

6.730

“Real” Semiconductor Project

GaAs

Part 1

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1. What is the crystal structure?

The crystal is a cubic sphalerite or zincblende structure, which consists of a face centered cubic lattice and a basis. The conventional basis consists of one GaAs molecule at the origin of the lattice. The basis is defined by a vector from one atom of the molecule at $(0,0,0)$ to the other atom at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. The crystal can also be viewed as two FCC lattices, one of Ga and the other of As, offset by the basis vector. [1] The crystal structure is shown below in Fig. 1. Gallium atoms are shown in black and arsenic atoms are shown in red. There are 14 gallium atoms shown, but only 4 arsenic atoms. However, given that 8 cells share each corner atom and 2 cells share each face atom, it is seen that there are actually 4 arsenic and 4 gallium atoms per cubic unit cell, i.e. 4 basis molecules per cell.

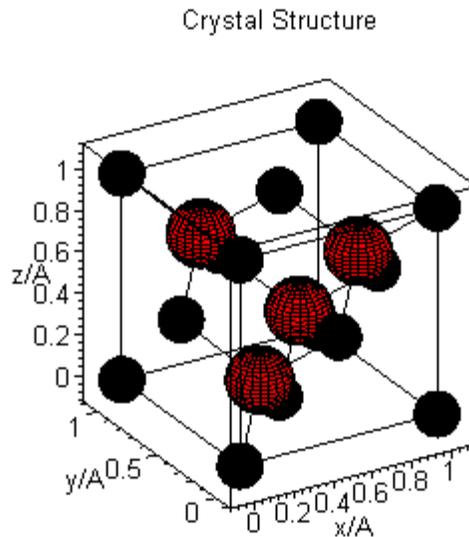


Figure 1. FCC cubic unit cell of GaAs

1. What is the lattice constant?

At $T=300$ K, the lattice constant, i.e. the length along any side of the cube, is $A=5.6325\text{\AA}$ [1].

2. What is the basis?

As stated earlier, the basis consists of one Ga atom and one As atom. The basis vector for GaAs is

$$\vec{b} = \frac{A}{4}(\hat{x} + \hat{y} + \hat{z}) \quad (1)$$

where \hat{x} , \hat{y} , \hat{z} are the cartesian unit vectors [2]. Fig. 2 shows the cubic unit cell again and a magnified view of the Ga-As basis.

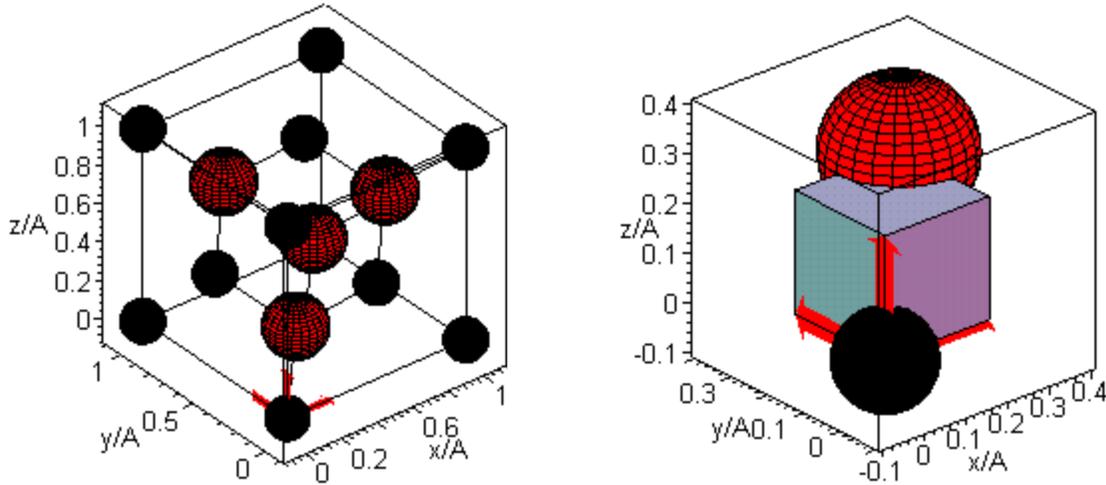


Figure 2. GaAs lattice with a magnified view of the basis

3. What are the primitive lattice vectors?

Since the lattice is face-centered cubic, the primitive lattice vectors are those of an fcc lattice. They are:

$$\vec{a}_1 = \frac{A}{2}(\hat{x} + \hat{y}) \quad (2)$$

$$\vec{a}_2 = \frac{A}{2}(\hat{y} + \hat{z}) \quad (3)$$

$$\vec{a}_3 = \frac{A}{2}(\hat{z} + \hat{x}) \quad (4)$$

The angle between any two primitive lattice vectors is 60° . \vec{a}_1 , \vec{a}_2 and \vec{a}_3 span a rhombohedron of volume $|\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)| = \frac{A^3}{4}$. Earlier, it was noted that there are 4 basis molecules per cubic unit cell. Since a primitive unit cell has only 1 basis molecule, its volume should be $\frac{1}{4}$ of the cubic unit cell, which is exactly what the calculation indicates. Fig. 3 shows the primitive lattice vectors for an fcc lattice [3].

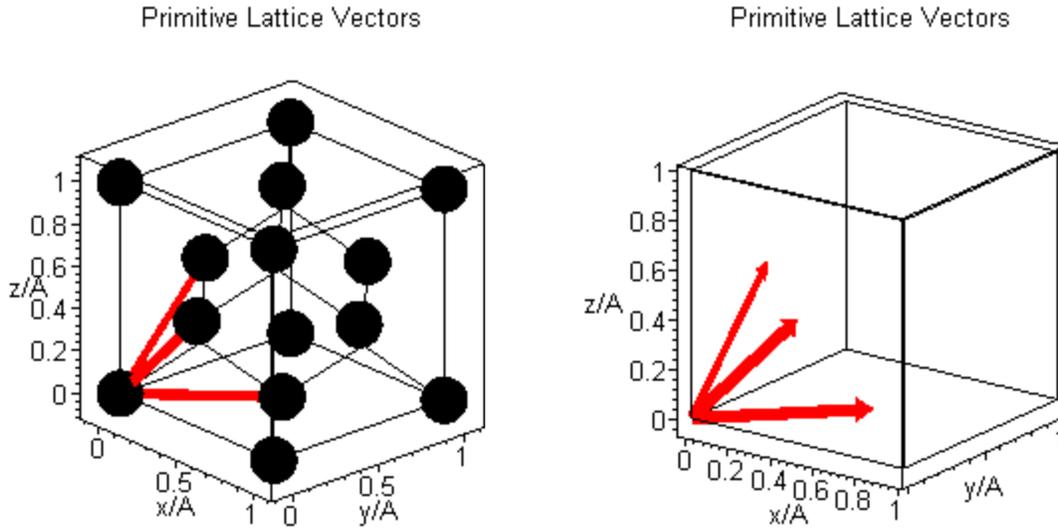


Figure 3. Primitive lattice vectors with and without lattice points

4. What is the structure of the reciprocal lattice?

6. What are the primitive reciprocal lattice vectors?

From the primitive lattice vectors defined above, the reciprocal lattice vectors are calculated as [2]

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \quad (5)$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_2 \cdot \vec{a}_3 \times \vec{a}_1} \quad (6)$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_3 \cdot \vec{a}_1 \times \vec{a}_2} \quad (7)$$

Performing the calculations indicated in Eq. (5), (6), and (7) with the values given in Eq. (2), (3), and (4) gives the following primitive reciprocal lattice vectors:

$$\vec{b}_1 = \frac{2\pi}{A} (\hat{x} + \hat{y} - \hat{z}) \quad (8)$$

$$\vec{b}_2 = \frac{2\pi}{A} (-\hat{x} + \hat{y} + \hat{z}) \quad (9)$$

$$\vec{b}_3 = \frac{2\pi}{A} (\hat{x} - \hat{y} + \hat{z}) \quad (10)$$

However, these are simply the primitive lattice vectors for a bcc lattice. Thus, it is apparent that the structure of the reciprocal lattice is body-centered cubic.

The structure of the primitive reciprocal lattice can also be described in terms of its Wigner-Seitz cell. The Wigner-Seitz cell is built in the following way. Consider all 8 vectors of the form $\frac{2\pi}{A}(\pm\hat{x} \pm \hat{y} \pm \hat{z})$. These are all reciprocal lattice vectors. Draw 8 planes normal to these 8 vectors at their midpoints. The smallest volume enclosed in this manner is an octahedron. The corners of the octahedron thus formed are also cut by the planes that are the perpendicular bisectors of 6 other reciprocal lattice vectors: $\frac{2\pi}{A}(\pm 2\hat{x})$; $\frac{2\pi}{A}(\pm 2\hat{y})$; $\frac{2\pi}{A}(\pm 2\hat{z})$ (these vectors are sums of vectors \vec{b}_i and \vec{b}_j from above). These planes form a cube, and therefore the Wigner-Seitz cell is a truncated octahedron in this cube. This Wigner-Seitz cell is usually referred to as the first Brillouin zone [3].

The surface of the truncated octahedron has 6 square faces (the intersections with the 6 faces of the cube), and 8 hexagonal faces. The article, Huisinga, M., "Ultraviolet photoelectron spectroscopy and electron stimulated desorption from CaF₂", FU Berlin Digitale Dissertation shows the first Brillouin zone, with important points of symmetry on it.

7. What are the atomic form factors for your material?

The atomic form factor is the amplitude of the wave scattered by an atom normalized by the amplitude of the wave scattered by one electron. The atomic form factor, f , is calculated as

$$f = \frac{2}{\xi} \int_0^{\infty} \rho(r) r \sin 2\pi r \xi \, dr \quad (11)$$

where ρ is the electron density and $\xi = \frac{2 \sin \theta}{\lambda}$ (θ is the angle of diffraction) [5]. It is

clear from Eq. (11) that $f = f\left(\frac{\sin \theta}{\lambda}\right)$. The atomic form factors for Ga and As for

different values of $\left(\frac{\sin \theta}{\lambda}\right)$ are given in Table 1 [6].

Table 1. Ga and As atomic form factors

$\frac{\sin \theta}{\lambda}$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2
Ga	31	27.8	23.3	19.3	16.5	14.5	12.7	11.2	10.0	8.9	7.9	7.3	6.7
As	33	29.7	25.0	20.8	17.7	15.6	13.8	12.1	10.8	9.7	8.7	7.9	7.3

The atomic form factors for Ga and As are approximately equal. The phenomenon can be explained by noting that in the molecule GaAs the “ions” Ga^- and As^+ have the same number Z of electrons.

1. Provide pictures of the crystal in the [100], [110], and [111] planes.

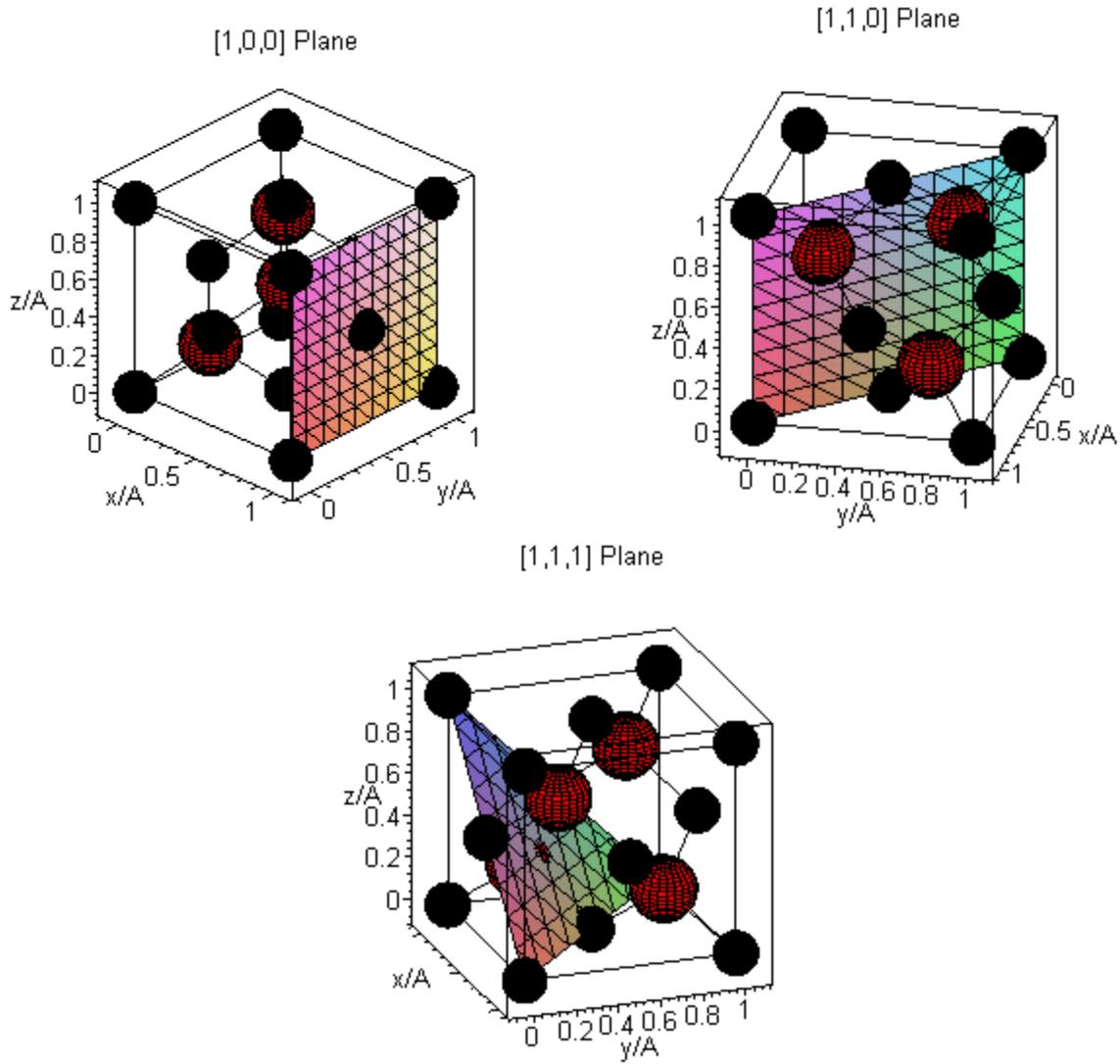


Figure 5. Crystal in the [100], [110], and [111] planes

1. Indicate the vertical positions of atoms with respect to the plane.

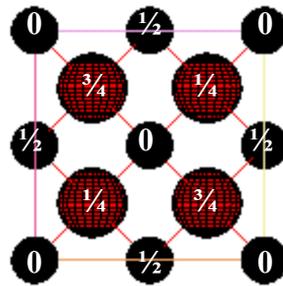


Figure 5. Vertical positions of atoms with respect to the bottom face of the cube [3]

1. Provide pictures of the reciprocal lattice in the [100], [110], and [111] planes.

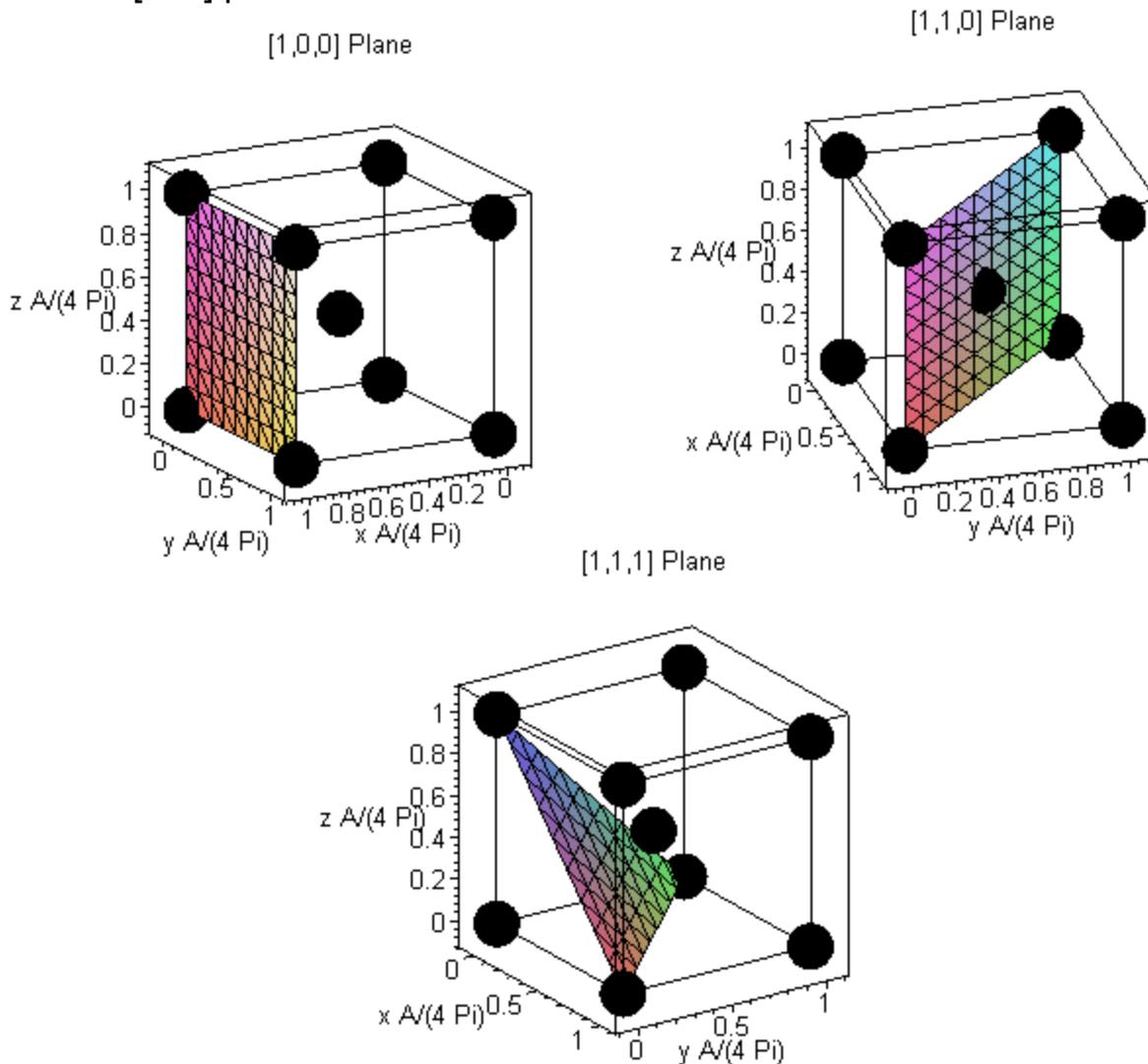


Figure 6. Reciprocal lattice in the [100], [110], and [111] planes

2. Calculate the structure factors.

The structure factor for a lattice of atoms is given as [6]

$$F_{hkl} = \sum_{n=1}^N f_n \exp(2\pi i(hu_n + kv_n + lw_n)) \quad (12)$$

where the summation is over the atoms in the unit cell; h, k, l are the Miller indices; and u, v, w are the fractional coordinates with respect to the cubic cell lattice vectors. Eq. (12) can be further simplified by separating out the basis and the lattice. For GaAs, this yields

$$F_{hkl} = \left[1 + \exp(i\pi(h+k)) + \exp(i\pi(h+l)) + \exp(i\pi(k+l)) \right] \left[f_{Ga} + f_{As} \left(1 + \exp\left(\frac{i\pi}{2}(h+k+l)\right) \right) \right] \quad (13)$$

The structure factor in Eq. (13) is separated into two terms. The first term is based only on the geometry of the lattice. It is observed that if $h, k,$ and l are mixed in terms of even and odd, this term will be identically zero; otherwise, it will be 4. The second term is based on the basis. The coefficient on the gallium form factor is either 1, $i,$ $-1,$ or $-i,$ depending on the sum of $h, k,$ and $l.$ Thus, the structure factor can take on the values: $4(f_{Ga} \pm f_{As}), 4(f_{Ga} \pm if_{As}),$ and 0. As mentioned earlier, the form factors will be angle dependent and thus vary for the different reciprocal lattice vectors. The structure factors for the reciprocal lattice vectors of interest are shown in Table 3 under Question 4.

3. Describe qualitatively an experimental set-up you could use to determine the crystal structure of your material by x-ray diffraction.

Summary of experimental method:

X-ray method:

Powder diffraction method

Operating wavelength:

1.5418Å from K_α emission of Cu source

Possible CMSE facilities:

RIGAKU 18kW Watt Rotating Anode X-ray Generator (Copper anode) Port #2

RIGAKU 12kW Watt Rotating Anode X-ray Generator (Copper anode) Port #1

Commonly used x-ray diffraction methods include the Laue method, the rotating-crystal method and the powder method. The Laue method was the first diffraction method ever used, and it satisfies the Bragg condition by continuously varying the wavelength of the incident beam during the experiment. The incident angle is fixed. On the other hand, the rotating-crystal and the powder methods use a monochromatic source but have the incident angle vary from 0° to 90° . Because of the different experimental setups, the Laue method usually serves to determine crystal orientation and assess crystal quality. The single crystal and the powder methods are generally used to determine unknown crystal structures.

Although the single crystal method is more powerful and sophisticated, it is also more complicated to use. A single scan with the crystal rotated only about one axis does not cover the Bragg angle from 0° to 90° for all possible planes, such as those perpendicular to the rotation axis. A more complete analysis would require successive rotation about other axes. It is therefore easier to use the powder diffraction method, which can also determine the structure of GaAs.

The powderized specimen of GaAs is placed in a holder, which rotates about an axis. The random orientation of the individual crystals in the specimen ensures the exposure of all possible planes during a single scan. The angle θ between the monochromatic incident beam and the lattice planes varies because of the random orientation of the planes. At particular instances, a set of lattice planes will make the correct Bragg angle with the incident beam to satisfy the diffraction condition

$$n\lambda = 2d_{h,k,l} \sin \theta \quad (14)$$

where n is equal to 1 for first order diffraction, and d is the spacing between the lattice planes with Miller indices $[hkl]$. The schematic of the diffractometer is shown in Fig. 7. It should be noted that while the crystal axis is rotated by θ , the detector arm is moved by 2θ .

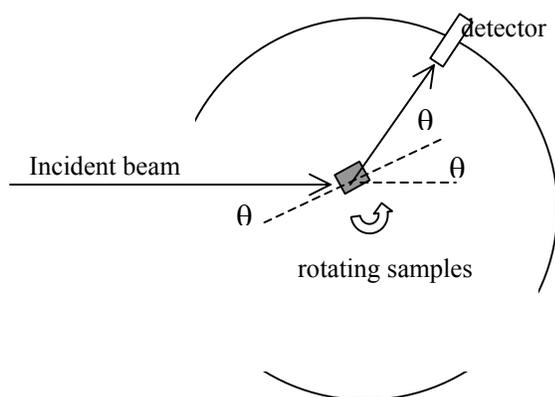


Figure 7: Experimental setup of the powder method. Angle θ varies from 0° to 90° . [7]

3. Specify what wavelength(s) of x-ray is (are) necessary in your set-up.

The wavelength of the incident beam λ should satisfy the condition

$$\lambda < 2d_{h,k,l} \quad (15)$$

This follows naturally from the Bragg condition in Eq. (14) since $\sin\theta$ is always less than 1. Here, the lattice spacing d will range from 1 to 6\AA , which means λ should not exceed 2\AA . Some commonly used x-ray sources and the corresponding wavelengths are listed in Table 2 [6].

Table 2. Commonly used x-ray K wavelengths

Sources	Wavelength [\AA]		
	$K_{\alpha 1}$	$K_{\alpha 2}$	K_{α} (weighed average)
Cr	2.28970	2.293606	2.29100
Fe	1.936042	1.939980	1.937355
Co	1.788965	1.792850	1.790260
Cu	1.540562	1.544390	1.541838
Mo	0.709300	0.713590	0.710730

Copper is a suitable choice for this experiment because its K_{α} characteristic wavelength at 1.5418\AA satisfies the requirements. In addition, it is the most commonly used. JCPDS files for a copper source are readily available, and the diffractometers in the CMSE are all fitted with a copper anode.

3. What centrally shared facilities in the Center for Materials Science and Engineering would be good for your material .

Since it is assumed that the GaAs is in bulk form, it is not necessary to have a diffractometer that can perform glancing angle/small angle analysis. The RIGAKU 18kW Watt unit (Port #2) or the RIGAKU 12kW Watt unit (Port #1) fitted with a copper anode would be a good choice.

4. Calculate the ratio of the intensities expected for the following lines of the diffraction pattern with respect to the [111] line: [100], [200], [220], [311] and [400].

The relative intensity of the diffraction lines are determined by three major factors:

- (1) the structure factor F described earlier
- (2) the Lorentz factor, which arises due to the fact that the intensity of diffraction is still appreciable at angles slightly different from the Bragg angle
- (3) the multiplicity factor p , which accounts for the fact that planes with different orientation can give rise to the same reflection if they have equal spacing. For instance, in a cubic structure, both [010] and [001] will contribute to the [100] reflection.

The intensity relation is given in Eq. (16) [6].

$$I = |F|^2 p \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \quad (16)$$

where I is the integrated intensity, F is the structure factor, p is the multiplicity factor, and θ is the Bragg angle. The ratio in parenthesis is the Lorentz factor. It should be noted that two other factors, the temperature and absorption factors, that affect the intensity are not included in Eq. (16). Their effects have opposite dependence on θ and thus, to a first approximation, cancel each other. Table 3 shows the calculated GaAs intensities for the different lines.

Table 3. Calculated intensities for different lines of diffraction for GaAs

Line	Distance [Å]	θ	$\frac{\sin \theta}{\lambda}$	f_{Ga}	f_{As}	$ F ^2$	p	Lorentz factor	Normalized Intensity
[111]	3.264	13.7°	0.1532	25.41	27.20	22165	8	33.01	100
[100]	5.653	7.84°	0.0884	28.17	30.08	0	6	104.6	0
[200]	2.827	15.8°	0.1769	24.34	26.09	48.788	6	24.10	0.121
[220]	1.999	22.7°	0.2502	21.29	22.89	31240	12	10.88	69.7
[311]	1.704	26.9°	0.2933	19.57	21.08	13235	24	7.396	40.1
[400]	1.413	33.1°	0.3538	17.79	19.13	21818	6	4.668	10.4

For each line, the distance between planes is computed. From this distance, $\frac{\sin \theta}{\lambda}$ is then computed. Using the value of $\lambda=1.5418\text{Å}$, θ and the Lorentz factor are calculated. The structure factor F is computed as described earlier. The form factors f_{Ga} and f_{As} are obtained from Appendix 12 [6]. The actual numbers used here are obtained through a linear interpolation between values in the appendix table. The multiplicity factor p is given in Appendix 13 [6]. In the literature, the line intensities for GaAs are normalized with respect to the [111] line as it is in Table 3.

5. What are the ratios if the material were Si? How could you use this information to distinguish Si from your material by x-ray diffraction?

Table 4 shows the experimental line intensities for silicon [8] as well as the previously calculated intensities for gallium arsenide. It is clear that the experimental line intensities for Si and GaAs are not drastically different. The relative ordering of the line intensities is the same and the relative magnitudes are somewhat similar as well.

Table 4. Comparison of experimental Si and calculated GaAs intensities

Line	Experimental Intensity	Calculated Intensity
	Si	GaAs
[111]	100	100
[100]	–	0
[200]	–	0.121
[220]	60	69.7
[311]	35	40.1
[400]	8	10.4

The difference between the two becomes even smaller when the experimental data for GaAs (taken from [9]) is used, as shown in Table 5.

Table 5. Comparison of experimental Si and experimental GaAs intensities

Line	Experimental Intensity	Experimental Intensity
	Si	GaAs
[111]	100	100
[100]	–	–
[200]	–	–
[220]	60	61
[311]	35	29
[400]	8	7

Thus, using the line intensities to distinguish Si from GaAs would require that the x-ray diffractometry be done quite carefully with little experimental error. However, this level of precision may be obtained in a laboratory, and thus the two crystals could be distinguished by comparing line intensities. The line intensity depends quite strongly on the geometry of the crystal lattice. Like GaAs, Si also has an fcc lattice with a lattice constant of 5.4309Å, compared to 5.6325Å for GaAs. This similarity helps to explain why the two crystals have such similar line intensities.

6. Compare your calculations of the x-ray ratios with experimental data for your material. Comment on the comparison.

Table 6 shows the comparison between experimental and calculated line intensities.

Table 6. Comparison of experimental and calculated GaAs intensities

Line	θ	Experimental Intensity GaAs	Calculated Intensity GaAs	Percent Error
[111]	13.7°	100	100	—
[100]	7.84°	—	0	—
[200]	15.8°	—	0.121	—
[220]	22.7°	60	69.7	14.2%
[311]	26.9°	35	40.1	38.4%
[400]	33.1°	8	10.4	49.1%

The agreement between the two is not particularly good, but this is to be expected. As mentioned earlier, the temperature and absorption factors have been neglected. These factors become increasingly important as the Bragg angle increases. Therefore, the error in this first order calculation should increase with θ , which is what is observed here. There are many other factors that have not been taken into account. In addition, there is some variation in the published experimental data. With this in mind, one can see that the agreement between calculated and experiment line intensities is acceptable.

References

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