

## High- $T_c$ Superconducting Membrane: (I) Theoretical Consideration for Gas Separation

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Magnetic separation of paramagnetic or ferromagnetic materials from diamagnetic ones has been widely studied in the context of various technologies. A selective separation of iron oxide impurity from ceramic raw materials is an old subject. In the present study, a new route to paramagnetic and diamagnetic gas separation is suggested using the magnetic properties of membranes.

In general, the cryogenic process is a well-established industrial technology to separate nitrogen and oxygen gases.<sup>1</sup> However, it is known to be inadequate for producing a small quantity of highly pure gases. This is the reason why many researchers have been exploring a new membrane process as an alternative, which should be very simple in equipment, not be energy consuming and, therefore, quite economic to separate gases.<sup>2-4</sup> In many cases, the main driving force to separate gases is the molecular sieving effect using microporous membranes such as zeolite, silica, and alumina ones. Such a sieving technique is efficient to separate gases with a large difference in molecular size, but not with similar molecular size like nitrogen, argon, and oxygen as listed in Table 1.

Recently, various materials have been developed and applied to gas separation procedures, based on the difference of chemical or physical properties. The polymer membranes made of polyaniline or polyamide, for example, can be used for gas separation, which prefers oxygen molecules to nitrogen ones.<sup>5-6</sup> In general the oxygen/nitrogen selectivity is often over 6 in polymer membranes, but unfortunately it suffers from low permeability. Even though the most permeable polymers developed so far show particular selectivity only, no better material is known beyond the upper bound of permeability square selectivity. On the other hand, inorganic membranes made of perovskites and molecular sieves like zeolite with alkali metal have also been extensively studied.<sup>7-8</sup> The former is based on the oxygen ionic conductivity and the separation factor of oxygen/nitrogen often reaches infinity, while the latter uses the quadruple moment difference between oxygen and nitrogen. But both should also suffer from low permeation and/ or low selectivity.

More recently, gas separation methods have been tried involving superconducting membranes and ferromagnetic ones.<sup>9-10</sup> Reich *et al.* reported that a superconducting membrane could be applied to gas separation using the diamagnetic property of a superconductor, based on the idea that the permeation of diamagnetic nitrogen molecules is preferable to that of paramagnetic oxygen molecules.<sup>9</sup> A ferromagnetic gauze was also used in magnetic gas separation, but it needs a strong magnetic field to induce a high selectivity. Even under a 10 T magnetic field induced by a superconducting magnet, however, the (O<sub>2</sub>/N<sub>2</sub>) selectivity does not exceed 2. More recently, K. Ishizaki *et al.* have demonstrated an example of a superconducting magnetic filter being applied to separate oxygen and argon gases, using a magnetic field gradient concept. That is, paramagnetic oxygen molecules can accumulate at the pore entrance, where the field gradient is the highest, and consequently permeate preferentially through the superconducting membrane, compared to diamagnetic nitrogen molecules. Also they theoretically calculated the magnetic force for oxygen molecules induced by the Meissner effect of a superconductor. A good model membrane in part of the geometrical shape, the applied field strength, and the pore size were postulated.

In this study, our primary attention has been paid to comparing the present results with the previous ones, in such a way that the solution to improving the separation efficiency in a superconducting membrane could be suggested.

In 1986, Bednorz and Muller discovered superconductivity for the first time in a layered perovskite, La<sub>2-x</sub>Ba<sub>x</sub>CuO<sub>4</sub>,

**Table 1.** Physical properties of various gas molecules

Gas molecules	Magnetic property at boiling temperature [ $\chi_m$ (10 <sup>-6</sup> cm <sup>3</sup> /mol)]	Boiling temperature (K)	Kinetic diameter (Å)
Oxygen (O <sub>2</sub> )	Paramagnetic (+3402 g) (+7667 liq)	90.1	3.46
Nitrogen (N <sub>2</sub> )	Diamagnetic (-12.05)	77.4	3.64
Argon (Ar)	Diamagnetic (-6.99)	87.3	3.35
Nitric acid (NO)	Paramagnetic (+1461)	121.4	~3.8
Carbon dioxide (CO <sub>2</sub> )	Diamagnetic (-20)	194.7	~4.0

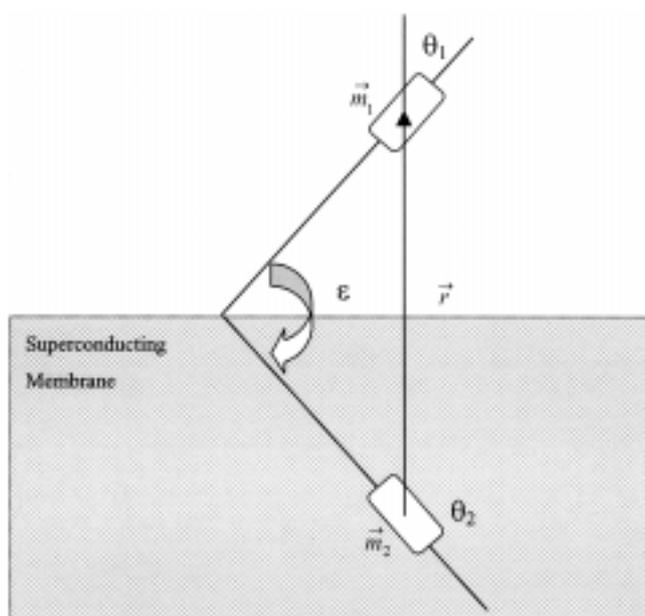
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**Table 2.** Various physical properties of high temperature superconductors

Super-conductor	Hc <sub>1</sub>		Hc <sub>2</sub> (mT)	T <sub>c</sub> (K)	Penetration Depth	
	a,b-axis (mT)	c-axis (mT)			a,b-axis (nm)	c-axis (nm)
Bi2201				20		
Bi2212	85		~89000	85	270	500
Bi(Pb)2223		650	~184000	110	250	178
YBCO	~25	~90	~120000	90	140	~500
Tl2223			~75000	125	173	480

which has a  $T_c > 30$  K, and later, various superconducting oxides had been discovered as shown in Table 2.<sup>12</sup> The characteristics of a superconductor are zero resistivity and perfect diamagnetism, termed the "Meissner effect", below the critical temperature ( $T_c$ ). The discovery of high temperature superconductors working at liquid nitrogen temperature is considered to be very important in terms of industrial applications due to its economic availability compared to conventional low temperature superconductors.

One of the important applications is thought to be membrane gas separation based on the Meissner effect, since the oxygen molecules are paramagnetic while the nitrogen or argon gases are diamagnetic. Therefore, a superconducting membrane could be used to separate such gases using the difference of magnetic properties. For example, the nitrogen molecules can pass through the diamagnetic superconducting membrane while the paramagnetic oxygen molecules would be expelled. Reich *et al.*, suggested a theoretical model to separate nitrogen and oxygen gases using the mirror principle of superconductors.<sup>9</sup> The mirror principle could be used to explain the magnetic interaction of a high  $T_c$  superconductor with a molecular magnet as shown in Figure

**Figure 1.** Mirror principle; interaction between a diamagnetic superconductor and a magnet.

1, and the interaction energy ( $E_{mag}$ ) between  $m_1$  and  $m_2$  could be calculated as follows;

$$E_{mag} = \frac{\vec{m}_1 \cdot \vec{m}_2}{r^3} - \frac{3(\vec{m}_1 \cdot r)(\vec{m}_2 \cdot r)}{r^5} = \frac{m^2}{r^3} (\cos\epsilon - 3\cos\theta_1\cos\theta_2)$$

$$\therefore \langle E_{mag} \rangle = \frac{3m^2}{2r^3} \quad (1)$$

Where  $\vec{m}_2$  is the mirror image of  $\vec{m}_1$ ,  $r$  is the effective distance between the molecular magnetic moment and the superconducting diamagnetic enclosure, and  $q_1 + q_2 = 180^\circ$ . On the other hand, the kinetic energy of gas molecules is given by

$$\langle E_{kinetic} \rangle = \frac{3}{2}kT \quad (2)$$

When a gas molecule interacts with six walls in a box, this becomes  $6\langle E_{mag} \rangle = 3/2kT$ , And therefore,

$$\frac{18m^2}{2r^3} = \frac{3}{2}kT$$

$$r^3 = \frac{6m^2}{kT} \quad (3)$$

On the other hand, the magnetic susceptibility is related to temperature as follows;

$$\chi(T) = \frac{m^2 N}{3kT} \Rightarrow m^2 = \frac{3kT\chi(T)}{N} \quad (4)$$

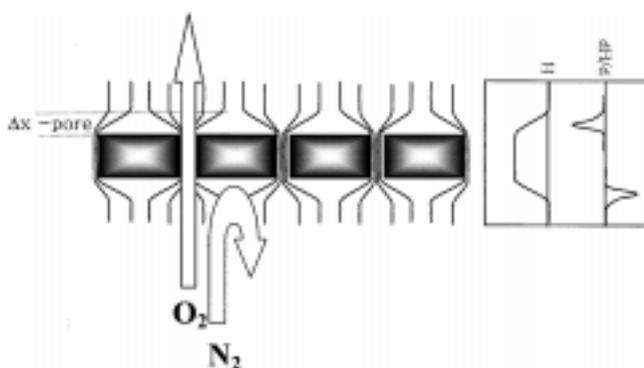
Where  $\chi(T)$  is the magnetic susceptibility,  $N$  is Avogadro's number, and  $k$  is the Boltzman constant. Therefore, the equilibrium distance between the magnetic interaction energy and the kinetic one can be derived as  $r^3 = 18\chi(T)/N$ , when the equation (4) is substituted into the equation (3).

Since the magnetic susceptibility of oxygen is  $1.08 \times 10^{-2}$  cm<sup>3</sup>/mol at 77 K, its  $r$  value of 0.68 Å can be simply calculated. Therefore, a size gain of  $2r = 1.36$  Å occurs for the oxygen molecule compared to a non-superconducting state.

In a previous study,<sup>9</sup> the authors seemed to be confused that the  $2r$  value of 1.36 Å was the distance between the superconductor wall and the interacting gas molecules, those which are in equilibrium between the magnetic energy of superconductor and the kinetic energy of gas molecules, so the size gain was expected to be sufficient to separate oxygen gas in air if the pore size of the membrane were designed less than 10 Å. However, the  $r$  value is in reality twice the distance between the superconductor plane and the center of the gas molecule at equilibrium according to our opinion, so that the real distance should be  $r/2$ , and the real size gain is only 0.34 Å, which is a negligible value. Moreover, when the gas penetrates through the superconducting membrane, it interacts with 4 superconducting planes instead of 6, which reduces the size gain to 0.3 Å. Therefore, the separation effect due to a size gain from the interaction

**Table 3.** Magnetic effect of a superconductor membrane for paramagnetic oxygen

Gas	Kinetic diameter	Size gain from diamagnetism of superconductor	Modified diameter	
Oxygen (O <sub>2</sub> )	3.46 Å	0.36 Å	3.82 Å	0.30 Å for cube
Nitrogen (N <sub>2</sub> )	3.64 Å	–	3.64 Å	
Size difference	0.18 Å	=	–0.18 Å	<b>No effect</b>

**Figure 2.** Gas separation using the magnetic property where the direction of the magnetic flux is parallel to the direction of the pressure gradient.

between diamagnetic superconductor and paramagnetic oxygen is thought to be less significant, as shown in Table 3, which means that the theoretical model based on the mirror principle is not to be applied to gas separation.

In the other study, if the superconductor is cooled down to below  $T_c$  under a magnetic field (FC), the magnetic flux expelled by a diamagnetic superconductor can be concentrated to the pore of the superconductor membrane as shown in Figure 2, which means that the field gradient is formed during concentration of the magnetic flux. Such a field gradient may force the paramagnetic or ferromagnetic materials to move in the concentrated magnetic field direction, and *vice versa* for diamagnetic materials. That is, the paramagnetic oxygen can be accumulated in front of the pore entrance while the diamagnetic nitrogen can pass through the superconducting body, where the magnetic field is most dilute. Thus the oxygen molecules collected preferentially at the pore may pass through the membrane by the pressure difference across it.

The force is applied to materials, affected by the applied magnetic field and the magnetic field gradient, as follows;

$$F = M \frac{dH}{dx} = \frac{M dB}{\mu_0 dx} = \frac{\chi_m dB}{\mu_0^2 dx} \quad (5)$$

Where  $M$  is the induced magnetization of a particle,  $\chi_m$  is the magnetic susceptibility,  $H$  is the applied field intensity,  $B$  is the induced magnetic field intensity,  $dB/dx$  is the magnetic field gradient, and  $\mu_0$  is the magnetic permeability of a vacuum. Two types of materials interact with the magnetic field and the field gradient inversely and the interaction

force is proportional to  $B$ ,  $(dB/dx)$ , and  $\chi_m$ . Ishizaki *et al.* found a value  $B(dB/dx)$  of 4 T<sup>2</sup>/m was required to separate argon and oxygen.<sup>10</sup> The magnetic susceptibility of liquid oxygen is  $0.767 \times 10^{-2}$  cm<sup>3</sup>/mol, which is  $(0.767 \times 10^{-2}) \times (10^{-6} \times 4\pi) \times (1.26 \times 10^{-6})$  in SI units. If a magnetic field of 1.8 T and a field gradient of 17 T/m are applied, the resulting force becomes;

$$F = \frac{0.767 \times 10^{-2} \cdot 10^{-6} \times 4\pi}{1.26 \times 10^{-6}} \times 17 \times 1.8 = 2.34 \text{ N/mol}$$

This value can be translated to 75 N/kg in kg unit, which is sufficient to lift up the oxygen molecules.

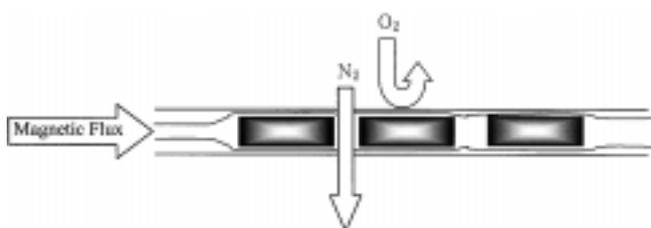
Also the magnetic susceptibility of oxygen gas at 90.1 K is  $+3.402 \times 10^{-3}$  cm<sup>3</sup>/mol, which is  $(0.3402 \times 10^{-2}) \times (10^{-6} \times 4\pi) \times (1.26 \times 10^{-6})$  m<sup>3</sup>/mol in SI units, so the force becomes  $F = (3.393 \times 10^{-2} \times H \times dH/dx)$  N/mole. This force, 1357 N/mol, could be induced by a magnetic field of 0.01 T and a field gradient of  $dH/dx = 4 \times 10^6$  T/m, where the concentrated field in a pore is 1T and the field concentrating distance is 250 nm.

However, the 1357 N/mol is insignificant in comparison to the force imposed by the pressure difference. If the membrane is composed of pores with an average size of 250 nm and a disk shape with a diameter of 4 cm, the magnetic flux could be concentrated by the 250 nm thickness. Only the gases in the space can interact with the magnetic field gradient, so the volume is  $2\pi^2 \text{ cm}^2 \times 0.25 \times 10^{-4} \text{ cm} = 3.14 \times 10^{-4}$  mL, which can be translated to  $1.402 \times 10^{-8}$  mol at 1 atm. Therefore the force is  $1.903 \times 10^{-5}$  N per molecule. On the other hand, if the pressure difference across the membrane is 0.01 atm, the interaction force with gas molecule becomes  $0.01 \times 10^5 \text{ Pa} (= \text{N/m}^2) = 1000 \text{ N/m}^2$ . If the area of the membrane is  $2\pi^2 \text{ cm}^2 = 12.5 \times 10^{-4} \text{ m}^2$  and the pore area is one third of the total area, the force becomes  $1000 \times 12.5 \times 10^{-4} \times 0.3 \text{ N} = 0.377 \text{ N}$  per molecule, which is still larger than the force exerted by the magnetic interaction. Therefore, it is not easy to separate oxygen and nitrogen molecules simply by the magnetic field and field gradient concepts.

It was therefore decided to consider the parameters required to influence the efficiency in separating nitrogen and oxygen as follows: (1) the minimum pressure, (2) the pore size limit of the membrane, (3) the membrane structure, (4) the proper magnetic field and field gradient. We are now able to summarize the following results.

**Pressure condition.** This is necessary to reduce the pressure difference between  $P_i$  and  $P_o$  to enhance the selectivity. If the pressure difference is small, the force induced is comparable to that of the magnetic field gradient. Therefore, a pressure difference of  $\sim 10^{-4}$  atm is needed to achieve the gas separation.

**Pore size.** A smaller pore size is essential to induce a larger field gradient, since it leads to a strong interaction between the magnetic field and paramagnetic oxygen. However, the size should be over 250 nm, which is the penetration depth of the superconductor. If the pore size is smaller than the penetration depth, the magnetic flux concentrated in the pore of the membrane would penetrate the superconduct-



**Figure 3.** Gas separation using the magnetic property where the direction of the magnetic flux is perpendicular to the direction of the pressure gradient.

ing body. Therefore, the field gradient would not be formed effectively.

**Membrane structure.** Even though the membrane structure is not so important, most superconductors have anisotropic structure. Such a structure can give a long penetration path as demonstrated by clay membranes, resulting in a large tortuosity and, therefore, a small permeation. Therefore, it is required to fabricate a membrane with more isotropic superconducting particles. It should be noted here that  $H_{c1}$  (the critical magnetic field) in the direction of the  $a, b$ -axes is different from that in the  $c$ -axis direction. Therefore, larger magnetic field intensity results if the superconducting particles can be aligned to an axis direction, so generating the field gradient more effectively. An important thing to be noted here is the thickness of the superconducting layer, which should be larger than the penetration depth of 250 nm.

**Magnetic field strength.** In order to induce an effective field gradient, the magnetic field intensity should be less than  $H_{c1}$  as listed in Table 2, where each superconductor has its specific  $H_{c1}$  and  $H_{c2}$  and the BSCCO has the largest  $H_{c1}$  value among the three different kinds of superconductor.

**Magnetic field direction.** The direction of an applied magnetic field should be the same as that of the pressure gradient. If the directions are mutually orthogonal, the magnetic flux passes through the membrane as shown in Figure 3. In such a case, the diamagnetic nitrogen penetrates very easily through the membrane but the paramagnetic oxygen does not, because the magnetic field cannot be concentrated in the pore. Therefore, the direction of the magnetic field should be

the same as the pressure gradient, as shown in Figure 2.

**Field cooling (FC) and zero field cooling (ZFC).** In order to concentrate the magnetic flux in the pore of a superconducting membrane, the membrane should be cooled under an applied magnetic field (FC). If the magnetic field is applied after cooling (ZFC), the superconducting body would expel the magnetic flux outside the membrane. In such a case a large field gradient would not be generated in the pore of the superconductor membrane.

Based on the above theoretical consideration, we are on the way to performing separation experiments using the magnetic properties of high  $T_c$  superconductors.

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