Laser Raman Scattering from Single Crystals of RuS₂ (Pyrite)

(Raman scattering/RuS$_2$/pyrite structure)

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Raman spectra have been studied in single crystals of RuS$_2$ at room temperature. Three, out of the five vibrational modes predicted from a group-theoretical analysis are observed. An analysis based on scattering intensity tensors is made to assign the observed peaks in the spectra. A comparison of Raman and infrared frequencies indicates that the sulfur-sulfur bonds and metal-sulfur bonds in RuS$_2$ and FeS$_2$ are of comparable strength.

INTRODUCTION

Transition-metal dichalcogenides of the form MX_2 (M=metal atom, X=S, Se, Te) crystallize in two types of structures : layered or otherwise (pyrite, marcasite, IrSe$_2$ and PdS$_2$). Compounds containing transition-metal atoms from groups IV—VI of the periodic table form layered structure, whereas those composed of metal atoms from groups VII, VIIIa, VIIIb or VIIIc crystallize predominantly in the pyrite structure. Both types of pyrite and layered crystals display a wide range of characteristics in their electrical (semiconductor, metal, superconductor) or magnetic properties.[1,2]

RuS$_2$ belongs to the family of the pyrite structure.[3] Recently, this material has attracted interest due to its potential application as an electrode in photoelectrochemical devices.[4,5] Up to a recent date, experimental works on RuS$_2$ had been done on powdered or polycrystalline samples because of difficulties in obtaining single crystals. However, Bichsel et al.[6] recently succeeded in growing large single crystals and it became possible to study the physical properties in detail. Their measurements of the electrical resistivity[6] and Hall effect[7] showed n-type semiconducting-like conduction in RuS$_2$. The energy gap was determined to be 1.22 eV by optical measurements.[6,7]

Concerning the lattice vibrations, Vaterlaus et al.[7] investigated the infra-

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red reflection spectra and found five phonon peaks in RuS_2. In order to discuss the lattice dynamics, we need to know Raman frequencies in addition to infrared data. In this paper, we present the results of the first Raman scattering experiments on single crystals of RuS_2.

STRUCTURE AND GROUP THEORETICAL ANALYSIS OF LATTICE MODES

Pyrite crystallizes in a cucic structure with the space group T_h^6 ($Pa3$). Primitive unit cell is shown in Fig. 1. A unit cell has cube edges $a_0 = 5.6095$ (5) Å[3] and contains 12 atoms with the following positions for the metal and chalcogen atoms ;
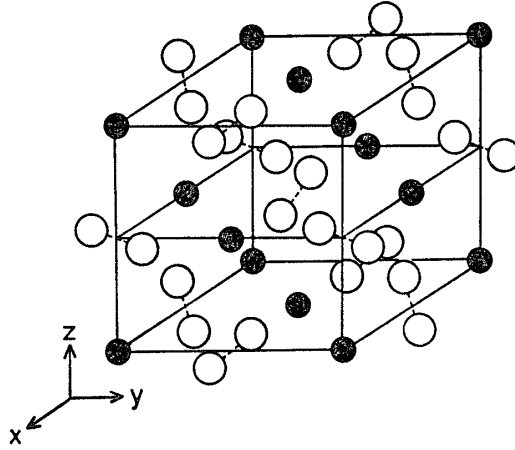

Fig. 1. Crystal structure and primitive unit cell of RuS_2. Ru atoms are represented by the full circles and S atoms are represented by the open circles.

metal atom : $0\ 0\ 0$; $0\ \frac{1}{2}\ \frac{1}{2}$; $\frac{1}{2}\ 0\ \frac{1}{2}$; $\frac{1}{2}\ \frac{1}{2}\ 0$,

chalcogen atom : $\begin{array}{c}+\\-\end{array}\left[u\ u\ u\ ; \frac{1}{2}+u,\ \frac{1}{2}-u,\ \bar{u}\ ; \ \bar{u},\ \frac{1}{2}+u,\ \frac{1}{2}-u;\ \frac{1}{2}-u,\ \bar{u}, \right.$

$\left. \frac{1}{2}+u, \right]$

where $u = 0.3879\,(14)$. The T_h factor-group operations and group theoretical procedures yield the following irreducible representation at the $\varGamma$ point in the simple cubic Brillouin zone :

$$\varGamma = A_g + E_g\,(2) + 3\,T_g\,(3) + 2\,A_u + 2\,E_u\,(2) + 6\,T_u\,(3) \tag{1}$$

The pyrite structure has two different centers of inversion. One is located at the site of metal atom and the other is located at the midpoint between two neighbouring sulfur atoms. The presence of the inversion symmetry separates all the 36 modes at the center of the Brillouin zone into even- and odd-parity modes. The even-parity modes A_g, E_g (doubly degenerate) and T_u

(triply degenerate) are Raman active. The six odd-parity T_u modes with triple degeneracy are split up into one acoustic and five infrared-active modes. The A_u and E_u modes are inactive.

The Raman tensors for T_h point group have the forms :[3]

$$A_g \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix} \quad E_g \begin{pmatrix} b & 0 & 0 \\ 0 & c & 0 \\ 0 & 0 & -(b+c) \end{pmatrix} \quad E_g \sqrt{\frac{2}{3}} \begin{pmatrix} \frac{1}{2}b+c & 0 & 0 \\ & -\left(b+\frac{1}{2}c\right) & 0 \\ 0 & 0 & \frac{1}{2}(b-c) \end{pmatrix}$$

$$(2)$$

$$T_g \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{pmatrix} \quad T_g \begin{pmatrix} 0 & 0 & d \\ 0 & 0 & 0 \\ d & 0 & 0 \end{pmatrix} \quad T_g \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

From these tensors, we expect that the A_g and E_g modes will appear in the spectra measured with the condition that the polarization of the scattered light is parallel to that of the incident light. The T_g modes will be observed in the configuration of crossed polarizations.

EXPERIMENTS

Single crystals of RuS$_2$ have been synthesized by chemical transport reactions. First, the compounds were prepared from the elements (Ru 99.9 % and S 99.999%) by reaction at 1100 °C during 240 hours in a silica glass crucible closed under vacuum. Then, the chemical transport has been achieved with the mixture of ICl$_3$ and S$_2$Cl$_2$ as the transport agent. The amount of the agent was approximately 10 mgcm^{-3}. A reaction in the temperature gradient 1040−1020 °C during 700 hours has produced large single crystals with dimensions up to $4 \times 4 \times 4$ mm^3 The structural parameters of the crystals have been investigated by X-ray analysis and the results have confirmed their correct structure of the pyrite type.

Experiments of Raman scattering have been made at room temperature by use of a Raman spectrometer (NR-1000, Japan Spectroscopic Co., Ltd.). The polarized spectra have been measured using the 5145 Å line from an argon-ion laser as the excting source and have been examined on several surfaces of the sample which were highly polished with alumina polishing powder. The excitation power level was at approximately 350 mW. The instrumental resolution is about 7 cm^{-1}.
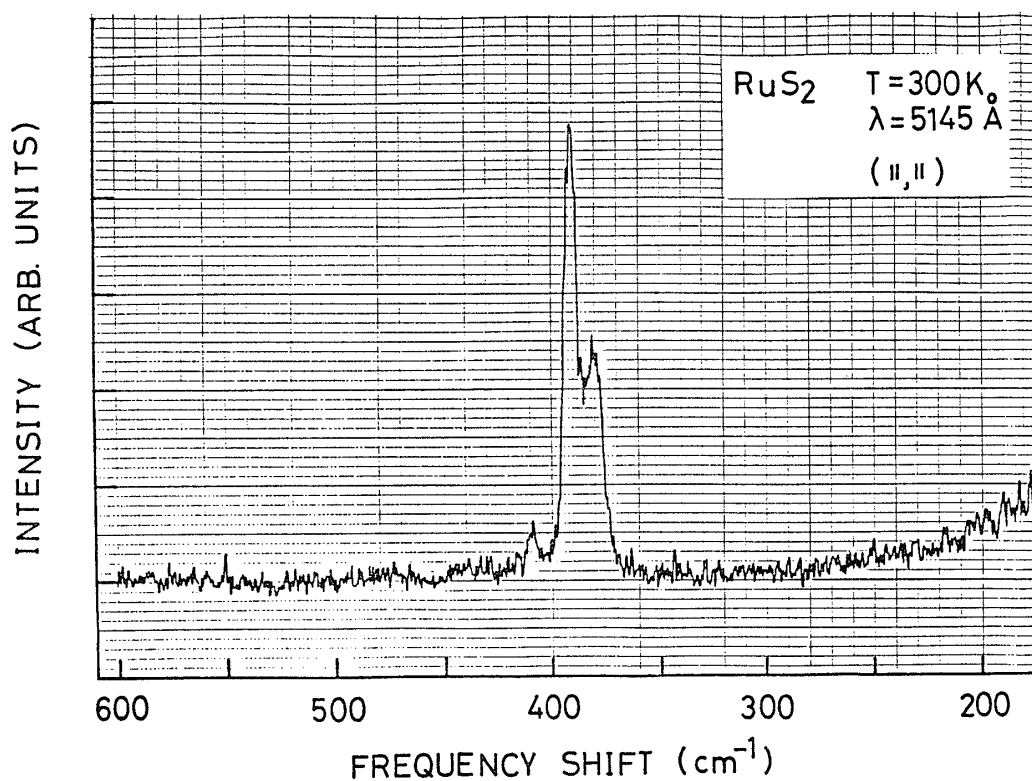
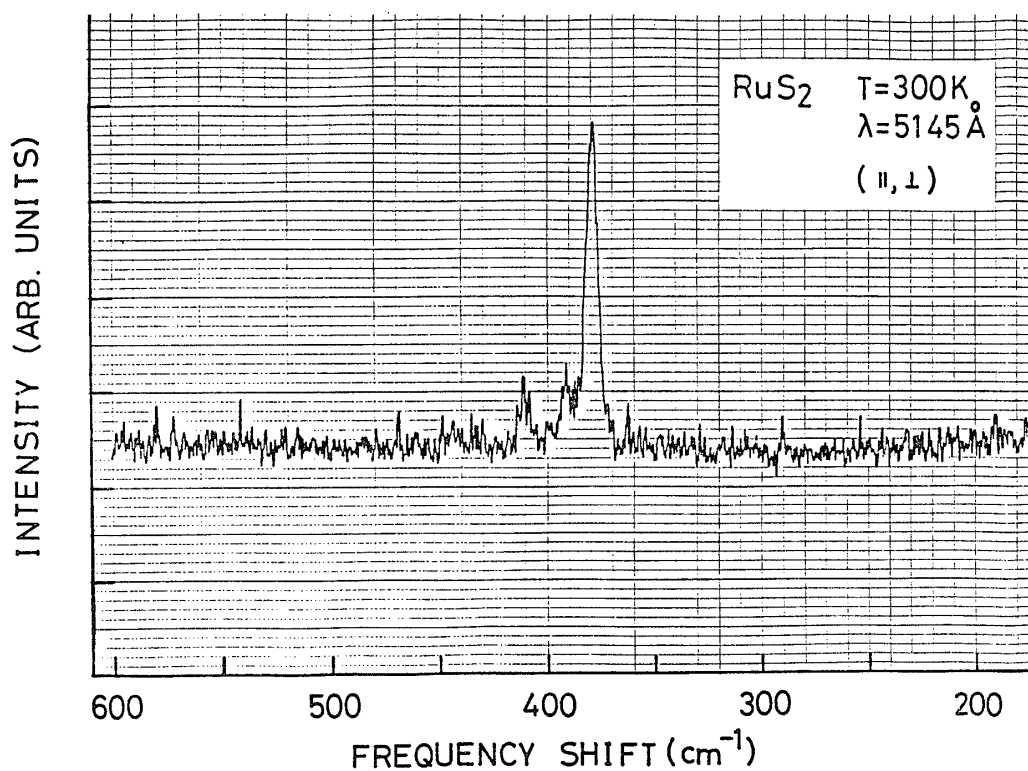Fig. 2. Raman spectrum of a RuS₂ single crystal at 300 K for (∥, ∥) polarization combination.

Fig. 3. Raman spectrum of a RuS₂ single crystal at 300 K for (∥, ⊥) polarization combination. The ordinate scale has been expanded by a factor of two compared with in Fig. 2. The spectra in Figs. 2 and 3 have been obtained on the same surface.

RESULTS AND DISCUSSION

Figure 2 shows the Raman spectrum obtained for parallel incident and scattered light polarizations ($\parallel$, $\parallel$). Figure 3 represents the spectrum for crossed incident and scattered polarizations ($\parallel$, $\perp$). Similar spectra have been observed from equivalent four surfaces The 391 cm^{-1} line which has the strongest intensity in the ($\parallel$, $\parallel$) configuration disappears within about 10 per cent in the crossed configuration. The other two peaks at 380 and 409 cm^{-1} appear in both, parallel and crossed configurations. The symmetry of the scattering tensors (2) for T_h symmetry predicts that we should observe the A_g and E_g modes in the ($\parallel$, $\parallel$) configuration and the T_g modes in the ($\parallel$, $\perp$) configuration. However, this does not agree with our observations and it follows that the examined surfaces of our experiments did not correspond to any of the (100), (010) or (001) surface.

In order to explain the observed spectra, we calculate the scattering intensity tensors for the (111) face. For a coordinate system with $X=[1\bar{1}0]$, $Y=[111]$ and $Z=[11\bar{2}]$, the scattering intensity tensors are found to have the following forms :

$$\alpha^2_{111}(A_g) = \begin{pmatrix} e & 0 & 0 \\ 0 & e & 0 \\ 0 & 0 & e \end{pmatrix}, \quad \alpha^2_{111}(E_g) = \begin{pmatrix} f & 7f & 4f \\ 7f & f & 4f \\ 4f & 4f & 4f \end{pmatrix}, \quad \alpha^2_{111}(T_g) = \begin{pmatrix} 17g & 2g & 5g \\ 2g & 11g & 5g \\ 5g & 5g & 8g \end{pmatrix} \quad (3)$$

where $e=a^2$, $f=(b^2+bc+c^2)/9$ and $g=d^2/9$. The equations show that, for the (111) face, the A_g mode should be observed only in the ($\parallel$, $\parallel$) configuration, whereas the E_g and T_g modes occur in both ($\parallel$, $\parallel$) and ($\parallel$, $\perp$) polarization configurations. The observed Raman spectra are in accord with the results of this calculation and, consequently, the measurements are found to have been done on the (111) surface or other equivalent surfaces. Thus, we assign the 391 cm^{-1} peak to A_g mode.

The other peaks at 380 and 409 cm^{-1} belong to the E_g or T_g mode. FeS₂ and RuS₂ are composed of transition-metals from the same column in the periodic table. The Raman spectra of FeS₂ were reported by Ushioda[8] and Macfarlane et al.[9] Comparing the spectra of FeS₂ with those of RuS₂, we notice similar changes of peak heights in ($\parallel$, $\parallel$) and ($\parallel$, $\perp$) polarization configurations. In the spectra of FeS₂, the A_g and E_g modes had much stronger intensity compared with that of the T_g mode which implies that the activity of the T_g mode is weak. Furthermore, the Raman frequencies of both compounds distribute in the same range as shown in Table I. Based on these similarities of the frequencies and intensities of the observed lines, we can relate the other strong peak at 380 cm^{-1} with E_g and the weak one at 409 cm^{-1} with T_g mode.

The two modes predicted to be Raman active by group theory have not

been observed. This appears to be quite possible since missing peaks were also reported in the spectra of FeS_2[8,9], $CoSe_2$[10], $CuSe_2$[10]. Two missing modes are considered to result from low scattering efficiency or from overdamping by free carriers which is likely to occur owing to relatively high conductivity of RuS_2[6,7].

The pyrite-type structure possesses two inversion centers, i. e. at the sites of metal atoms and at the midpoints between the sulfur atoms in the neighbouring pairs. In a vibrational mode with an even representation, displacements of atoms which are related through an inversion center are in opposite directions. Furthermore, atoms at sites of inversion symmetry have no displacements in an even-parity mode. Therefore, in Raman-active modes, the two sulfur atoms move in opposite directions with equal amplitudes, whereas the metal atoms remain at rest. On the other hand, in the infrared-active modes, pairs of sulfur atoms vibrate as rigid units in opposition to the motion of the metal atoms. Thus, it follows that the Raman frequencies are mainly determined by the strength of the sulfur-sulfur bonds and the infrared frequencies are largely determined by the strength of the metal-sulfur bonds.

Table I. Frequencies of Raman and infrared modes observed in RuS_2 and FeS_2.

Raman frequencies (cm^{-1})			IR frequencies (cm^{-1})		
Vibrational symmetry	FeS_2[a]	RuS_2[b]	Vibrational symmetry	FeS_2[c]	RuS_2[d]
E_g	351	380		293	242
A_g	385	391		348	336
T_g	441	409			366
T_g				402	391
T_g				415	402

a) Reference 8.
b) Present work.
c) Reference 11.
d) Reference 7.

The frequencies of Raman-active and infrared-active modes[7,11] observed in RuS_2 and FeS_2 are listed in table I. As has been already noted, the Raman frequencies of both compounds distribute in the same range of the frequency. This result is well explained by the above mentioned symmetry arguments about atomic displacements. On the other hand, the infrared frequencies in RuS_2 are lower than those in FeS_2 by a factor of 0.93 in average. This difference can be understood by an application of mass scaling to the vibrations of a simple linear-chain molecule (pair of sulfur atoms-metal-pair of sulfur atoms). In this model, Raman frequencies depend only upon the mass of sulfur atom, whereas infrared frequencies depend on

both masses of sulfur and metal atoms proportionally to $[M(2m)/\{M+2(2m)\}]^{1/2}$. The ratio is estimated to be 0.85 and is found to be approximately equal to the observed value. The agreement and the same frequencies of the Raman frequencies indicate that the metal-sulfur bonds as well as the sulfur-sulfur bonds in RuS₂ and FeS₂ are of comparable strength.

A valence force model for the transition-metal dichalcogenides with pyrite structure was proposed by Lutz et al.[12]. The valence force field consists of short and long range M-X, X_2-X_2 and M-M stretching constants and seven force constants were introduced. At the present time, the number of experimentally known parameters is not sufficient to discuss the lattice dynamics in that force model.

SUMMARY

Large single crystals of RuS₂ have been grown by chemical transport reactions with ICl_3 and S_2Cl_2 as transport agent. Using these crystals, we have performed the first Raman scattering measurements on RuS₂. The observed three peaks in the Raman spectra have been related with the A_g, E_g and T_g modes predicted by group theory. Two missing T_g modes have been attributed to low scattering efficiency and/or overdamping by free carriers due to relatively high conductivity of this material. The applications of mass scaling to the observed Raman and infrared data have given nearly the same strengths of force constants in RuS₂ and FeS₂. A comparison of the presented Raman data with a proposed force model will be made in future.

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