

The numbers in square brackets in the right-hand margin indicate the provisional allocation of maximum marks per sub-section of a question. Unseen parts are printed in red.

[Part marks]

1. (a) A *lattice* is a mathematical construction, an infinite array of points in space for which the environment of any point is identical with the environment of any other point. A *basis* is an arrangement of atoms or ions that are associated with each lattice point to make a crystal. A *unit cell* is a region that can be repeated by translation to reproduce the whole structure. The conventional cubic unit cell for the face-centred cubic lattice contains 4 lattice points. [4]

- (b) The primitive translation vectors of the face-centred cubic lattice are those joining a lattice point at the origin to three of its nearest neighbours, and so they may be chosen as $\mathbf{a} = a\left(\frac{1}{2}, \frac{1}{2}, 0\right)$, $\mathbf{b} = a\left(\frac{1}{2}, 0, \frac{1}{2}\right)$, $\mathbf{c} = a\left(0, \frac{1}{2}, \frac{1}{2}\right)$. Now we can use the definitions of the reciprocal lattice vectors, as follows:

$$\begin{aligned}
 \mathbf{A} &= 2\pi \frac{\mathbf{b} \times \mathbf{c}}{|\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}|} \\
 &= \frac{2\pi}{a} \frac{\left(\frac{1}{2}, 0, \frac{1}{2}\right) \times \left(0, \frac{1}{2}, \frac{1}{2}\right)}{\left|\left(\frac{1}{2}, \frac{1}{2}, 0\right) \cdot \left(\frac{1}{2}, 0, \frac{1}{2}\right) \times \left(0, \frac{1}{2}, \frac{1}{2}\right)\right|} \\
 &= \frac{2\pi}{a} \frac{\left(-\frac{1}{4}, -\frac{1}{4}, \frac{1}{4}\right)}{\left|\left(\frac{1}{2}, \frac{1}{2}, 0\right) \cdot \left(-\frac{1}{4}, -\frac{1}{4}, \frac{1}{4}\right)\right|} \\
 &= \frac{2\pi}{a} \frac{\left(-\frac{1}{4}, -\frac{1}{4}, \frac{1}{4}\right)}{\left|-\frac{1}{4}\right|} \\
 &= \frac{2\pi}{a} (-1, -1, 1) \\
 \mathbf{B} &= 2\pi \frac{\mathbf{c} \times \mathbf{a}}{|\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}|} \\
 &= \frac{2\pi}{a} \frac{\left(0, \frac{1}{2}, \frac{1}{2}\right) \times \left(\frac{1}{2}, \frac{1}{2}, 0\right)}{\left|\left(\frac{1}{2}, \frac{1}{2}, 0\right) \cdot \left(\frac{1}{2}, 0, \frac{1}{2}\right) \times \left(0, \frac{1}{2}, \frac{1}{2}\right)\right|} \\
 &= \frac{8\pi}{a} \left(-\frac{1}{4}, \frac{1}{4}, -\frac{1}{4}\right) \\
 &= \frac{2\pi}{a} (-1, 1, -1) \\
 \mathbf{C} &= 2\pi \frac{\mathbf{a} \times \mathbf{b}}{|\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}|}
 \end{aligned}$$

$$\begin{aligned}
&= \frac{2\pi}{a} \frac{\left(\frac{1}{2}, \frac{1}{2}, 0\right) \times \left(\frac{1}{2}, 0, \frac{1}{2}\right)}{\left|\left(\frac{1}{2}, \frac{1}{2}, 0\right) \cdot \left(\frac{1}{2}, 0, \frac{1}{2}\right) \times \left(0, \frac{1}{2}, \frac{1}{2}\right)\right|} \\
&= \frac{8\pi}{a} \left(\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4}\right) \\
&= \frac{2\pi}{a} (1, -1, -1),
\end{aligned}$$

though other choices of sign are possible. Allow 1 mark for correct selection of real space lattice vectors, 1 for correct definition of reciprocal lattice vectors. [5]

- (c) *Missing orders* describe cases in which a simple application of Bragg's law to the conventional unit cell predicts a diffracted beam, but interference between atoms of the basis or, for nonprimitive unit cells, between the bases at different lattice points, reduces the intensity to zero. [1]

If a cubic crystal with cubic cell side $a = 0.42$ nm is illuminated with x-rays of wavelength $\lambda = 0.154$ nm, the exit angles away from the incident beam will be 2θ , where θ is given by Bragg's law

$$2d \sin(\theta) = n\lambda,$$

or

$$\sin(\theta) = \frac{\lambda \sqrt{h^2 + k^2 + l^2}}{2a},$$

and five lowest-order diffracted beams will have (h, k, l) equal to $(1, 0, 0)$, $(1, 1, 0)$, $(1, 1, 1)$, $(2, 0, 0)$ and $(2, 1, 0)$. The corresponding angles 2θ are 21.28 degrees, 30.05 degrees, 37.03 degrees, 43.02 degrees and 48.40 degrees. Allow 1 mark for quoting Bragg's law, 1 for $\sqrt{h^2 + k^2 + l^2}$, 1.5 for the angles, 0.5 for converting to the double angle. [4]

If the crystal has a face-centred cubic structure the observed reflections have h , k and l all even or all odd, and so only the (111) and (200) reflections will be observed. [1]

- (d) If RbF forms face-centred cubic crystals, with a basis of Rb^+ at $(0, 0, 0)$ and F^- at $(\frac{1}{2}, 0, 0)$ then each ion has six nearest neighbours, arranged along the positive and negative x , y and z axes. [1]

If the energy per ion pair is

$$U(r) = A \exp(-r/\rho) - \frac{\alpha q^2}{4\pi\epsilon_0 r},$$

where r is the nearest-neighbour separation, q is the charge on an ion, and $\alpha = 1.748$, then the positive term represents short-range repulsion between the closed-shell ions, arising from the Pauli exclusion principle, and the negative term represents the long-range Coulomb attraction between like charges. [1]

The equilibrium separation is given by $\partial U/\partial r = 0$, so

$$\frac{A}{\rho} \exp(-r/\rho) = \frac{\alpha q^2}{4\pi\epsilon_0 r^2},$$

and if $\rho = 0.03$ nm and the nearest-neighbour separation is $r_0 = 0.282$ nm this gives

$$\begin{aligned} A &= \frac{\alpha q^2}{4\pi\epsilon_0 r_0^2} \rho \exp(r_0/\rho) \\ &= \frac{1.748 (1.602 \times 10^{-19})^2}{4\pi \times 8.854 \times 10^{-12} (0.282 \times 10^{-9})^2} 0.03 \times 10^{-9} \exp(0.282/0.03) \\ &= 1.84 \times 10^{-15} \text{ J} \end{aligned}$$

the units should be given, but no marks deducted if not. Allow 1 mark for $dU/dr = 0$. Note that if, in error, the condition is taken as $U=0$ one finds $A = 1.73 \times 10^{-14}$ J, for which allow 1 mark.

[3]

2. (a) Either the periodic or fixed boundary condition model is acceptable. For periodic boundaries, consider a crystal in the form of a cube of side L : in each direction assume running waves of the form

$$\phi(x, t) = Ae^{i(kx - \omega t)},$$

and require

$$\phi(x + L, t) = \phi(x, t)$$

so that

$$e^{ikL} = 1$$

or

$$k = n \frac{2\pi}{L}$$

giving a density of states in each dimension of

$$g(k) = \frac{L}{2\pi}$$

or an overall density of states in k -space of

$$g(\mathbf{k}) = \left(\frac{L}{2\pi}\right)^3.$$

Now the number of states with $k = |\mathbf{k}|$ between k and $k + dk$ is the density of states multiplied by the volume of a shell of thickness dk in k -space, so that

$$g(k)dk = 4\pi k^2 g(\mathbf{k})dk = 4\pi \left(\frac{L}{2\pi}\right)^3 k^2 dk.$$

But the number of states with frequency between ω and $\omega + d\omega$ is the same, for the isotropic solid, as the number in the shell between $k(\omega)$ and $k(\omega) + (dk(\omega)/d\omega)d\omega$, so that

$$g(\omega)d\omega = 4\pi \left(\frac{L}{2\pi}\right)^3 k^2 \frac{dk(\omega)}{d\omega} d\omega,$$

and, writing $L^3 = V$, we have

$$g(\omega) = \frac{V}{2\pi^2} k^2 \frac{dk}{d\omega}.$$

For full marks, require evidence of 1-D density of states, idea of spherical symmetry, and relation between k -space and ω -space density of states.

- (b) The Debye model assumes that the allowed vibrations of a solid may be represented by non-interacting nondispersive elastic waves, with velocity independent of direction, occupied according to the Bose-Einstein distribution. The Debye frequency ω_D represents a correction to the theory, compensating for the incorrect assumption about dispersion by cutting off the frequency spectrum in such a way as to include the correct total number of degrees of freedom (or, equivalently, to obtain the correct specific heat in the high temperature limit). No marks for stating that it is a cut-off frequency, or the highest frequency that can occur in the lattice, or similar.

[5]

[3]

[2]

(c) If the thermal energy of a three-dimensional crystal is written as

$$U(T) = A \int_0^{\omega_D} \frac{\omega^3}{\exp(\hbar\omega/k_B T) - 1} d\omega,$$

where A is independent of temperature, then we may obtain the specific heat by differentiation:

$$C(T) = \frac{\partial U}{\partial T} = A \int_0^{\omega_D} \frac{\omega^3 \frac{\hbar\omega}{k_B T^2} \exp(\hbar\omega/k_B T)}{[\exp(\hbar\omega/k_B T) - 1]^2} d\omega.$$

Now it is convenient to convert the integral to dimensionless form by writing

$$x = \frac{\hbar\omega}{k_B T},$$

so that

$$\omega = \frac{k_B T x}{\hbar}$$

giving

$$\begin{aligned} C(T) &= A \int_0^{x_D} \frac{\left(\frac{k_B T x}{\hbar}\right)^3 \frac{x}{T} \exp(x) k_B T}{[\exp(x) - 1]^2 \hbar} dx \\ &= A \left(\frac{k_B}{\hbar}\right)^4 T^3 \int_0^{x_D} \frac{x^4 \exp(x)}{[\exp(x) - 1]^2} dx, \end{aligned}$$

where

$$x_D = \frac{\hbar\omega_D}{k_B T}. \quad [2]$$

At low temperatures, x_D may be taken to be infinite and the integral over x becomes a constant, so $C(T) \propto T^3$. [1]

At high temperatures x is small, so we expand

$$\frac{x^4 \exp(x)}{[\exp(x) - 1]^2} \approx \frac{x^4(1 + x \dots)}{[1 + x + \dots - 1]^2} \approx x^2,$$

and then

$$\begin{aligned} C(T) &= A \left(\frac{k_B}{\hbar}\right)^4 T^3 \int_0^{x_D} x^2 dx \\ &= A \left(\frac{k_B}{\hbar}\right)^4 T^3 \frac{x_D^3}{3} \\ &= A \left(\frac{k_B}{\hbar}\right)^4 T^3 \frac{1}{3} \left(\frac{\hbar\omega_D}{k_B T}\right)^3 \\ &= A \frac{k_B \omega_D^3}{3\hbar}, \end{aligned}$$

which is independent of temperature. Allow 1 mark each if the T^3 and T^0 dependencies are quoted, not derived. [2]

(d) We know that the thermal conductivities of insulators are given by [2]

$$\kappa = \frac{1}{3}Cv\Lambda,$$

where C is the specific heat, v the sound velocity, and Λ the phonon mean free path. We may take v to be independent of temperature. The specific heat does not depend on the sample size, so all we need to consider is the mean free path. (i) at 4 K we expect boundary scattering to dominate: thus we expect [2]

$$\frac{\kappa_{\text{single crystal}}}{\kappa_{\text{polycrystal}}} \approx \frac{10^{-3}}{10^{-6}} = 1000.$$

(ii) at 1000 K phonon-phonon scattering dominates, which is size-independent, so we expect [1]

$$\frac{\kappa_{\text{single crystal}}}{\kappa_{\text{polycrystal}}} = 1.$$

3. (a) A degenerate Fermi gas is one in which, for the majority of occupied states, the occupation probability is close to unity. Alternatively, one may express this as the fact that the chemical potential is large compared with $k_B T$. [2]

When two metals are brought into contact, electrons flow from one to the other in order to equalise the chemical potentials. The flow of charge sets up a potential difference – the *contact potential*. [1]

Thermal emission is the escape of electrons with high enough energies over the confining potential barrier at the surface of the metal. [1]

In *field emission* the application of a strong electron field distorts the potential outside the metal to form a narrow barrier through which electrons can tunnel. [1]

- (b) If the density of states in a free electron gas is written as

$$g(E) = B\sqrt{E},$$

then the Fermi energy is defined by

$$N = \int_0^{E_F} g(E) dE,$$

where N is the total number of electrons in the sample, so that

$$N = B \left[\frac{2}{3} E^{3/2} \right]_0^{E_F} = \frac{2}{3} B E_F^{3/2}.$$

Hence we know B , and [2]

$$g(E_F) = \frac{3N}{2E_F}.$$

Note that there was a misprint in the paper – $2/3$ instead of $3/2$ – so give full marks for either. Given that for a sample of volume V

$$B = V \left(\frac{2m_e}{\hbar^2} \right)^{3/2} / (2\pi^2),$$

and, from our previous result,

$$E_F = \left[\frac{3N}{2B} \right]^{2/3},$$

so for gold with an electron concentration of $5.9 \times 10^{28} \text{ m}^{-3}$ [4]

$$E_F = \left[\frac{6\pi^2 N}{2V} \right]^{2/3} \frac{\hbar^2}{2m_e} = \left[3\pi^2 5.9 \times 10^{28} \right]^{2/3} \frac{(1.05 \times 10^{-34})^2}{2 \times 9.11 \times 10^{-31}} = 8.78 \times 10^{-19} \text{ J} = 5.48 \text{ eV}.$$

If we require

$$g(E_F) = \frac{3N}{2E_F} = \left[\frac{1.602 \times 10^{-19}}{40} \right]^{-1},$$

then

$$N = \frac{40}{1.602 \times 10^{-19}} \frac{2 \times 8.78 \times 10^{-19}}{3} = 146.1,$$

implying a cube of side given by

$$L^3 5.9 \times 10^{28} = 146.1,$$

or

$$L = 1.35 \text{ nm.}$$

[3]

Note that following through with the incorrect formula gives $E_F = 3.19 \text{ eV}$, and a volume $3.24 \times 10^{-27} \text{ m}^3$, whereas using the correct E_F with the incorrect $g(E_F)$ gives $5.57 \times 10^{-27} \text{ m}^3$

(c) The key points are

- the underlying smooth curve represents nearly free electron states, arising from the s orbital of gold; [1]
- the structure between about 0 eV and +6 eV arises from the more tightly bound d states; [1]
- we can expect absorption of light corresponding to excitation of electrons from below the Fermi energy to above it. Whereas this absorption would be almost independent of energy for a free electron metal, here there will be a sharp increase of absorption for energies above about 2 eV (Fermi energy minus energy of top of d levels). Thus reflected light contains a decreased amount of green and blue, giving gold its characteristic yellowish colour. For the colour, give some credit for discussing the mixture of wavelengths, and for involving absorption/optical transitions. [4]

4. (a) If the matrix elements of the Hamiltonian H between atomic functions $\phi_j(r)$ centred on sites j satisfy

$$\begin{aligned}\int \phi_i^*(r)H\phi_i(r) dr &= -\alpha \\ \int \phi_i^*(r)H\phi_j(r) dr &= -\beta \text{ if } n \text{ and } m \text{ are nearest neighbours,} \\ \int \phi_i^*(r)H\phi_j(r) dr &= 0 \text{ otherwise}\end{aligned}$$

and in addition

$$\int \phi_i^*(r)\phi_j(r) dr = \delta_{ij},$$

where the integrals are taken over the whole crystal.

If we take

$$\psi_k(r) = \sqrt{\frac{1}{N}} \sum_{n=1}^N e^{ikna} \phi_n(r)$$

then

$$\begin{aligned}\int \psi_k^*(r)\psi_k(r) dr &= \frac{1}{N} \sum_{n=1}^N e^{-ikna} \sum_{m=1}^N e^{ikma} \int \phi_n^*(r)\phi_m(r) dr \\ &= \frac{1}{N} \sum_{n=1}^N \sum_{m=1}^N e^{ik(m-n)a} \delta_{mn} \\ &= \frac{1}{N} \sum_{n=1}^N 1 \\ &= 1,\end{aligned}$$

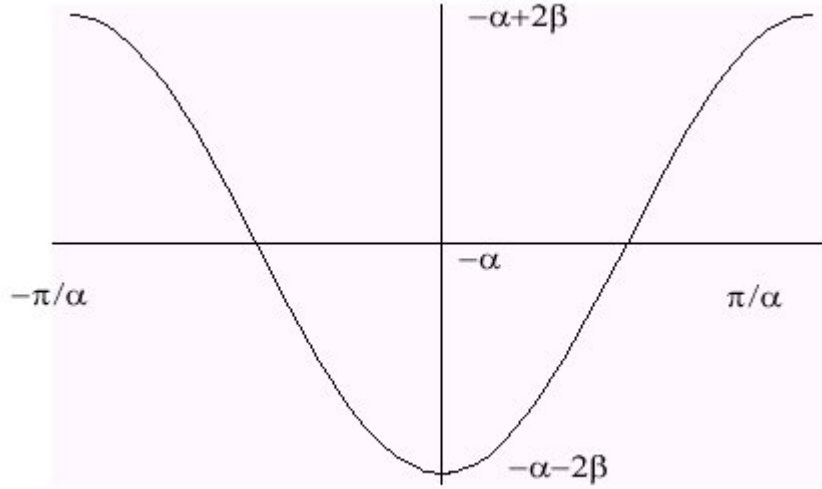
so the wavefunction is normalised. Award 0.5 mark for stating the normalisation condition. [2]

We evaluate the expectation value of the energy (implicitly using the normalisation) as

$$\begin{aligned}E(k) = \int \psi_k^*(r)H\psi_k(r) dr &= \frac{1}{N} \sum_{n=1}^N e^{-ikna} \sum_{m=1}^N e^{ikma} \int \phi_n^*(r)H\phi_m(r) dr \\ &= -\frac{1}{N} \sum_{n=1}^N \alpha - \frac{1}{N} \sum_{n=1}^N e^{ika} \beta - \frac{1}{N} \sum_{n=1}^N e^{-ika} \beta \\ &= \frac{1}{N} \sum_{n=1}^N 1 \\ &= -\alpha - 2\beta \cos(ka),\end{aligned}$$

where we have used the fact that $N + 1$ is equivalent to 1. [3]

- (b) The sketch shows the resulting dispersion relation for values of k between $-\pi/a$ and π/a . [1]



The cosine is bounded above and below by 1 and -1 respectively, so the energy ranges from $-\alpha - 2\beta$ to $-\alpha + 2\beta$, giving a band width of 4β . [1]

The effective mass is given by [1]

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2}.$$

in this case [1]

$$\frac{1}{m^*} = \frac{2a^2}{\hbar^2} \beta \cos(ka),$$

so near the bottom of the band, where $k = 0$, $\cos(ka) = 1$ and [1]

$$m^* = \frac{\hbar^2}{2\beta a^2},$$

while near the top of the band $k = \pi/a$, $\cos(ka) = -1$, and [1]

$$m^* = -\frac{\hbar^2}{2\beta a^2}.$$

As the valence band is usually narrower than the conduction band, and as the effective mass is inversely proportional to β , which is proportional to the bandwidth, one expects a hole in a semiconductor to be heavier than an electron. [1]

- (c) If electric field \mathcal{E} is applied to the system, the rate of change of the electron group velocity is [1]

$$\frac{dv_g}{dt} = \frac{1}{m^*} \frac{d\hbar k}{dt} = -\frac{2a^2}{\hbar^2} \beta \cos(ka) |e| \mathcal{E}.$$

Now the total current will be the current carried by each electron, $-|e|v_g$, multiplied by the number of electrons in the range k to $k + dk$, and integrated over k between $-\pi/a$ and π/a for the full Brillouin zone. In one dimension $g(k)$ is a constant, so

$$\frac{d\mathcal{J}}{dt} = ge^2 \mathcal{E} \frac{2a^2}{\hbar^2} \beta \int_{-\pi/a}^{\pi/a} \cos(ka) dk = 0,$$

that is, no current will be established. [3]

(d) The overlap between wavefunctions for any two different values of k will be

$$\begin{aligned}\int \psi_k^*(r)\psi_{k'}(r) dr &= \frac{1}{N} \sum_{n=1}^N e^{-ikna} \sum_{m=1}^N e^{ik'ma} \int \phi_n^*(r)\phi_m(r) dr \\ &= \frac{1}{N} \sum_{n=1}^N \sum_{m=1}^N e^{i(k'm-kn)a} \delta_{mn} \\ &= \frac{1}{N} \sum_{n=1}^N e^{i(k'-k)na} \\ &= \frac{1}{N} e^{i(k'-k)a} \frac{1 - e^{i(k'-k)Na}}{1 - e^{i(k'-k)a}}\end{aligned}$$

where we have used, in the last step, the formula for the sum of a geometric progression. Now the allowed values of k and k' are of the form $2\pi/(Na)$, so the numerator in the last expression is zero and the states ψ_k and $\psi_{k'}$ are orthogonal for $k \neq k'$.

[4]

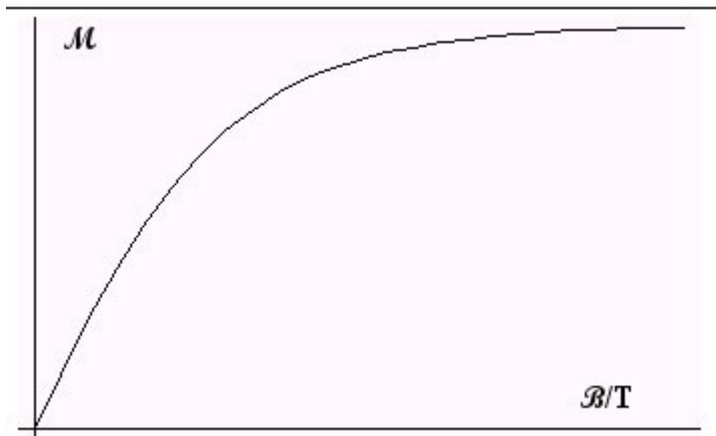
5. (a) Diamagnetism is caused by currents induced in the material as a result of the imposition of an external field. Paramagnetism is caused by the alignment of pre-existing magnetic moments by the application of the field. A superconductor below its transition temperature acts as a perfect diamagnet. [4]

(b) The *quenching* of orbital angular momentum is caused by electrostatic crystal fields. These fields split the degeneracy of the different m_L orbitals, by energies that are large compared with magnetic energies, and the eigenstates are linear combinations of the spherical harmonic states, aligned along crystal directions. This means that the application of a magnetic field can no longer freely reorient the projection of $\mathbf{L} - m_L$ is no longer a good quantum number. In rare earths the spin-orbit coupling is strong enough to couple \mathbf{S} and \mathbf{J} together even in the presence of crystal fields, so m_J remains a good quantum number. The difference arises because the f orbitals which are partly-filled in the rare earths are closer to the nuclei, and the nuclei have larger charges, than is the case in the transition metals. [6]

(c) If there are n ions per volume with spin magnetic moments, with $S = 1$, we know that the Landé factor will be $g_J = 2$ and the expectation value of the magnetisation is found from the Boltzmann distribution, knowing that the energy of a dipole $m = g_J \mu_B m_J$ in a field \mathcal{B} is $-m\mathcal{B}$, and is

$$\begin{aligned} \mathcal{M} &= n \frac{2\mu_B e^{2\mu_B \mathcal{B}/(k_B T)} + 0 - 2\mu_B e^{-2\mu_B \mathcal{B}/(k_B T)}}{e^{2\mu_B \mathcal{B}/(k_B T)} + 1 + e^{-2\mu_B \mathcal{B}/(k_B T)}} \\ &= 2n\mu_B \frac{2 \sinh(x)}{2 \cosh(x) + 1}, \end{aligned}$$

where $x = 2\mu_B \mathcal{B}/(k_B T)$. The form of the magnetisation as a function of \mathcal{B}/T is shown below. [3]



In the limit of small \mathcal{B}/T we may use the fact that x is small, so that [1]

$$\begin{aligned} \sinh(x) &\approx x \\ \cosh(x) &\approx 1 \end{aligned}$$

and thus

$$\mathcal{M} \approx 2n\mu_B \frac{2x}{2+1} = 2n\mu_B \frac{2 \times 2\mu_B \mathcal{B}/(k_B T)}{3} = \frac{8n\mu_B^2 \mathcal{B}}{3k_B T},$$

so the susceptibility is

$$\chi = \frac{\mathcal{M}}{\mathcal{H}} = \frac{\mu_0 \mathcal{M}}{\mathcal{B}} = \frac{8n\mu_0\mu_B^2 \mathcal{B}}{3k_B T}.$$

This is in accord with Curie's law, $\chi = C/T$, with $C = 8n\mu_0\mu_B^2/(3k_B)$. [4]

The low-field susceptibility at 300 K with 10^{27} ions per cubic metre is therefore [2]

$$\chi = \frac{8 \times 10^{27} \times 4\pi \times 10^{-7} \times (9.273 \times 10^{-24})^2}{3 \times 1.38 \times 10^{-23} \times 300} = 6.96 \times 10^{-5}.$$