

STUDY OF STOPPING CROSS-SECTION FACTORS OF He IONS IN SOME METAL FLUORIDE FILMS

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الخلاصة :

تم قياس معاملات مقاطع الإيقاف المستعرضة (ϵ) لأيونات الهليوم في أغشية رقيقة مفلورة مصنوعة من المواد MgF_2 ، LaF_3 ، NdF_3 ، و ThF_4 وذلك باستخدام التبعثر الخلفي مقروناً بطرق ضوئية. وقد قورنت قيم (ϵ) المقاسة مع القيم المحسوبة من قاعدة براغ باستعمال بيانات جداول المقاطع الذرية المستعرضة. ووجدنا أن الفرق بين القيم المحسوبة والمقاسة في حدود ١٧٪، ولكن يُتوقع أن يكون الخطأ الكلي بين نتائج القياس والحساب أكثر من ذلك.

ABSTRACT

Stopping cross section factors, $[\epsilon]$, of helium ions, in thin evaporated films of MgF_2 , LaF_3 , NdF_3 , and ThF_4 , have been measured by backscattering combined with optical methods. The measured values of $[\epsilon]$ are compared with those calculated from the Bragg's rule using the tabulated atomic cross sections. The differences between the measured and calculated values were as high as 17%, but the combined uncertainty arising from the measurement and calculation is estimated to be larger than this value.

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1. INTRODUCTION

Knowledge of electron stopping of light ions (such as He ions) in matter is of basic interest in atomic and molecular physics and in elemental analysis by nuclear techniques [1]. In many applications of ion-beam techniques, target materials are compounds rather than pure elements. Nevertheless, there is still a lack of basic understanding [2] of how chemical bonds influence the stopping behavior of light ions. This deficiency is partly due to a lack of precise measurements, which could be used to test the validity of existing theoretical models [3, 4].

In the present work, we have followed a different approach to the existing method [3] of backscattering in determining stopping cross-section factors of light ions in thin solid films, where, by using the Lorenz–Lorentz law, the uncertain molecular density of the films has been replaced with parameters that can be measured more accurately, such as molecular density of the corresponding bulk material and the refractive indices of the film and bulk material [5]. This method was applied to determine the stopping cross-section factors of He ions in thin films of MgF_2 , LaF_3 , NdF_3 , and ThF_4 . Our experimental work presented here has been motivated by the apparent lack of data on the metal fluorides.

2. EXPERIMENT

Thin films of MgF_2 , LaF_3 , NdF_3 , and ThF_4 were deposited on fused silica and carbon substrates in a Leybold model L560 box coater pumped by a turbo molecular pump. The system was pumped to a base pressure of less than 10^{-6} mbar. The purity of source material was as follows: MgF_2 (99.99%), LaF_3 (99.9%), NdF_3 (99.3%), and ThF_4 (99.99%). All the materials were evaporated using thermally heated molybdenum boats. In all cases, the films were deposited on substrate heated to 300°C . The rate of evaporation in each case was controlled by a quartz crystal monitor and was 0.7 nm/s. The source to substrate distance was 40 cm.

After the films were deposited, they were removed from the coating chamber and exposed to the ambient atmosphere, prior to measurement of optical and Rutherford backscattering spectrometry (RBS) spectra. Transmission measurements on the films were performed using a Bausch and Lomb spectrophotometer, model Spectronic 2000. The refractive indices (n_f) and thickness (t_f) of the films were determined from the transmission spectra. The RBS was applied using 2 MeV He^{2+} ions. The system has been described in detail elsewhere [6]. Briefly, a solid state detector (Tennelec model PD-50-100-14-CB) was placed in the chamber at a scattering angle of 164° , with an effective solid angle of 1.75 msr. The system resolution for the He^{2+} beam used, including detector resolution, straggling and the electronics set-up, was 17 keV [6]. The collected RBS spectra were then fitted by the code RUMP [7] to determine the relative concentrations of various elements in the compound samples. For all the compounds it was found that the films were stoichiometric within experimental uncertainty, *i.e.* $\pm 3\%$.

3. RESULTS

A typical RBS measurement was made on a target in the form of a thin metal fluoride film on a fused silica (or carbon) substrate. The energy difference, ΔE , between particles scattered from the surface of the film and those scattered from the film–substrate interface is related to the thickness (t_f) of the film by the energy loss, that is (Equation 5.41 in reference [8] and appendix in reference [9])

$$\Delta E = N_f [\epsilon] t_f, \quad (1)$$

where $[\epsilon]$ is the stopping cross-section factor and N_f is the molecular density (*i.e.* number of molecules/cm³ in the film). In the present work, ΔE was measured from the RBS spectra (such as the one shown in Figure 1), t_f was measured by an optical method, and N_f was determined from the molecular density of the corresponding bulk material and the refractive indices of the film and bulk material, using the Lorenz–Lorentz law. Thus, the stopping cross-section factor, $[\epsilon]$, was calculated using Equation 1.

The variation of the refractive index (n), at a given wavelength, with the molecular density (N , molecules/cm³) of a perfectly transparent material is given by the Lorenz-Lorentz (LL) law as

$$[(n^2-1)/(n^2+2)][1/N] = \text{Constant.} \tag{2}$$

The LL-law is found to be accurate ($\pm 1\%$) for many materials, even being correct for cases in which there is a phase change (solid to liquid or liquid to vapor) [10, 11]. Recently, the variation of the index of refraction with density $\rho (= NM/N_A$, where N_A is Avogadro's number and M is the molecular mass) of titanium oxide samples in the form of thin films and bulk crystalline form, was found to follow the LL-law [5]. In the present work, the molecular density (N_f) of the film was replaced, using the LL-law by refractive index (n_f) of the film, refractive index (n_b), and the molecular density (N_b) of the corresponding bulk material, such that:

$$N_f / N_b = \{(n_f^2 - 1) / (n_f^2 + 2)\} / \{(n_b^2 - 1) / (n_b^2 + 2)\}. \tag{3}$$

First an attempt was made to determine the refractive indices (n_f) and thickness (t_f) of transparent fluoride films (in the spectral region from 250 nm to 850 nm) on a transparent silica substrate, using a method given by Khawaja [12]. In this method, the refractive index is calculated from the measured transmittance spectra at normal incidence beginning with an approximate film thickness, which may be obtained from the position of the consecutive minima and maxima of the

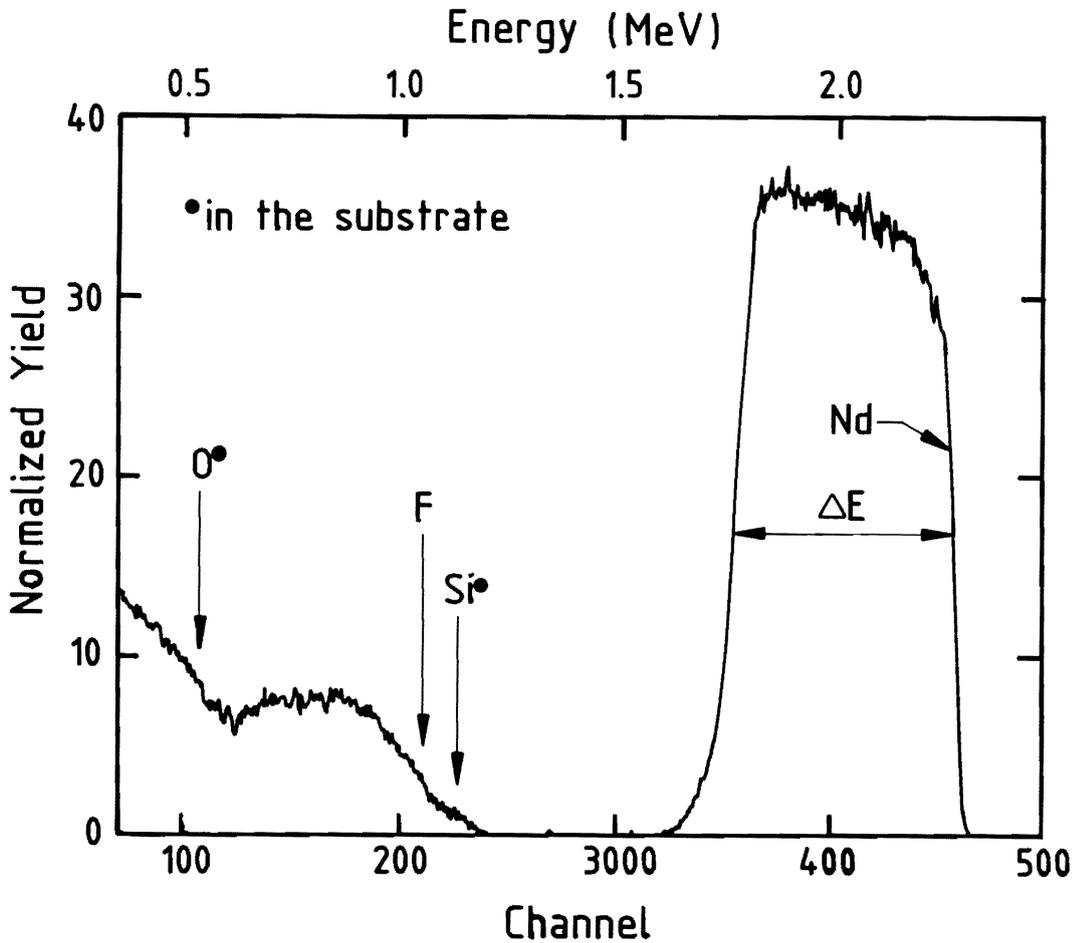


Figure 1. Energy Spectra of ⁴He Backscattered from a 493 nm Thick NdF₃ Film on Fused Silica Substrate for Incidence Energy of 2.0 MeV.

transmission curve, and then the thickness may be adjusted in an attempt to obtain a closed dispersion curve. For all the fluoride films, no choice of thickness was possible for which acceptable closure of the dispersion curve over the whole wavelength range could be obtained. A similar situation was observed for films of ZrO_2 [13]. It was concluded that the measured transmittance was not that appropriate to a perfectly plane parallel uniform thin films such as is assumed for the determination of the formula used.

Thermally evaporated fluoride films are known to be optically inhomogeneous [14–16]. This results from the fact that the films have columnar structure [14–16], with column diameter changing (*i.e.* change in density of the film), with distance from the substrate side (or air side) of the film. This density gradient in a thin film would ultimately result in a corresponding gradient in the refractive index of the film. Henceforth, such a film would be optically inhomogeneous.

Finally, the average refractive indices of the films at different wavelengths were calculated from the transmittance curves using the peak minima and maxima envelope technique given by Swanepoel [17]. The film thickness used in the present work was that for which we could get closest to an acceptable dispersion while using the method of reference [12].

The molecular film density (N_f , number of molecules per cm^3) was determined from film refractive index (n_f), bulk refractive index (n_b) and bulk molecular density (N_b), using the LL-law. In determining N_f , for MgF_2 and LaF_3 the bulk data were taken from [18]. The calculated values of N_f were for MgF_2 96% and LaF_3 97% of the corresponding bulk materials. Values are not readily available for the bulk refractive indices of NdF_3 and ThF_3 . It is known [14–16] that the density (g/cm^3) of fluoride films increases with substrate temperature (T_s), for example, the density of MgF_2 films was reported to be 0.72 [16] and 0.80–0.84 [14] of the bulk value for $T_s = 30^\circ\text{--}40^\circ\text{C}$ and 0.98 of the bulk value for $T_s = 300^\circ\text{C}$. The densities of NdF_3 and LaF_3 for $T_s = 30^\circ\text{C}$ are reported [14] to be the same, that is 0.80 of that of corresponding bulk values. In the present work ($T_s = 300^\circ\text{C}$), following above, we have assumed the film density of all films to be close to 0.97 of that of corresponding bulk materials. Therefore, the uncertainty in N_f may be less than $\pm 2\%$.

A typical RBS spectrum from a NdF_3 film of thickness 493 nm, is shown in Figure 1. Similar spectra were obtained from the other films. In Figure 2 the energy width, *i.e.* energy loss (ΔE) of the He^{2+} beam between the surface and interface (film–substrate) as shown in Figure 1, is plotted against the film thickness (t_f) for NdF_3 films. Similar results were obtained from the other materials. However in case of MgF_2 , due to isotopic effects the Mg peak was asymmetrical, therefore the

Table 1. Comparison of Measured and Calculated Stopping Cross-Section Factors, $[\epsilon]$ and Cross-Section at $E_0 = 2$ MeV He Ions, $\epsilon(E_0)$.

Material	N_f [ϵ] ^a (10^8 eV/cm)	Stopping cross-section factor [ϵ] (10^{-15} Vcm ² /molecule)		Stopping cross-section at 2 MeV He ions, $\epsilon_{Mol}(E_0)$ (10^{-15} Vcm ² /molecule)	
		Measured	Calculated ^b	Extracted ^c from [ϵ]	Calculated ^d using Bragg's rule
MgF_2 ^e	64.0	215	206	127	120
LaF_3 ^f	85.9	481	460	242	231
NdF_3 ^f	99.7	527	451	265	227
ThF_4 ^f	79.8	668	580	335	291

^a N_f [ϵ] is measured from the slope of ΔE versus t_f plots (Figure 2). The molecular density, N_f , number of molecules per cm^3 , was taken to be 0.97 of the bulk molecular density (as described in the text).

^b Calculated using Equation 6, for the parameters K and ϵ 's taken from reference [8].

^c Extracted from measured [ϵ] using Equation 7, while the parameters K and ϵ 's were taken from reference [8].

^d Calculated using Bragg's rule Equation 5a for the atomic cross-sections taken from reference [8].

^e For energy loss fluoride peak was used.

^f For energy loss metal (La, Nd, and Th) peaks were used.

fluorine peak was used in determining the energy width ΔE . In all the other fluorides, metal peaks were used. The parameter $N_f [\epsilon]$ as determined from the slopes of the straight lines (such as Figure 2) are listed in Table 1. The values of N_f were determined from the measured n_f as mentioned earlier. The measured stopping cross-section factor $[\epsilon]$ of the He ions in various dielectrics are listed in Table 1.

For the range of the thicknesses of the films that was used in the present work, almost linear plots of ΔE versus t_f for films of Ta₂O₅ [9], Pt, Al₂O₃, SiO₂, etc. have previously been observed (pages 145–149 in reference [8]). This linear relationship provides the basis for the frequently used surface energy approximation in thin films. In the surface energy approximation, the stopping cross-section factor $[\epsilon]$ is given by (Equation 3.12 in reference [8])

$$[\epsilon] = K \epsilon_{\text{Mol}}(E_0) / |\cos\theta_1| + \epsilon_{\text{Mol}}(KE_0) / |\cos\theta_2|, \quad (4)$$

where K is the ratio of projectile energy before and after scattering, E_0 is the incident beam energy, $\epsilon_{\text{Mol}}(E_0)$ and $\epsilon_{\text{Mol}}(KE_0)$ are the molecular stopping cross-sections at energies E_0 and KE_0 , respectively, $\theta_1 = 0^\circ$ is the incident angle of the beam and $\theta_2 = 164^\circ$ is the scattering angle. Assuming additivity of atomic cross-sections, ϵ 's, to obtain ϵ_{Mol} of a compound (*i.e.* Bragg's rule), one gets:

$$\epsilon_{\text{Mol}}(E_0) = \epsilon_{\text{M}}(E_0) + n\epsilon_{\text{F}}(E_0), \quad (5a)$$

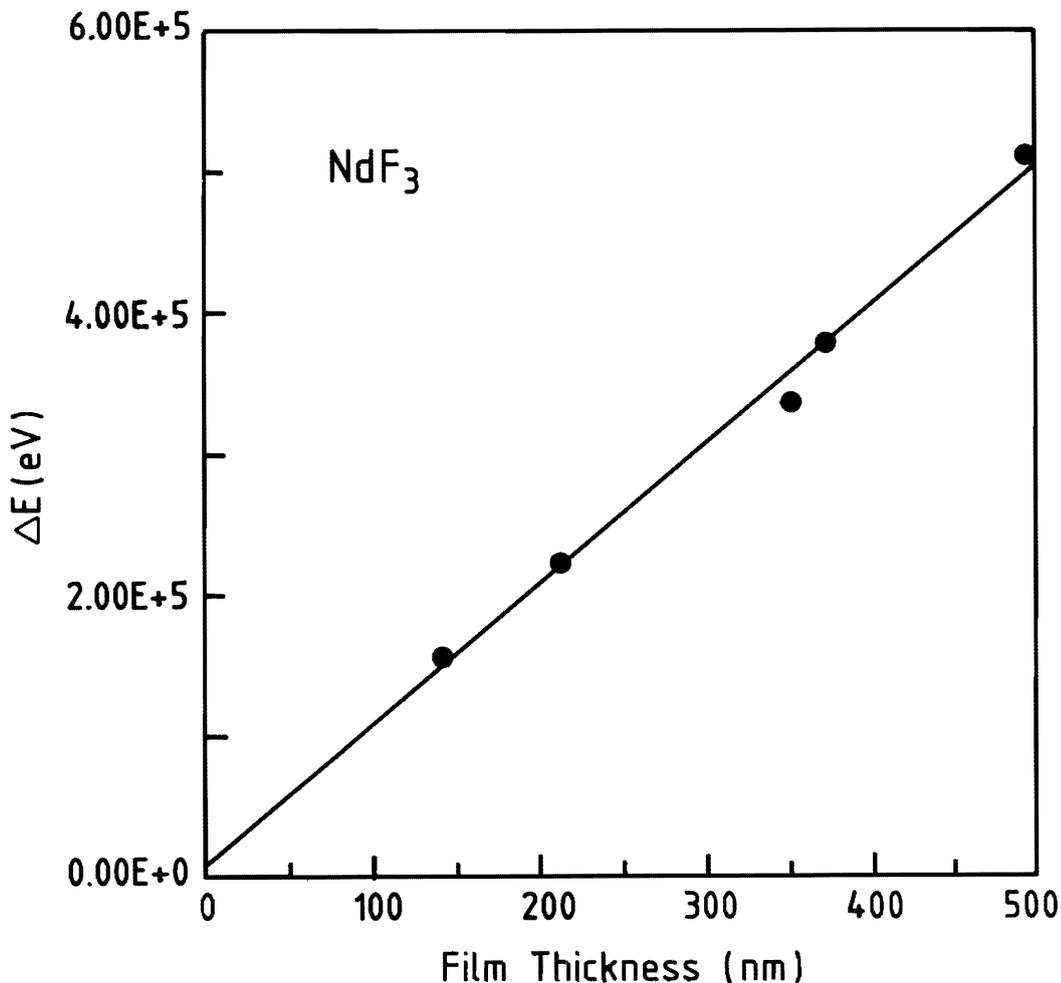


Figure 2. Energy Loss ΔE in the NdF₃ Films as Obtained from Backscattering Spectra (see Figure 1) Plotted as a Function of the Film Thickness (t_f) which is Obtained from the Spectrophotometric Method. The dots represent data. The straight line is the least-square linear fit to the data.

and

$$\epsilon_{\text{Mol}}(KE_0) = \epsilon_{\text{M}}(KE_0) + n\epsilon_{\text{F}}(KE_0). \quad (5b)$$

Thus Equation (4) can be written as:

$$[\epsilon] = K [\epsilon_{\text{M}}(E_0) + n\epsilon_{\text{F}}(E_0)] + [\epsilon_{\text{M}}(KE_0) + n\epsilon_{\text{F}}(KE_0)] / |\cos\theta_2| \quad (6)$$

where ϵ_{M} (or ϵ_{F}) is the atomic stopping cross-section, M stands for metal atom (Mg, La, Nd, or Th) and F for fluorine atom, n is the number of fluorine atoms in a molecule of a metal fluoride. In determining ΔE from RBS spectrum, if metal peak is used the K is represented by K_{M} , while in the case of fluorine it is K_{F} . The cross-section factors, $[\epsilon]$, were calculated from Equation (6) for the parameters K and ϵ taken from Table III on page 354, and Table VI on page 362, respectively, in reference [8]. The calculated values of the cross-section factors are listed in Table 1.

The energy of backscattered particles depends on the energy loss along both incoming and outgoing paths. Consequently, from the backscattering measurements one obtains values for the stopping cross-section factor $[\epsilon]$ rather than the stopping cross-section ϵ . However, one can extract values of ϵ from $[\epsilon]$, as suggested on page 279 in reference [8], by using:

$$\epsilon_{\text{Mol}}(E_0) = [\epsilon] / \{ K / |\cos\theta_1| + \epsilon_{\text{Mol}}(KE_0) / \epsilon_{\text{Mol}}(E_0) |\cos\theta_2| \}. \quad (7)$$

Applying Bragg's rule (Equation 5) and using the atomic cross-sections from reference [8] the ratio $\epsilon_{\text{Mol}}(KE_0) / \epsilon_{\text{Mol}}(E_0)$ was obtained. Thus, from Equation 7 we were able to calculate $\epsilon_{\text{Mol}}(E_0)$ for the measured $[\epsilon]$. The values of $\epsilon_{\text{Mol}}(E_0)$ are listed in Table 1. These values are compared with those directly obtained using Bragg's rule (Equation 5a) for the atomic cross-sections taken from reference 8.

4. DISCUSSION

The measured stopping cross-sections in fluoride films are up to 17% higher (Table 1) than those calculated. However, the combined uncertainty arising from both measurement and calculation, as discussed below, may be a little higher than this value. Exact determination of combined uncertainty arising from the measurement and calculation of the stopping cross-section factors may not be easy. However, in the following we attempt to identify possible sources that may contribute to the combined uncertainty.

The accuracy of the stopping cross-section factors as determined in the present work, is estimated to be around 13%, where about 5% arises from film thickness (t_f), 2% from molecular density of the film (N_f) and 6% from RBS measurement (due to system energy resolution alone). Fluoride films have rough surfaces because of columnar structure [14–16]. Surface roughness contributes to higher uncertainty in the measurement of film thickness, as compared with that for films with relatively smoother surfaces. Generally, a film with columnar structure has a hill and valley structure at the surface of the film. The surface roughness is averaged out in the optical method, as discussed in detail in reference [19]. The rough surface layer (average distance between the top of the hill and the bottom of the valley) has been estimated for films of some other materials to be less than about 10% of the total thickness of a film [20, 21]. Assuming that the optical method averages the thickness of this rough surface layer to half its value and similar surface roughness exist in the fluoride films, then the uncertainty in the film thickness t_f may be less than 5%.

Moreover, the Bragg's rule introduces further uncertainty as it makes the assumption that chemically binding atoms form into molecules (chemical effects) and any change in physical state on going from element to compound or between different phases of the same material (phase effect), have negligible effect on stopping power. Furthermore, the atomic stopping cross-sections used in the above calculations, have been derived from empirical sets of values and may be in error by as much as 10% but are typically good to within a few percent (page 339 in reference [8]). The validity of additivity of element stopping (the Bragg's rule) has been tested in a wide range of work [4] and breakdown of Bragg's rule is now well established [4]. For example the phase effect on stopping cross-section differences for proton in H_2O as vapor and ice could contribute up to 15% deviations [22]. Some methods have been developed which take into account chemical effects, for example see reference [23–25]. However, the purpose of the present work was to measure the stopping cross-section factors and not

necessary to prove a test of Bragg's rule. Due to its simplicity, the Bragg's rule was used to provide a rough estimate of the cross-section factors for comparison.

5. CONCLUSIONS

Stopping cross-section factors have been determined by backscattering combined with optical methods in some metal fluoride films. The measured stopping cross-section factors in fluoride films are higher by up to 17% than those calculated using Bragg's rule. However, the combined uncertainty arising from the measurement and from the calculation is expected to be larger than this value, so the results can not be used as a test of Bragg's rule.

ACKNOWLEDGMENT

This work is part of KFUPM/RI project LRL, supported by the King Fahd University of Petroleum and Minerals.

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Paper Received 27 October 1996; Revised 7 April 1997; Accepted 11 June 1997.