = 115 K), V = 366.1(1) Å^3, D_x = 3.436, $\lambda(\text{Mo}K\alpha_1)$ = 0.7093 Å, μ = 113.9 cm^{-1}, $R_w(F^2)$ = 0.060 for 2613 observations and 66 variables, $R(F)$ = 0.022 for 2534 observations having $F_o^2 > 2\sigma(F_o^2)$; $KLaGeSe_4$—space group $P2_1$, M = 566.44, Z = 2, a = 6.875(3), b = 7.002(2), c = 8.942(4) Å, β = 107.84(2)° (T = 115 K), V = 409.8(3) Å^3, D_x = 4.590, $\lambda(\text{Mo}K\alpha_1)$ = 0.7093 Å, μ = 267.8 cm^{-1}, $R_w(F^2)$ = 0.100 for 3083 observations and 66 variables, $R(F)$ = 0.041 for 2965 observations having $F_o^2 > 2\sigma(F_o^2)$. The other compounds synthesized appear to crystallize in the same structure type. The structure consists of two-dimensional $^2_\infty[LnMQ_4^-]$ layers separated by K^+ cations in trigonal prismatic sites. The layers consist of LnQ_7 distorted monocapped trigonal prisms and MQ_4 tetrahedra that share edges and corners. The resultant structure is related to those of Eu_2GeS_4 and $ScPS_4$. The diffuse reflective UV–visible spectrum of $KLaGeS_4$ has been measured. From measurements of magnetic susceptibility vs temperature both $KNdGeS_4$ and $KGdGeS_4$ show Curie–Weiss behavior.

Introduction

The search for new complex chalcogenides has led to the synthesis of a number of new quaternary chalcogenides in this laboratory (*1–4*). These compounds display a wide range of structural features that can be described by the packing of metal–chalcogen polyhedra. In previous publications we have reported two groups of compounds with the general formula $A^IM^{III}M^{IV}Q_4$ (*5, 6*), where A = alkali metal, M^{III} = Ga/In/Cr, and M^{IV} = Ge/Sn/Zr. These are pseudoternary compounds since M^{III} and M^{IV} disorder. The compounds may be related to the parent MQ_2 structure by substitution of half of the tetravalent metal atoms by an equal amount of trivalent metal and monovalent alkali metal atoms. The resultant quaternary compounds have a layered structure similar to those of the binaries, with the alkali metal ions filling the gaps between the layers. We anticipated that new structural features would be found if the cation disorder could be avoided through the use of elements with different coordination preferences (*7*). Consequently, attempts were made to synthesize new quaternary chalcogenides that contain three metal elements from different major blocks of the Periodic Table, namely an *s*-block alkali- or alkaline-earth metal, a *p*-block main-group metal, and a *d*-block transition metal or an *f*-block lanthanide. In this paper the synthesis and crystal structures of a new series of quaternary chalcogenides $AM^{III}M^{IV}Q_4$ (A = K; M^{III} = Ln = La, Nd, Gd, Y; M^{IV} = Si, Ge; Q = S, Se) are reported. The new structure type $KLnMQ_4$ described here has crystallographically distinct sites for the three different

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metal atoms and there is no disorder. It is related in an interesting way to the structures of Eu_2GeS_4 and $ScPS_4$.

Experimental

Syntheses. The compounds $KLnMQ_4$ (Ln = La, Nd, Gd, Y; M = Si, Ge; Q = S, Se) were prepared by the reaction of elemental Ge or Si (both AESAR, 99.999%) with binary chalcogenides K_2Q_5 (prepared from the stoichiometric reaction of elemental K (AESAR, 99%) and S (Alfa, 99.9995%) or Se (Aldrich, 99.999%) in liquid ammonia under an atmosphere of argon), and Ln_2Q_3 (La_2S_3 from Strem, 99.9%, the rest prepared by high-temperature reactions of rare earth metals (all from Johnson Matthey, 99.9%) with S or Se). The starting materials were placed in quartz tubes that were subsequently evacuated to 10^{-5} Torr and sealed. After a preliminary study, an elemental ratio of 1 : 1 : 1 : 4 for K : Ln : M : Q was used. The quartz tubes were heated gradually to 500°C, where they were kept for 24 hr before being successively brought to 700°C for 24 hr and 1000°C for 150 hr. The tubes were then cooled at a rate of 4°C/hr to 300°C and then the furnace was shut off. Except for the neodymium system, colorless crystals of the sulfides and yellow-brown crystals of the selenides had grown in the tubes. The crystals of $KNdGeS_4$ appear green under normal fluorescent light, but the color nearly vanishes with illumination by an intense incandescent light or sunlight. In each system semiquantitative EDAX analysis with the microprobe of an Hitachi S-570 scanning electron microscope confirmed the presence of all four elements in a ratio of approximately 1 : 1 : 1 : 4. These compounds appear to be modestly stable in air. They decompose gradually in the presence of water.

Bulk samples of these compounds were prepared by reaction of stoichiometric amounts of starting materials at 1000°C for 10 days with an intermittent grinding.

Crystallographic study of $KLaGeS_4$. A plate-like crystal of approximate dimensions 0.18 by 0.15 by 0.05 mm was selected for data collection. Intensity data were collected by the θ–2θ scan technique on a Picker diffractometer. From systematic absences the compound crystallizes in space group $P2_1$ or $P2_1/m$ of the monoclinic system. The lattice constants were determined by least-squares analysis of the setting angles of 50 reflections in the range $37° < 2\theta$ (Mo$K\alpha_1$) $< 42°$ that had been automatically centered at 115 K. The refined cell constants and additional relevant crystal data are given in Table I. Six standard reflections measured every 100 reflections throughout data collection showed no significant variations in intensity.

The initial data processing was carried out on a Stardent computer with programs and methods standard in this laboratory (*8*). Conventional atomic scattering factors (*9*, *10*) were used and anomalous dispersion corrections (*11*) were applied. With the direct methods program SHEL86 (*12*) a reasonable solution was found only in the noncentrosymmetric space group $P2_1$. Data were corrected for absorption and averaged. The residual for averaging is 6.1%. An isotropic refinement led to an R index of 0.045 on F. An anisotropic refinement was carried out on F_o^2 with the use of all of the data. The values of R and R_w on F_o^2 converged to 0.057 and 0.077, respectively. An attempt to establish the direction of the polar axis by comparison of Friedel pairs of reflections was inconclusive. Consequently, the refinement program SHELXL-92 (*13*) was used to refine the Flack parameter x (*14*). The resultant value of 0.50(1) is strong evidence that the crystal chosen is a racemic twin. The final refinement was carried out on a model with two components that are racemic twins; it resulted in a value of R_w on F_o^2 of 0.060 and a twinning fraction of 0.52(1). The conventional R index on F_o for those 2534 reflections having $F_o^2 > 2\sigma(F_o^2)$ is 0.022. The residual electron densities have heights less than 0.4% of the height of a La atom. The program package SHELXTL PC

TABLE I

CRYSTAL DATA AND EXPERIMENTAL DETAILS FOR $KLaGeS_4$ AND $KLaGeSe_4$

Compound	$KLaGeS_4$	$KLaGeSe_4$
Formula weight	378.84	566.44
Space group	C_2^2–$P2_1$	C_2^2–$P2_1$
a, Å	6.653(1)	6.875(3)
b, Å	6.679(2)	7.002(2)
c, Å	8.643(2)	8.942(4)
β, °	107.57(1)	107.84(2)
V, Å^3	366.1	409.8
Z	2	2
T of data collection, K	115[a]	115[b]
Crystal volume, mm^{-3}	1.5×10^{-3}	1.6×10^{-3}
Crystal shape	Plate, bounded by {001}, {20$\bar{1}$}, (01$\bar{1}$), (0$\bar{1}$1), (2$\bar{1}$$\bar{1}$)	Plate, bounded by {20$\bar{1}$}, {010}, {001}, ($\bar{1}$10)
Radiation	Graphite monochromated Mo$K\alpha$ ($\lambda(K\alpha_1)$ = 0.7093 Å)	Graphite monochromated Mo$K\alpha$ ($\lambda(K\alpha_1)$ = 0.7093 Å)
Linear abs. coeff., cm^{-1}	113.9	267.8
Transmission factors[c]	0.259–0.684	0.047–0.186
Detector aperture, mm	Horizontal, 5.5; vertical, 5.5; 32 cm from crystal.	Horizontal, 4.0; vertical, 3.0; 20 cm from crystal.
Take-off angle, °	2.5	3.0
Scan speed, ° min^{-1}	2.0 in 2θ	$4° \le 2\theta \le 54°$, 3.1[d] in 2θ $54° \le 2\theta \le 66°$, 2.1[d] in 2θ.
Scan type	θ–2θ	ω–2θ
Scan range, °	1.1° below $K\alpha_1$ to 1.1° above $K\alpha_2$	0.7° below $K\alpha_1$ to 0.7° above $K\alpha_2$
$\lambda^{-1}\sin\theta$ limits, Å	0.0492–0.7678; $4° \le 2\theta(\text{Mo}K\alpha_1) \le 66°$	0.0492–0.7678; $4° \le 2\theta(\text{Mo}K\alpha_1) \le 66°$
Background counts	10 sec at each end of the scan	5 sec at each end of the scan
Data collected	$\pm h \pm k \pm l$	$+h \pm k \pm l$
Number of unique data including those with $F_o^2 < 0$	2613	3083
Number of unique data with $F_o^2 > 2\sigma(F_o^2)$	2534	2965
Number of variables	66	66
$R_w(F^2)$[e]	0.060	0.100
R (on F for $F_o^2 > 2\sigma(F_o^2)$)	0.022	0.041
Error in observation of unit weight, e^2	0.89	1.23

[a] The low-temperature system for the Picker diffractometer is based on a design by J. C. Huffman, Ph.D. thesis, Indiana University, 1974.

[b] The low-temperature system for the Nonius CAD4 diffractometer is from a design by Professor J. J. Bonnet and S. Askenazy and is commercially available from Soterem, Z. T. de Vic, 31320 Castanet-Tolosan, France.

[c] The analytical method was used for the absorption correction (J. de Meulenaer and H. Tompa, *Acta Crystallogr.* **19**, 1014–1018 (1965)).

[d] Reflections with $\sigma(I)/I > 0.33$ were rescanned up to a maximum of 60 sec in the range $4° \le 2\theta \le 54°$, and 100 sec in the range $54° \le 2\theta \le 66°$.

[e] $w^{-1} = \sigma^2(F_o^2) + (0.04 \times F_o^2)^2$ for $F_o^2 \ge 0$ and $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 < 0$.

(*15*) was used for the ensuing molecular graphics generation.

Crystallographic study of $KLaGeSe_4$. A plate-like crystal of approximate dimensions 0.17 by 0.15 by 0.07 mm was selected for data collection. The lattice constants were determined from least-squares analysis of the setting angles of 25 reflections in the range $35° < 2\theta\,(\text{Mo}K\alpha_1) < 45°$ that had been automatically centered at 115 K on a

TABLE II

POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS

Atom	x	y	z	U_{eq} (Å^2)[a]
		$KLaGeS_4$		
La	0.23221(2)	−0.00003(2)	0.55430(2)	0.00626(7)
Ge	0.21624(5)	0.52591(6)	0.31258(4)	0.00591(12)
K	0.27155(13)	0.0149(2)	0.06556(8)	0.0133(3)
S(1)	0.0147(2)	0.25795(14)	0.27989(12)	0.0078(3)
S(2)	0.0188(2)	0.26895(14)	0.73214(12)	0.0074(3)
S(3)	0.41368(13)	0.5286(2)	0.15277(10)	0.0092(3)
S(4)	0.59168(13)	0.06456(15)	0.43019(10)	0.0088(3)
		$KLaGeSe_4$		
La	0.23227(6)	0.00001(5)	0.55461(4)	0.0077(2)
Ge	0.21582(11)	0.52911(10)	0.31393(8)	0.0074(3)
K	0.2594(3)	0091(3)	0.0632(2)	0.0164(7)
Se(1)	0.00996(12)	.5633(9)	0.27761(9)	0.0086(3)
Se(2)	0.02955(11)	0.2736(10)	0.73514(9)	0.0083(3)
Se(3)	0.41336(11)	0.53303(12)	0.14668(8)	0.0112(3)
Se(4)	0.58513(12)	0.07535(10)	0.42294(8)	0.0094(3)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

CAD4 diffractometer. The refined cell constants and additional relevant crystal data are given in Table I. Intensity data were collected by the ω–2θ scan technique on the CAD4 diffractometer. Six standard reflections measured every 3 hr throughout data collection showed no significant variation in intensity. Systematic absences are consistent with space groups $P2_1$ or $P2_1/m$ of the monoclinic system. We assumed that $KLaGeS_4$ and $KLaGeSe_4$ were isostructural and hence the refinement was carried out as described above. Refinement of the model with two components that are racemic twins resulted in values of R_w of 0.100, and the fraction of the second component of 0.52(2). The conventional R index on F_0 for those 2965 reflections having $F_o^2 > 2\sigma(F_o^2)$ is 0.041. The residual electron densities have height of about 1.2% of that of a La atom in this structure.

The program MISSYM (*16*) was used to test for additional potential symmetry in these two structures. It detected a possible inversion center consistent with space group $P2_1/m$. Indeed, the atomic coordinates for all atoms except those of $Q(4)$ can be related approximately by a center of symmetry. Attempts to refine these structures in space group $P2_1/m$, however, were unsuccessful. That the correct space group is $P2_1$ rather than $P2_1/m$ was established from the observation of green light from second harmonic generation when some $KLaGeS_4$ samples were placed in the path of a Nd:YAG laser beam (λ = 1.06 μm).

No unusual trends were found in either structure in an analysis of the goodness of fit as a function of F_o and scattering angle. Final values of the atomic parameters and equivalent isotropic thermal parameters for both compounds appear in Table II. Final anisotropic thermal parameters and structure amplitudes are given in Tables III and IV.[1]

Unit cell measurements. The unit cell dimensions of several other members of this series were determined either from least-squares analysis of the setting angles of reflections automatically centered on a Picker

[1] See NAPS Document 05013 for 26 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or $9.55 for photocopy. All orders must be prepaid.

TABLE V

SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

	$KLaGeS_4$	$KLaGeSe_4$
La–Q(1)	2.935(1)	3.062(2)
La–Q(1)	2.964(1)	3.077(2)
La–Q(2)	2.967(1)	3.098(2)
La–Q(2)	2.987(1)	3.100(2)
La–Q(3)	2.898(1)	3.023(2)
La–Q(4)	2.933(1)	3.050(2)
La–Q(4)	3.123(1)	3.210(2)
Ge–Q(1)	2.203(1)	2.340(2)
Ge–Q(2)	2.206(1)	2.349(2)
Ge–Q(3)	2.175(1)	2.308(2)
Ge–Q(4)	2.220(1)	2.354(2)
K···Q(1)	3.301(2)	3.410(3)
K···Q(1)	3.472(2)	3.520(3)
K···Q(2)	3.329(2)	3.420(3)
K···Q(2)	3.395(2)	3.480(3)
K···Q(3)	3.216(1)	3.347(3)
K···Q(3)	3.404(2)	3.508(3)
K···Q(3)	3.578(2)	3.828(4)
K···Q(4)	3.244(2)	3.342(3)
Q(1)–La–Q(1)	120.05(2)	120.60(4)
Q(1)–La–Q(2)	67.36(3)	66.75(4)
Q(1)–La–Q(2)	82.40(3)	82.32(4)
Q(1)–La–Q(3)	137.72(3)	137.53(4)
Q(1)–La–Q(4)	82.86(3)	81.09(4)
Q(1)–La–Q(4)	131.94(3)	133.03(4)
Q(1)–La–Q(2)	82.26(3)	82.05(4)
Q(1)–La–Q(2)	70.15(3)	72.05(4)
Q(1)–La–Q(3)	92.09(3)	91.24(4)
Q(1)–La–Q(4)	152.74(3)	153.85(3)
Q(1)–La–Q(4)	74.15(3)	73.47(4)
Q(2)–La–Q(2)	120.45(2)	120.87(4)
Q(2)–La–Q(3)	150.21(3)	151.92(3)
Q(2)–La–Q(4)	95.00(3)	95.31(5)
Q(2)–La–Q(4)	70.18(3)	72.21(4)
Q(2)–La–Q(3)	84.15(3)	82.05(4)
Q(2)–La–Q(4)	131.78(3)	129.21(4)
Q(2)–La–Q(4)	140.21(3)	140.36(3)
Q(3)–La–Q(4)	76.84(3)	78.86(4)
Q(3)–La–Q(4)	80.12(3)	79.73(4)
Q(4)–La–Q(4)	79.39(3)	80.92(4)
Q(1)–Ge–Q(2)	101.74(4)	101.53(5)
Q(1)–Ge–Q(3)	112.72(4)	111.76(5)
Q(1)–Ge–Q(4)	111.54(4)	113.12(5)
Q(2)–Ge–Q(3)	114.52(4)	113.69(5)
Q(2)–Ge–Q(4)	104.67(4)	104.52(5)
Q(3)–Ge–Q(4)	111.08(4)	111.65(5)

diffractometer at 115 K or from precession photographs taken at room temperature.

Physical measurements. A diffuse reflective UV-visible spectrum of $KLaGeS_4$ was taken at room temperature on an Hitachi U-3000 spectrophotometer over the wavelength range 240 to 700 nm. Barium sulfate was used as a reference. Magnetic susceptibility measurements of $KNdGeS_4$ and $KGdGeS_4$ were made at 10 kG over the temperature range 6–300 K with a Quantum Design SQUID magnetometer. Field dependency measurements were also made at 6 and 300 K and the magnetization of all samples was linearly proportional to the applied field strengths from 2 to 10 kG. All magnetic susceptibility data were corrected for core diamagnetism.

Results and Discussion

Selected distances and angles for $KLaGeS_4$ and $KLaGeSe_4$ are given in Table V. The unit cell parameters of several other members that are apparently isostructural are listed in Table VI. These materials crystallize in the structure type illustrated in Fig. 1 for the $KLaGeS_4$ structure. In these

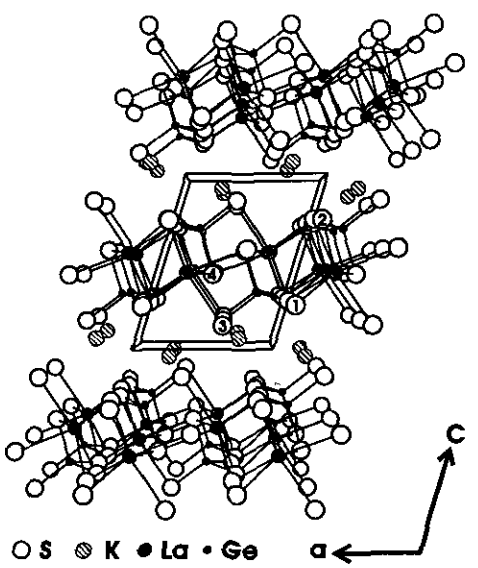

FIG. 1. View of the $KLaGeS_4$ structure along the *b* axis.

TABLE VI

UNIT CELLS OF THE COMPOUNDS K$LnMQ_4$

Compound	a (Å)	b (Å)	c (Å)	β (°)	T (K)
$KYSiS_4$	6.37(2)	6.56(2)	8.61(3)	108.1(4)	295
$KYGeS_4$	6.42(2)	6.60(1)	8.49(2)	107.0(1)	115
$KNdGeS_4$	6.57(2)	6.69(2)	8.67(2)	107.8(3)	295
$KGdGeS_4$	6.50(2)	6.67(2)	8.64(3)	108.0(3)	295
$KLaSiS_4$	6.57(2)	6.60(2)	8.69(3)	107.2(4)	295
$KLaSiSe_4$	6.81(2)	6.94(2)	9.06(2)	108.4(3)	295
$KLaGeS_4$	6.653(1)	6.679(2)	8.643(2)	107.57(1)	115
$KLaGeSe_4$	6.875(3)	7.002(2)	8.942(4)	107.84(2)	115

structures there are two-dimensional layers $^2_\infty[LnMQ_4^-]$ (M = Ge, Si; Q = S, Se) separated by K^+ ions. Figure 2 shows a perspective view of a $^2_\infty[LaGeQ_4^-]$ layer while Fig. 3 shows a polyhedral representation. La atoms are coordinated by seven chalcogen atoms at the corners of a monocapped trigonal prism and Ge atoms are coordinated by four chalcogen atoms at the corners of a tetrahedron. The La–Q bond lengths range from 2.898(1) to 3.123(1) Å in $KLaGeS_4$ and from 3.023(2) to 3.210(2) Å in $KLaGeSe_4$. The Ge–Q bond lengths range from 2.175(1) to 2.220(1) Å in $KLaGeS_4$ and from 2.308(2) to 2.354(2) Å in $KLaGeSe_4$. These values compare well with those in the literature. For example, La–S bond lengths vary from 2.804(4) to 3.274(3) Å in La_2SnS_5 (*17*); La–Se bond lengths vary from 3.048(2) to 3.232(2) Å in La_2SeSiO_4 (*18*); Ge–S bond lengths vary from 2.181(3) to 2.262(3) Å in $Na_6Ge_2S_7$ (*19*); and Ge–Se bond lengths vary from 2.337(5) to 2.365(5) Å in $GeSe_2$ (*20*). The Q–Ge–Q bond angles range from 101° to 115° in the present structures. With reference to Fig. 3 note that two of the three edges formed by the rectangular faces of the trigonal prisms are shared to form chains along the b direction, while the third edge is shared with a GeQ_4 tetrahedron. The tetrahedron in turn shares its other two vertices with two trigonal prisms in the adjacent

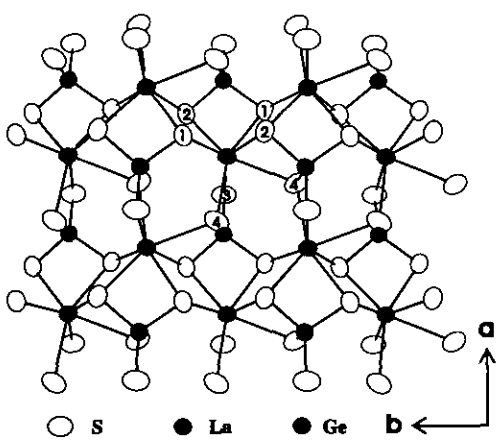

FIG. 2. View of a $^2_\infty[LnGeS_4^-]$ layer along the c^* axis. The thermal ellipsoids are shown at 99.99% probability level.

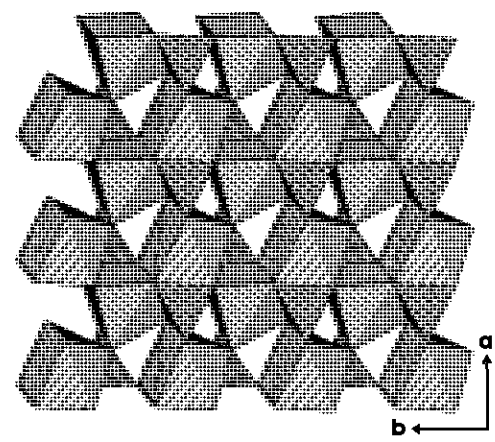

FIG. 3. A polyhedral presentation of a $^2_\infty[LnGeS_4^-]$ layer. The triangular face of the trigonal prism faces the viewer.

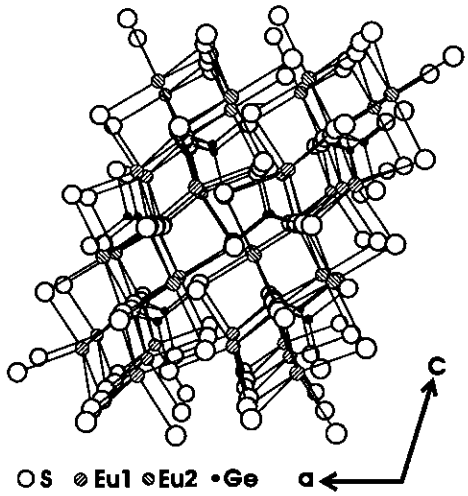

FIG. 4. View of the Eu_2GeS_4 structure along the *b* axis.

chain. These chains are cross-linked not only by GeQ_4 tetrahedra, but also by capping of one rectangular face of each trigonal prism by a chalcogen atom in the neighboring chain.

This structure is related to that of Eu_2GeS_4 (*21*). That structure (Fig. 4) has two Eu^{2+} sites, both of which are seven-coordinated, and the structure extends in all three dimensions. The substitution of Ln^{3+} for Eu(1) and K^+ for Eu(2) results in the $KLaGeQ_4$ structure type. Although the framework of the two structure types is similar, as a result of the very electropositive nature of K^+ the $KLaGeQ_4$ structure comprises alternating $^2_\infty[LnMQ_4^-]$ and K^+ layers. K^+, which is larger than Eu^{2+}, is eight-coordinated and the $KLaGeQ_4$ structure type is distorted slightly from that of Eu_2GeS_4. The K···S interactions in $KLaGeS_4$ range from 3.216(1) to 3.578(2) Å while the K···Se interactions in $KLaGeSe_4$ range from 3.342(3) to 3.828(4) Å.

The noncentrosymmetric nature of the $KLaGeQ_4$ structure arises mainly from the distortion of the trigonal prisms that allows capping of an adjacent *Ln* atom by a *Q*(4) atom. As shown in Figs. 2 and 3, all caps point in the same direction along the polar *b* axis. This destroys the center of inversion. To clarify this point, a comparison can be made with the structure of $ScPS_4$(*22*). Figure 5 shows a layer of that structure. It is formed by connecting ScS_7 monocapped-trigonal prisms and PS_4 tetrahedra. As in the $KLaGeQ_4$ structure, the trigonal prisms form zigzag chains along the *a* direction. The chains are connected by PS_4 tetrahedra and by capping of trigonal prisms. The difference between the two structures is in the way those caps point. In the $ScPS_4$ structure the caps on two sides of a chain point in alternating directions, while in the $KLaGeS_4$ structure they point in one direction. In $ScPS_4$ the center of symmetry is preserved but the symmetry of the system is lowered to triclinic.

In the $KLaGeQ_4$ structure the enantiomer is formed upon the reversal of the capping direction. That racemic twinning occurs is not too surprising in view of the structure. The layers in these compounds are held together primarily by ionic forces; local reversal of the direction of the polar axis should not introduce too much stress in the structure.

The structures of two layered quaternary chalcogenides $CaYbInQ_4$ (Q = S and Se) have recently been reported (*23*). While these compounds have similar formulas to the present ones their structures are very different. In $CaYbInQ_4$, Ca and Yb cations

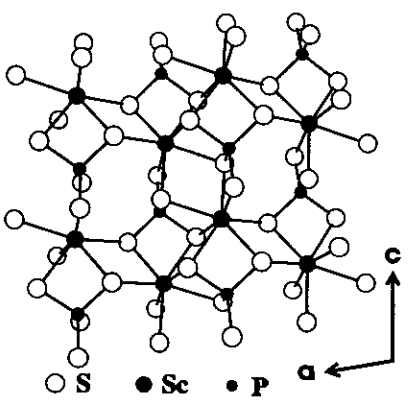

FIG. 5. View of a $ScPS_4$ layer along the b^* axis.

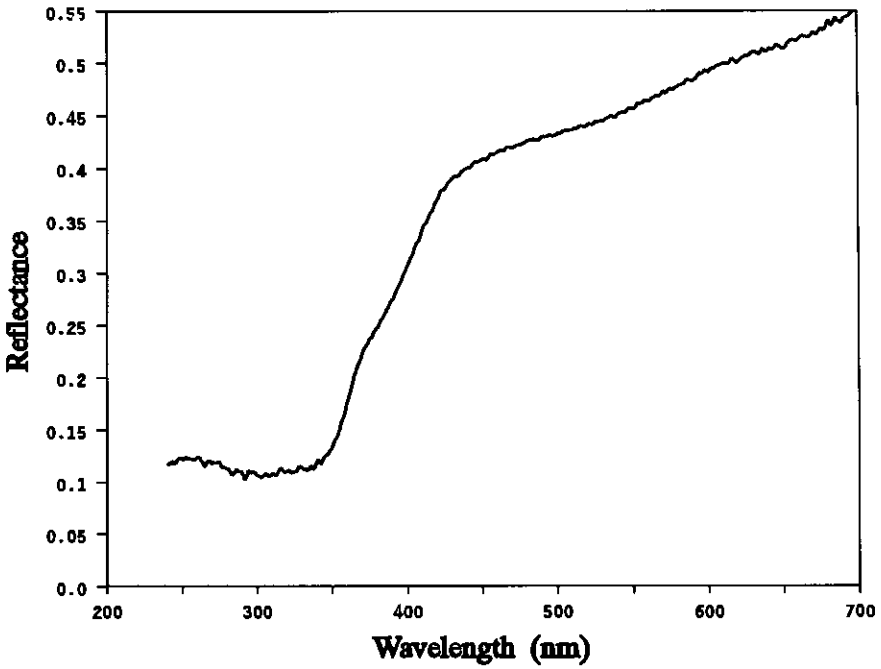

FIG. 6. Diffuse reflective UV–visible spectrum of $KLaGeS_4$.

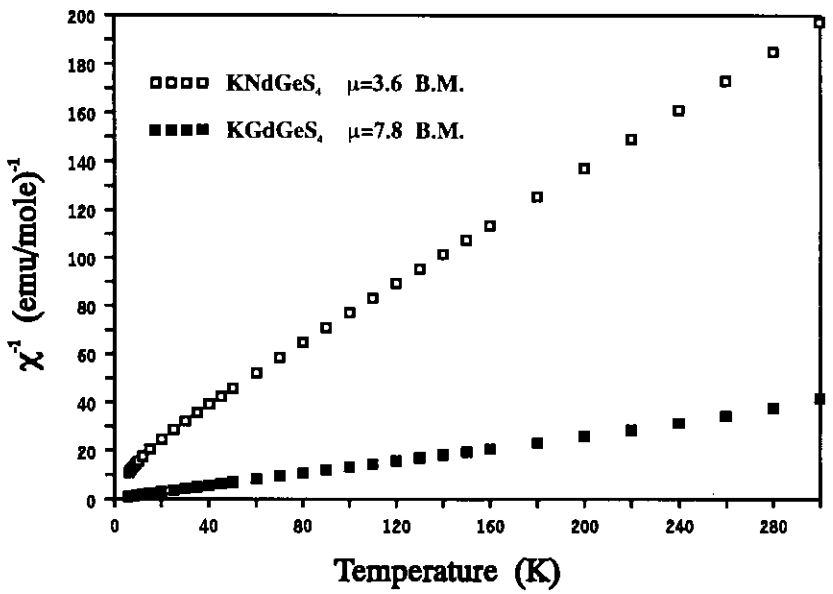

FIG. 7. Measured magnetic susceptibilities of $KNdGeS_4$ and $KGdGeS_4$.

are disordered and occupy octahedral sites, and the resultant layers consist of edge-sharing octahedral chains connected only by InQ_4 tetrahedra.

Figure 6 shows the diffuse reflective UV–visible spectrum of $KLaGeS_4$. From a plot of $(\alpha h\nu)^2$ vs $h\nu$, where α is the absorption coefficient and $h\nu$ is the photon energy, a direct band gap of 3.4(1) eV may be derived; alternatively, from a plot of $(\alpha h\nu)^{1/2}$ vs $h\nu$ an indirect band gap of 2.8(1) eV may be derived (*24*). The data do not enable us to distinguish between these two alternatives.

Plots of the reciprocal molar magnetic susceptibilities of $KNdGeS_4$ and $KGdGeS_4$ as a function of temperature are shown in Fig. 7. Both compounds show Curie–Weiss behavior. The measured magnetic moments, 3.6(1) μ_B for $KNdGeS_4$ and 7.8(1) μ_B for $KGdGeS_4$, are consistent with the theoretical values for Nd^{III} and Gd^{III}, respectively (*25*).

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