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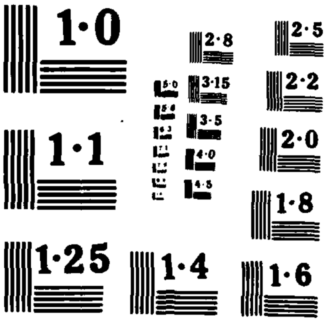
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A STUDY OF STRUCTURAL PHASE TRANSITIONS USING LIGHT SCATTERING TECHNIQUES

Final Technical Report

by

W. Taylor

April 1984

United States Army

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Raman and Brillouin light-scattering spectroscopy have been used to study a variety of materials including Ag_3AsS_3 (proustite), Ag_3SbS_3 (pyrargyrite), $NaKC_4H_4O_6.4H_2O$ (Rochelle salt), $CaC_4H_4O_6.4H_2O$ (calcium tartrate), $Li_2B_4O_7$ (Lithium diborate), $BaTiO_3$ (barium titanate), $Pb_5Ge_3O_{11}$ (lead germanate) $C_3N_3H_3$ (s-triazine) and $SrTiO_3$ (strontium titanate). Most of these materials undergo structural phase transitions of one kind or another and the spectroscopic date have been used to help identify and characterise these

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transitions where they exist. The presence of order-disorder phenomena is shown to be important in several instances but not necessarily directly involved in the phase-transition mechanism.

In a subsidiary study a molecular crystal dynamics computer simulation has been carried out, successfully modelling the anharmonic behaviour of the crystal naphthalene.

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Introduction

We have used the techniques of Raman and Brillouin spectroscopy to study a variety of materials whose common characteristic is that they undergo structural phase transitions. A considerable amount of information can be obtained from these studies. For example, in cases where detailed structural information is lacking the techniques can be used to help identify the changes in point group symmetry of the material on passing through the transition. In some cases soft mode and/or central-peak scattering is found which provides valuable information about the kind of phase-transition involved. Brillouin scattering experiments give independent values for the elastic constants which can be compared with ultrasonic measurements. Line-shape and line-strength anomalies can be used as indicators of disorder effects whether related or not to any phase transition.

1. Characterisation of structural phase transitions

The techniques of Raman scattering can assist significantly in the location, identification and characterisation of structural phase transitions. The principal material we have studied is proustite[1,2] (Ag_3AsS_3), which has some unusual and interesting properties and applications in infrared electro-optics and acousto-electronics. In particular we have been able to formulate definite conclusions about the symmetry changes at the two phase transitions despite the lack of suitable structural information normally supplied by X-ray and neutron diffraction. The superior performance of the computer-controlled triple-grating spectrometer and the ability to remove polarization leak-through effects by computer has enabled us to produce spectra of the soft mode in proustite which are free of noise and stray light despite the very low frequency and cross-section of the mode and which allow the reliable extraction of soft-mode parameters. However it was not possible to extract these parameters at temperatures close to T_c because the mode becomes overdamped and its frequency too low. In any case one-phonon fitting procedures are inappropriate very close to T_c as explained below (Section 4).

The superior performance of our spectrometer systems has also enabled us to examine and cast doubt on claims in the Russian literature for the existence of phase transitions at 210 K in Ag_3AsS_3 and at 9 K in Ag_3SbS_3 (pyrargyrite, an isomorph of proustite).[1,2,3] These claims are important because they affect the plausibility of the various proposed transition schemes. In both cases we find no real evidence in the Raman spectra for these transitions; in the case of proustite this allows a definite conclusion that the point-group sequence through the three phases is $3m \rightarrow 3 \rightarrow m$ (or $C_{3v} \rightarrow C_3 \rightarrow Cs$). Final confirmation of this scheme awaits improved X-ray or neutron diffraction structure determinations but these are expected to be performed soon by colleagues at this institution.

Also under this heading we include our work[4] (in collaboration with Dr. G.L. Paul of the University of New South Wales) on $Li_2B_4O_7$ (lithium diborate) a material which has some unusual properties and applications in the field of surface-acoustic waves. Stimulated by work at RSRE (Malvern) and Plessey we have recorded the Raman spectrum of this material over a wide temperature range since the existence of an elastic constant anomaly near room temperature pointed to the possibility of a phase transition. In the event none was found, but the exercise was still valuable as it led to the first observation and analysis of the zone-centre Raman-active modes in this material. We have also determined the elastic constants of the crystal by Brillouin spectroscopy and measured the dispersion of the refractive index in the visible region.

We have also carried out a very detailed study of the Raman spectrum and a full group theory analysis of the original ferroelectric, Rochelle Salt ($NaKC_4H_4O_6.4H_2O$). This material has received remarkably little attention from spectroscopists despite ease of growth. (The large number of atoms per cell and consequently rich phonon spectrum is possibly to blame.) We find remarkably little significant change in the spectra at either of the two phase transitions in this material. As in KH_2PO_4 the bands assigned to proton modes show little evidence of being affected by the transitions. We are preparing for publication[5] a report on this work together with an analysis of the spectra of the related crystal calcium tartrate ($CaC_4H_4O_6.4H_2O$) in collaboration with Dr. D.J. Lockwood of the National Research Council of Canada.

In a subsequent study of the Rayleigh-Brillouin spectrum of Rochelle salt by Fabry-Perot interferometry we have been able to confirm the existence of 'dynamic central-peak' scattering in the 2GHz region similar to that observed by other workers. This is consistent with the existence of dielectric relaxation in this frequency regime and supports the conjecture that the transitions in this material are order-disorder in nature.

2. Disorder effects

Disorder is of considerable interest both in relation to phase transitions and other areas (for example in the extreme cases of liquids and amorphous solids). The existence of silver-ion disorder in Ag_3AsS_3 has been suggested as being implicated in both phase transitions and this is important because it would have a direct bearing on the nature of the phase transitions for example as to their order-disorder or displacive character. We therefore have embarked on a close study[1,2,3] of the temperature dependence of the Raman spectra of both Ag_3AsS_3 and Ag_3SbS_3. These experiments have revealed, in both materials, the anomalous behaviour of the temperature dependence of linewidths of modes involving the silver ions. Analysis of these effects lead us to the conclusion that silver-ion disorder sets in and increases steadily above 50 K in both Ag_3AsS_3 and Ag_3SbS_3 and that there is no direct connection between this and the existence of phase transitions in Ag_3AsS_3. As before, improved neutron diffraction studies are needed to provide better information on the exact details of the Ag-disorder.

Another and well-known material in which disorder has been claimed to occur is $BaTiO_3$ in which first-order Raman modes are observed to persist well above the tetragonal to cubic 1st order transition though alternative theories involving impurity and other effects have been put forward. We have collaborated[6,7] with Dr. G. Burns of IBM Yorktown in a series of refractive index (n) measurements which have demonstrated that the deviations from linear behaviour of n vs. T observed in $BaTiO_3$ do not occur in either pure or doped lead germanate. This confirms that impurities are not the cause of nonlinear n(T) above T_c; the true cause of the deviations in $BaTiO_3$ probably originates in the displacive to order-disorder crossover which occurs on approaching T_c from above. These experiments also reveal remarkably high values for the quadratic electro-optic coefficents of lead germanate.

3. Molecular crystals

We have remeasured[8] the lattice mode region of the Raman spectrum of s-triazine ($C_3N_3H_3$) over a wide range of temperatures above and below the ferroelastic phase transition at 198 K using superior resolution and narrower temperature intervals than hitherto. A considerable amount of experimental and theoretical effort has been devoted to understanding this crystal and it is now known to undergo a proper ferro-elastic transition driven [illegible] a soft acoustic mode. Recent theories seek to provide a detailed description of the phase transition by taking account of coupling between corresponding optic and acoustic modes. This coupling manifests itself in the temperature dependence of the Raman spectrum and thus the theory can be tested by a careful measurement of the temperature dependence of the external modes. We find good agreement between theory and experiment, in particular the crossing-over of modes predicted in the model is confirmed. We have also completed an improved group theoretical correlation of the two phases using recent new information on the low temperature structure.

4. Soft mode parameters by Raman scattering

Since the first observation of ferroelectric soft modes by Raman scattering in BaTiO$_3$ and KH$_2$PO$_4$ using damped harmonic oscillator models, many workers have analysed soft mode spectra in terms of essentially single-phonon oscillators. However more careful measurements[9] revealed inescapable discrepancies particularly close to the transition temperature. It is now apparent[10] that the failure of these analyses is due to neglecting the significant contribution from two-phonon scattering processes close to T_c. This effect has been demonstrated most clearly in comparisons of neutron and Raman scattering cross-sections and we have collaborated[11,12] in making measurements on the soft mode spectra of Pb$_5$Ge$_3$O$_{11}$ and SrTiO$_3$ for this purpose. The importance of this work is considerable as it casts doubt on the validity of nearly all past attempts to analyse soft mode spectra.

5. Computer simulation of molecular crystal dynamics

A realistic molecular dynamics calculation for naphthalene has been carried out[13] and a comparison made between the simulation and the crystallographic data. The molecular dynamics sample consisted of 4096 molecules arranged in a volume with cyclic boundary conditions, each molecule being associated with one processing element of the ICL DAP computer. The potential functions used were the same as those used for lattice dynamics, and were developed from atom-atom 6-exp functions. A comparison with a lattice dynamical result establishes the correctness of the program. Temperature was introduced in the usual molecular dynamics way, resulting in a true modelling of anharmonic behaviour. The calculation proceeds at zero pressure throughout, yielding the temperature variation of the crystalline unit cell, the mean molecular orientation and the rigid-body thermal vibration tensors T and L. These were compared with the recently reported results measured by neutron scattering from powder samples and analysed through constained refinements. The variation of unit cell volume with temperature is particularly close to the experimental result, though discrepancies begin to be significant in measurements involving the orientational behaviour of the molecules.

This is the most extensive molecular dynamics calculation of its type yet undertaken, and comes at a very opportune time as there is a growing awareness of the value of large-scale computer simulations to the extent that computers are now being designed for this work which will be considerably more powerful than our dual-DAP facility. We hope to remain in the forefront of this work, a position that the present grant has helped us to achieve.

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Dear Dr. Lehnigk,

Ref : Contract No. DAJA37-82-C-0060

I am pleased to enclose copies of publications relating to the above contract. Our Final Technical Report on the Contract has been submitted under separate cover.

Yours sincerely,

W. Taylor

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THE LOW-TEMPERATURE RAMAN SPECTRA OF PYRARGYRITE (Ag_3SbS_3)

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The Raman spectrum of pyrargyrite (Ag_3SbS_3) has been recorded at temperatures in the range 4-293 K. For the pure material there is no evidence of any phase transition in this range, though changes in relative intensities may indicate the ordering of Ag atoms below ~80 K. In particular, no soft mode was observed. Several new bands have been revealed and the contribution of leak-through modes has been assessed. The influence of sample imperfections on the spectrum is also examined.

1. Introduction

Interest in pyrargyrite, Ag_3SbS_3, has been stimulated by its potential applications in non-linear optics. The possible existence of a structural phase transition in this material between 77 and 4.2 K was suggested by Dovgii et al.[1] on the basis of optical absorption measurements; subsequent NQR[2] and permittivity[3] investigations indicate the occurrence of a 2nd order transition at 9.7 K. Recent results[4] *on its piezoelectric properties have* been interpreted as evidence of a second transition at ~140 K. Pyrargyrite is isomorphous with proustite, Ag_3AsS_3, which exhibits transitions at 58 K (2nd order) and 29 K (1st order).

The room temperature phase of pyrargyrite has space group C^6_{3v} (trigonal 3m) and its first-order Raman spectrum should consist of $6A_1$ and 13E modes, the A_1 and E modes being selected by the X(ZZ)Y and X(ZX)Y scattering geometries respectively[5]. The spectrum at 65 K was reported by Byer et al.[5] who found it to agree with the group theoretical predictions and made mode assignments. Haller and Rebane[6] have since measured the spectrum at 12 and 5 K, that is just above and below the supposed 9.7 K transition temperature. Recent results for proustite[6,7,8] show a soft mode in the spectrum of the intermediate phase between the 29 and 58 K transitions. The aim of the present work was to determine whether a corresponding soft mode occurred in pyrargyrite and to make a detailed comparison of the spectra above and below the supposed transitions at 9.7 and 140 K.

2. Experimental

A sample of synthetic pyrargyrite obtained from the Royal Signals and Radar Establishment was oriented using X-ray diffraction photographs and cut (to dimensions ~ 6 × 5 × 3 mm), polished and mounted such that the c-axis of the crystal was vertical in the scattering plane. For the purpose of comparison a sample of naturally occurring pyrargyrite[9] from Peru was also examined. The directions of the crystallographic axes for this sample were deduced from the crystal habit and a cuboid of dimensions 6 × 6 × 7 mm was cut with the c-axis perpendicular to two opposite faces. Both samples were dark red and weakly transparent.

Cooling was achieved using a Thor S-500 continuous flow cryostat, the temperature of the crystal, which was in helium exchange gas, being monitored by a silicon diode mounted on the sample holder and a chromel-Au (+0.07 at % Fe) thermocouple attached to the crystal. The *sensors were calibrated at 4.2 K by immersion* in a flask of liquid helium. The sample temperature was controlled to within ±0.1 K using a Thor E3010 II controller.

The spectra were excited with ~65 mW or less of 676.4 nm radiation from a Kr-ion laser, the beam being passed through a prism filter to eliminate plasma emission lines. A microcomputer-controlled Coderg T800 triple spectrometer was used to record the spectra, which were obtained with a 90° scattering configuration. The slit width was 200 μm, yielding a resolution of ~1 cm^{-1}

3. Results and Discussion

The X(ZZ)Y and X(ZX)Y spectra of the synthetic sample were recorded at room temperature and at several temperatures between 180 and 4 K; the spectra at four of these temperatures (145, 77, 16 and 4 K) are shown in Figures 1 and 2. In the case of the A_1 modes (Figure 1) the results are in general agreement[10] with those reported by other workers[5,6]. The four spectra are essentially similar, the main difference between them being in the width and relative intensity of the bands, which sharpen considerably as the temperature decreases. Five intense bands together with several weaker features are apparent in the spectra of Figure 1. The frequencies of the A_1 modes at 4 K are listed in Table 1. On an expanded intensity scale numerous very weak bands at frequencies characteristic of the E modes are also observable in the spectra for temperatures below ~40 K. The frequencies of

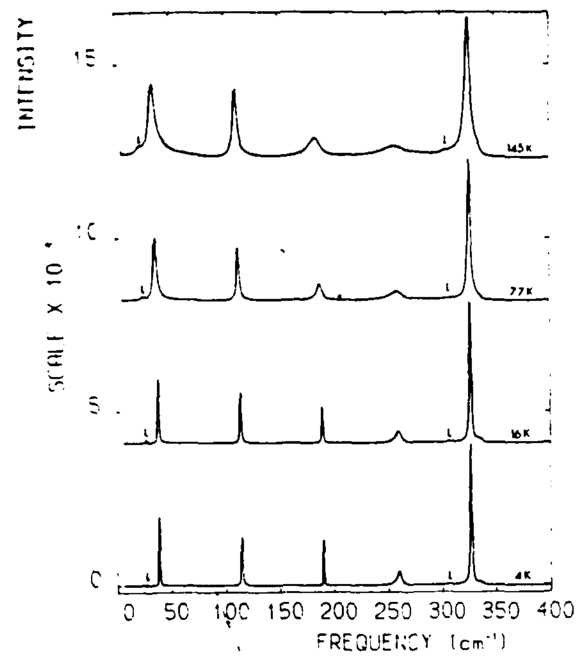

Figure 1. The X(ZZ)Y Raman spectrum of Ag_3SbS_3. Leakthrough modes indicated by 'L'.

the weak features visible in Figure 1 also correspond with bands in the E mode spectrum. The presence of E mode frequencies in the A_1 mode spectrum was also observed by Haller and Rebane who noted that a similar effect occurs in the spectra of proustite in the intermediate phase as a result of the structural change occurring at the 58 K transition. The results obtained in the present study show that these weak features do not appear abruptly at any one temperature but emerge gradually as the temperature decreases. In addition, the relative intensities of these weak bands — with the exception of a feature at 337 cm^{-1} — match those of the corresponding bands in the E mode spectrum. These facts suggest that the weak structure, apart from the 337 cm^{-1} band, is probably due to leak-through and does not arise from any phase transition. Byer et al. take the weak feature at 306 cm^{-1} to be one of the six bands predicted by group theory for the first order A_1 mode spectrum; our results, however, indicate that this peak is a leak-through mode and that the feature at 337 cm^{-1} is probably the sixth A_1 band. The intensity of the strongest leak-through E mode is ~2% of that of the strongest A_1 mode. The principal leak-through modes in Figure 1 are labelled 'L'.

The spectrum of the mineral sample was measured at room temperature and 145, 105, 77 and 5 K. As a result of the imperfections in this sample the leak-through component of the spectra was approximately a factor of 10 larger than in the case of the synthetic sample. However, when the A_1 spectra of the mineral sample were corrected for this by computer subtraction of the E spectra suitably scaled, they were found to be similar to those obtained for the synthetic sample.

Figure 2 shows the E spectra of the synthetic sample at 145, 77, 16 and 4 K. The frequencies of the E modes at 4 K are listed in Table 1. We attribute a number of bands in the E spectra to leak-through since their frequencies and relative intensities match those of bands in the A_1 spectrum. As is usual, the leak through is more pronounced in these, the off-diagonal spectra, than in the A_1 spectra: the intensity of the strongest leak-through A_1 mode is about 10% of that of the strongest E mode. The leak-through component has been computer subtracted from the 16 and 4 K spectra but to facilitate comparison with the data obtained by other workers it has been left in the 145 and 77 K spectra. The principal leak-through features in these spectra are labelled 'L' in the figure.

As was the case for the A_1 spectra, the four E spectra are essentially similar (allowing for the leak-through correction) and differ only with respect to the width and relative intensity of the bands, which sharpen considerably as the temperature decreases. The 77 K spectrum is in good agreement with that obtained at 65 K by Byer et al. As a result of the superior resolution achieved in the present study the bands in the 77 K spectrum are sharper than in the 65 K spectrum of Byer et al. and we have been able to resolve a weak feature at 273 cm^{-1}. The 16 and 4 K spectra, however, differ significantly from the 12 and 5 K spectra reported by Haller and Rebane. The frequencies of the bands in the 16 K spectrum are in reasonable agreement with those in the 12 K spectrum observed by Haller and Rebane but there are many differences in relative intensities between the two spectra. Furthermore, whereas the 16 and 4 K spectra of Figure 2 are virtually identical, the 12 and 5 K spectra of Haller and Rebane differ, although, again, only in terms of relative intensities.

The 16 and 4 K spectra exhibit several weak features that were not observed by Haller and Rebane. These features emerge gradually as the temperature decreases and are observable below ~ 30 K; they cannot be attributed to leak-through. Eighteen bands were observed in the 0-400 cm^{-1} region of the low-temperature, leak-through corrected E spectra. These bands can be grouped into 8 singlets and 5 doublets, making 13 modes in all in agreement with group theory. Our results suggest that the mode assignment carried out by Byer et al. should be modified to take into account the 273 cm^{-1} band which they do not resolve and also the fact that the 113 cm^{-1} band in their spectrum is probably a leak-through mode.

Whereas the A_1 spectra of the synthetic and mineral samples are similar at all temperatures this is not true for the E spectra. Figure 3 shows the E mode spectrum of the mineral sample at 145 and 5 K. Above ~140 K the E mode spectra of the two samples are identical after correction for leak-through, but as the temperature decreases below 140 K the relative intensities of the bands in the spectrum of the mineral sample gradually change so that the low temperature spectra of the mineral and synthetic samples differ markedly in terms of relative intensities. In particular, the 190 cm^{-1} band is considerably enhanced in the low temperature spectrum of the

Table 1. Frequencies in cm^{-1} of the Raman bands of synthetic pyrargyrite at 4 K, excluding leak-through modes. Curly brackets indicate doublet components. sh — shoulder; * — second order bands.

A_1 modes	E modes
	22
	28
39	
	40
	46
	65
	91
	102
115	
190	190
	221
	226
	256
260	
	270
	276
	307
	316
	320
326	
	332
	sh 335
sh 337	
529^*	
	643^*
670^*	

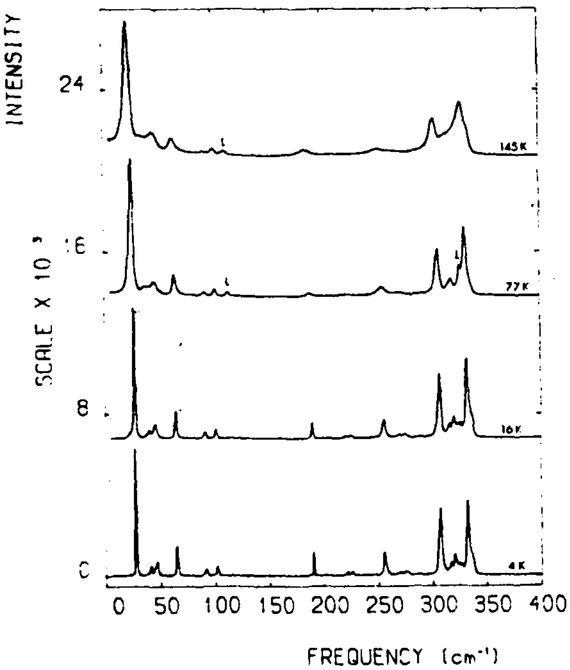

Figure 2. The X(ZX)Y Raman spectrum of Ag_3SbS_3. The 16 and 4 K spectra have been corrected for leak-through. Leak-through modes in the 145 and 77 K spectra are indicated by 'L'.

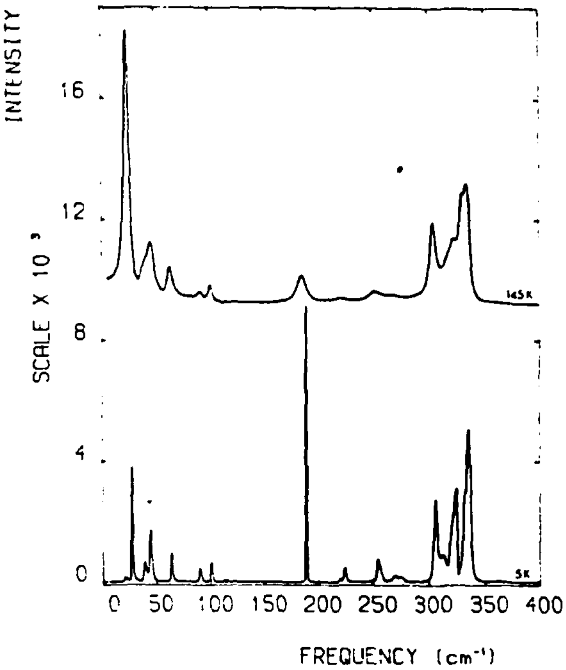

Figure 3. The X(ZX)Y Raman spectrum of a mineral sample of Ag_3SbS_3. Both spectra have been corrected for leak-through.

mineral sample, as comparison of the 4 and 5 K spectra in Figures 2 and 3 shows. Although the 5 K spectrum of the mineral sample is not identical with the 5 K spectrum obtained by Haller and Rebane it is similar and certainly bears a closer resemblance to their data than does the 4 K spectrum of the synthetic sample.

Haller and Rebane observe a band at 16 cm^{-1} in their 12 K results which they suggest corresponds to the soft mode in the intermediate phase of proustite. However, we observe no band near 16 cm^{-1} in any of the spectra of either the mineral or the synthetic sample nor do we find any band exhibiting the expected temperature dependence of a soft mode. The feature they observe is possibly the 15 cm^{-1} emission line associated with the 676.4 nm Kr laser line.

In addition to the bands shown in Figures 1 - 3 the A_1 and E spectra exhibit several weak peaks in the range 400-1000 cm^{-1}. At 90 K these occur at 529 and 670 cm^{-1} (A_1 spectrum) and at 643 cm^{-1} (E spectrum) and are presumably due to second order processes. The 670 cm^{-1} band probably corresponds to the weak feature at 738 cm^{-1} in the A_1 spectrum of proustite[7].

As far as phase transitions are concerned our results indicate that in the case of the synthetic sample either there are no transitions at 9.7 and 140 K or these transitions have no effect on the Raman spectrum; between 293 and 4 K there are no abrupt changes in the Raman spectrum, which is essentially the same at all temperatures. The difference between the E spectra of the synthetic and mineral samples at low temperatures implies that this spectrum is sensitive to the presence of imperfections in the material since the mineral sample is certainly of poorer quality than the synthetic one. This, together with the similarity between the 5 K E spectrum of the mineral and that reported by Haller and Rebane, suggests that the spectral change observed by these authors between 12 and 5 K is due to the presence of imperfections in their sample.

Although the spectra of the synthetic sample show no evidence of an abrupt structural transition as the temperature decreases from 293 to 4 K, gradual changes do occur in the relative intensities of certain bands even after correction for the Bose-Einstein factor. In particular, the 190 cm^{-1} peak in the A$_1$ spectrum sharpens and grows considerably as the temperature decreases. Figure 4 is a plot of the ratio between the as-measured intensity at 190 cm^{-1} and that at 326 cm^{-1} as a function of temperature: there is a significant upturn in the ratio at ~80 K. In the mineral sample a similar effect occurs and in addition the 190 cm^{-1} band in the E spectrum is considerably enhanced at low temperatures, as Figure 3 shows. According to the analysis carried out by Byer et al. the modes at 190 cm^{-1} in the A$_1$ and E spectra involve the stretching of S-Ag bonds and it is therefore possible that the marked sharpening of these bands is a result of ordering of the silver atoms with decreasing temperature, for which there is evidence from NQR measurements[11]. Recent neutron diffraction results[12] indicate the existence of a similar ordering in proustite below the 58 K transition.

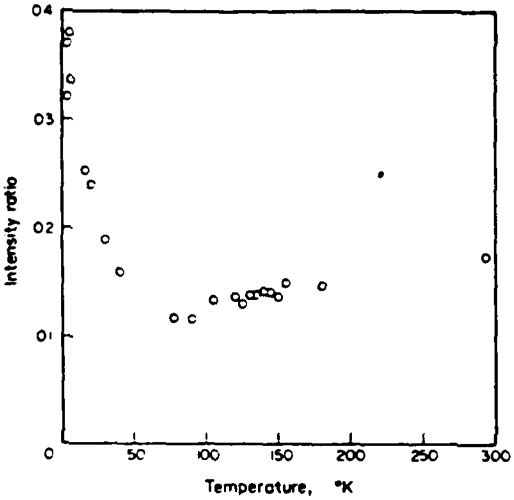

Figure 4. The ratio of the as-measured intensities of the 190 and 326 cm^{-1} bands of the A$_1$ spectrum of the synthetic sample plotted as a function of temperature.

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A RAMAN STUDY OF Ag_3AsS_3 (PROUSTITE)

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Abstract Anomalous behaviour of the linewidth and intensity of certain modes has been observed in the Raman spectrum of Ag_3AsS_3. The modes affected involve Ag-S stretching vibrations and it is suspected that the anomalies may be connected with the onset of silver ion conductivity.

INTRODUCTION

We have carried out an extensive study[1,2,3] of the Raman spectra of Ag_3AsS_3 and its isomorph Ag_3SbS_3 (pyrargyrite). This work confirms the existence of two structural phase transitions in proustite (at 29 K and 58 K) but provides no evidence for any other transitions in proustite or for any transitions at all in pyrargyrite. A very low frequency soft mode is observed in proustite[1,4] below and associated with the 58 K (2nd order) transition. The Raman results, taken together with all other data, indicate[3] that at this transition the room temperature trigonal structure (space group R3c) transforms to a trigonal and perhaps weakly ferroelectric phase (space group R3). The lower (29 K) transition is first-order and is accompanied by an abrupt change to a new monoclinic structure (space group Cc). In this phase proustite becomes ferroelectric with a reorientable polarization in the x-y plane[5]. Both transitions are accompanied by large dielectric anomalies in the x-y plane[5].

Proustite is known to exhibit appreciable ionic conductivity at room temperature due to silver-ion transport[6,7]. The electronic contribution to the conductivity is extremely small due to the relatively large energy gap of 2eV. Furthermore it has been assumed that one or both phase transitions could involve silver ion disorder[8]. Recent neutron results indicate steadily increasing anisotropy of the thermal vibration ellipsoid of the silver ions with increasing temperature[9] and also the onset of silver ion disorder around 80 K[10]. One might expect to see some evidence for these effects in the Raman spectra. For this reason we have carefully studied the temperature dependence of linewidths and intensities in the Raman spectra over a wide temperature range.

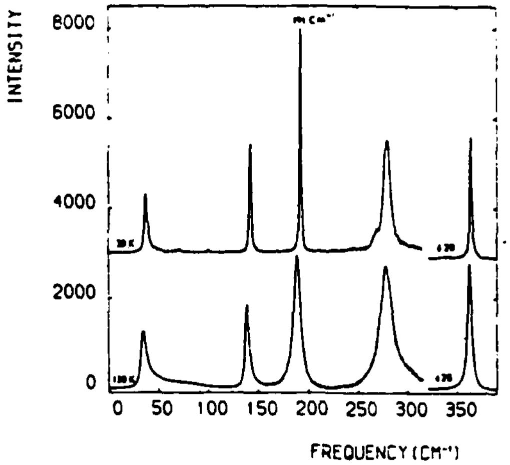

FIGURE 1   x(zz)y Raman spectra of proustite at two temperatures (corrected for thermal population factor and frequency dependence).

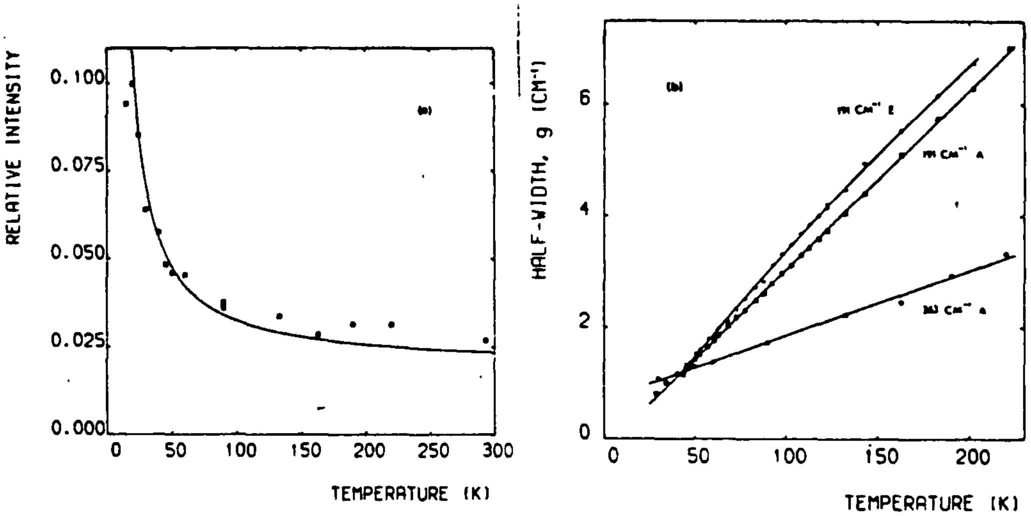

FIGURE 2   (a) Data points show ratio of peak intensities of the 191 cm^{-1} and 363 cm^{-1} A modes; solid line is predicted ratio using fitted Lorentzian linewidths. (b) Temperature dependence of halfwidths.

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RESULTS AND DISCUSSION

Our examination[2,3] of intensity changes in the spectra revealed that between 30 K and 130 K the peak intensity of the mode at 191 cm^{-1} in the A symmetry spectrum falls rapidly compared to other modes in the spectrum (Figure 1). In Figure 2a we have plotted the ratio between the 191 cm^{-1} mode and an A mode at 363 cm^{-1}; the data have been corrected for the temperature and frequency dependence of the scattering. The Figure clearly shows the anomalous behaviour of the 191 cm^{-1} mode. It was decided to record in greater detail the temperature dependence of the lineshape of several modes including the anomalous 191 cm^{-1} mode. The profiles of most of the lines were satisfactorily fitted by a standard Lorentzian function. In figure 2b we plot the Lorentzian damping constant (g = half-width at half maximum) for three lines: the 191 cm^{-1} A symmetry mode, its E symmetry counterpart at the same frequency and an A symmetry mode at 363 cm^{-1} which is representative of the rest of the modes in the spectrum. Here we see that g for all three modes increases as temperature(T) but that for the 191 cm^{-1} mode g vs. T has a much steeper slope.

It is interesting to compare Figures 2a and 2b. The peak intensity of a Lorentzian is inversely proportional to its width (measured by g) and thus the observed linear dependence of g on T should lead to a reciprocal dependence of the peak intensities. To test this we have inserted the observed g values in the Lorentz formula to obtain a prediction for the relative peak intensities. This predicted behaviour is plotted in Figure 2a as a solid line. We see that the fit to the experimental data points is fairly good below 100 K; the agreement above 100 K is less good possibly due to absorption effects caused by the shift of the absorption edge with temperature.

The 191 cm^{-1} mode corresponds to a stretching vibration of Ag-S bonds[3], so that the gradual onset of silver-ion disorder might be the cause of the observed sharp reduction in intensity and increased broadening. Although the fall in intensity occurs in the same region as the two phase transitions (29 K and 58 K), it does not show any discontinuities which one could directly correlate with them and in any case we have shown above that the rapid initial fall in intensity of the mode is consistent with the steady linear rise in g over the whole temperature range. Furthermore we have found that a similar and even more pronounced effect occurs in the isomorphous crystal pyrargyrite[2] in which (according to our Raman data and the X-ray and neutron data) no phase transitions are observed. Thus it appears that silver ion disorder, if it exists, is probably unrelated to the existence of the phase transitions in proustite.

In superionic crystals, such as AgI, sharp one-phonon Raman lines are drastically broadened with the approach of the superionic transition and disappear above it[11]. In proustite the conductivity is always too low to be considered superionic, but the increase in silver ion disorder and associated rise in silver ion conductivity with temperature might be expected to affect some Raman lines as in AgI and as in fact we report here.

The experimental and theoretical literature[12] on Raman linewidths shows that g generally varies approximately linearly with temperature over a wide range though with different slopes for different modes, eventually saturating at very low temperature. The anomaly we observe here, that the linewidths of certain modes increase at a faster rate than others, is consistent with the neutron diffraction result[9] that the thermal vibration ellipsoid for Ag-S vibrations shows a marked increase in anisotropy with increasing temperature. Oddly however the linewidths of these modes do not appear to saturate at low temperature, at least within the temperature range studied here.

Acknowledgement

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