REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
Sept 30, 94

3. REPORT TYPE AND DATES COVERED
Final 1 Sep 93-31 Aug 94

4. TITLE AND SUBTITLE
Actuators of Mica Layer Structures

5. FUNDING NUMBERS
DAAL03-90-G-0076

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Marquette University
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8. PERFORMING ORGANIZATION REPORT NUMBER

DTIC
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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
ARO 27572.4-MS-SM

11. SUPPLEMENTARY NOTES
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12a. DISTRIBUTION/AVAILABILITY STATEMENT
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12b. DISTRIBUTION CODE

19951204 094

3.

A mechanism for a thermal actuating systems depends on the anomalously high thermal expansion of some crystals with layer structures. These have reversible thermal expansions in excess of 10^{-1} °C^{-1}; expansions of several thousand percent over a temperature range of a few hundred degrees centigrade have been reported. Stresses can be as high as 3 MPa, reversible thermal strains of ~ 5000%, and work densities greater than 10 MJ/m^3 have been obtained.

DTIC QUALITY INSPECTED 3

(Continued on reverse side)

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

19. SECURITY CLASSIFICATION OF ABSTRACT
UNCLASSIFIED

20. LIMITATION OF ABSTRACT
UL

Crystals that behave in this fashion are phlogopite micas and also some intercalated graphites which expand perpendicular to the silicate or graphitic layers. Other layer structures have comparable properties.

Extraneous, non-structural gases or liquids are entrapped between the layers. On increase of temperature, the separation of the layers increases, changing into a dome-shaped lenticular bubble where the lateral spacing, perpendicular to the layers can expand from ~ 1 nm to ~ 10 μm, particularly at the liquid-gas phase transition. The resulting solid-gas composite expands more like a gas, with the atomic layers acting as flexible membranes.

Implantation of rare gases Xe, Kr, Ar, He into muscovite mica of normal thermal expansion behavior produces the same anomalous thermal expansion effects. The rare gases Xe and Kr can be observed and identified unambiguously within the silicate layers and in the bubbles that develop, using RBS, and by low temperature electron diffraction of the solidified Xe and Kr.

FINAL REPORT

ACTUATORS OF MICA LAYER STRUCTURES

by

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ARPO Proposal Number 27572-MS-SM

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ACTUATORS OF MICA LAYER STRUCTURES

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Summary

A mechanism for a thermal actuating systems depends on the anomalously high thermal expansion of some crystals with layer structures. These have reversible thermal expansions in excess of $10^{-1}\ ^{\circ}C^{-1}$; expansions of several thousand percent over a temperature range of a few hundred degrees centigrade have been reported. Stresses can be as high as 3 MPa, reversible thermal strains of ~ 5000%, and work densities greater than 10 MJ/m^3 have been obtained.

Crystals that behave in this fashion are phlogopite micas and also some intercalated graphites which expand perpendicular to the silicate or graphitic layers. Other layer structures have comparable properties.

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Thermal Expansion of Phlogopite Mica

The thermal expansion of phlogopite mica is illustrated in Fig. 1, using a thermomechanical analyzer (TMA) with a mica specimen approximately 300 μm thick.

The behavior can be summarized as follows:

1. At about 100°C, the mica expands markedly perpendicular to the silicate layers, due to a liquid to gas phase change of H_20.

2. At higher temperatures, the expansion is comparable to that of a gas rather than a solid. This is shown by extrapolating to zero expansion which occurs at ~ 0°K which agrees with ideal gas behavior.

3. An estimate of the quantity of H_20 present can be made from the expansion at the phase change and is ~ 100 ppm.

4. The steep change at ~ 100°C is displaced to higher temperatures on increasing the applied pressure in the TMA, and agrees with the b.p. change with pressure reported for H_20; see Fig. 2.

5. The first heating cycle is always anomalous; the heating-cooling curve shown in Fig. 1 is valid after the first heating cycle. Subsequently, the specimen is stable for at least 100 thermal cycles, providing the upper temperature limit is not changed.

6. The hystersis effect of the heating-cooling cycle is persistent and reproducible; this is demonstrated in Fig. 3 where three-hour isothermal steps were used for the heating and cooling cycle.

7. Isothermal studies are shown in Fig. 4 showing the phlogopite mica to be stable at 585°C for 24 hours.

8. High temperature transmission electron microscope studies have followed the appearance and development of bubbles within the mica with temperature; see Fig. 5A.

The thermal behavior of the phlogopite mica can be explained by the following:

(a) Excess, non-structural water is entrapped between the silicate layers.

(b) This water is not able to diffuse out of the mica structure even after long periods of time at temperatures up to ~ 600°C.

(c) Lenticular flaws develop between the silicate layers as the liquid H_20 undergoes a phase change to H_20 vapor.

(d) These lenticular flaws expand perpendicular to the silicate layer.

It has not been possible to identify unambiguously the excess H_20. Differential Calorimetric Scanning studies reveal a very small thermal effect at ~ 100-120°C. However, the amount of H_20 present is very small ~ 100 ppm. Low temperature TEM has not been able to observe ice diffraction patterns within the lenticular flaws; the diffraction pattern becomes complex with the superposition of several patterns.

To confirm the gas-bubble explanation of the anomalous thermal expansion, rare gas has been implanted into a muscovite mica of normal thermal expansion properties.

Helium Implanted into Muscovite Mica

Muscovite mica of normal thermal expansion properties has been implanted with He ion (at 1.5 MeV) to give a distribution as shown in Fig. 6. Bubbles are observed in the mica as shown in Fig. 7. The thermal expansion has been measured by TMA on specimen ~ 100 μm thick, obtained by stacking the 5 μm-thick implanted specimens, and the results are presented in Fig. 8. The thermal expansion can be ~ 8% at 500°C, which is an order of magnitude greater than for the original muscovite mica, and the expansion varies with applied pressure.

It is not possible to identify unambiguously the presence of the rare gas He. To accomplish this, heavier rare gases, Xe, Kr, Ar, have been implanted.

Muscovite Mica Implanted with Xe, Kr, Ar

Xe, Kr and Ar have been implanted into muscovite mica at 180 keV [implantation equipment at higher energies was not available]. The rare gas formed bubble within the mica, and the location of the gas was identified by

1. RBS; see Fig. 9 for the case of Xe. A decrease is observed in the signal of K, located between the silicate layers and this decrease is removed by annealing. This suggests that the implanted Xe is located between the silicate layers.

2. Solid Xe and Kr can be observed at low temperatures by TEM; liquid He stage is required for the Kr, liquid N stage for the Xe see Fig. 5B. Electron diffraction at low temperatures of the solid Xe and Kr showed f.c.c. structures to be present with lattice parameters not reduced, indicating no undue pressure effects.

3. Electron fluorescence studies EDAX of the solids within the bubbles confirmed the presence of Xe and Kr.

4. The quantity of Xe and Kr gas present has be determined from the volume of the gas bubbles present, assumed to be spherical, and using the equation of state of the rare gases. Good agreement has been obtained between the known amount of implanted gas, the RBS signal, and the bubble-count method.

Mechanism of Anomalous Thermal Expansion

The model of the thermal expansion behavior of the mica is illustrated in Fig. 10. The lenticular bubbles give rise to a very large lateral thermal expansion, which can be ~ several thousand percent, even in the case where the angle θ is less than 5°. The schematic in Fig. 10B shows a typical density and distribution of lenticular bubbles within a phlogopite mica specimen observed in a TEM. In Fig. 11, the effect of a small longitudinal change is illustrated and can give rise to a considerable lateral thermal expansion.

The work performed by the phlogopite mica at the phase change, using ΔT 5°C, Δx 500% and an applied pressure of 200 kPa, is of the order of a MJ/m^3. In the case of the bromine intercalated graphite, the work performed is ~ 100 MJ/m^3.

Other layer structures tend to have comparable anomalous thermal expansion properties. A table I is given of such compounds. Some preliminary measurements have been carried out using a fine capacitometer system, where the layer crystals act as spacers between the capacitor plates.

Related Phenomena

Thermo-rheological fluids. An effect analogous to electro-rheology is observed on heating a fluid with a phlogopite mica dispersion. With increase of temperature, the viscosity of the oil-mica mixture increases markedly when the phlogopite mica flaws expand. Some preliminary experiments have been undertaken.

Shape Memory Ceramics. Phlogopite mica flakes have been encapsulated into a molten boric oxide glass. At about 450°C, pressure is applied on cooling to room temperature. On reheating to about 450°C, the glass softens and the specimen expands markedly (~ 20%) to its original size. The enclosed mica becomes free to expand.

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Participating Scientific Personnel

Yang, Xin	"Anomalous Thermal Expansion of Phlogopite Mica"	M.S. Thesis (1990)
Xu, Q.	"Anomalous Thermal Expansion of Muscovite Mica Implanted with Noble Gases"	M.S. May (1992)
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Dr. W.A. Chiou		Northwestern University Evanston, IL
Dr. J. Chaumont		Université Paris/Osay, France

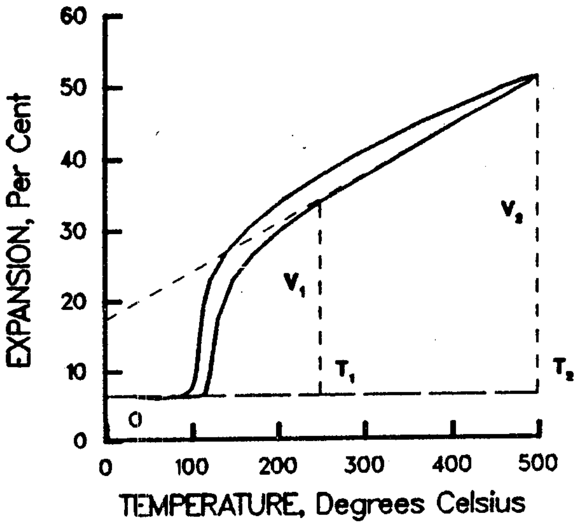


Fig. 1. Linear thermal expansion of phlogopite mica. The region above 120°C has been extrapolated to absolute zero, corresponding to 0% thermal expansion in agreement with the ideal gas law.

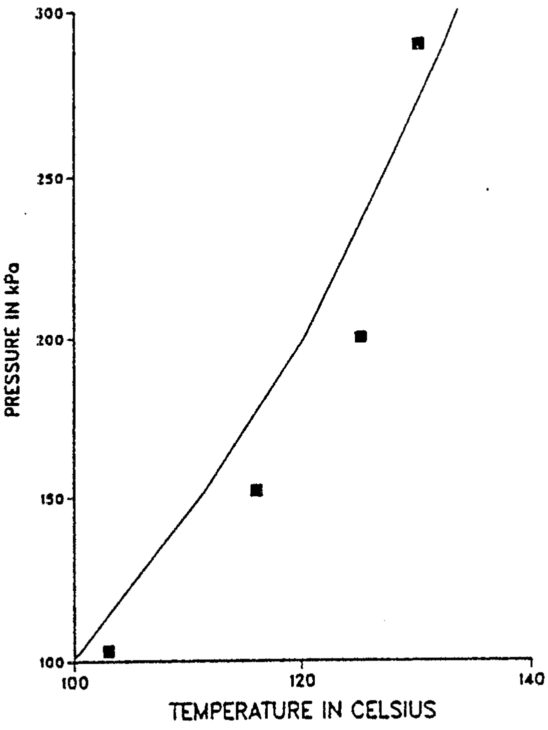


Fig. 2. The solid curve represents the variation of the boiling point of water with pressure, plotted from standard tables. The experimental data points are onset temperatures of the maximum expansion of phlogopite.

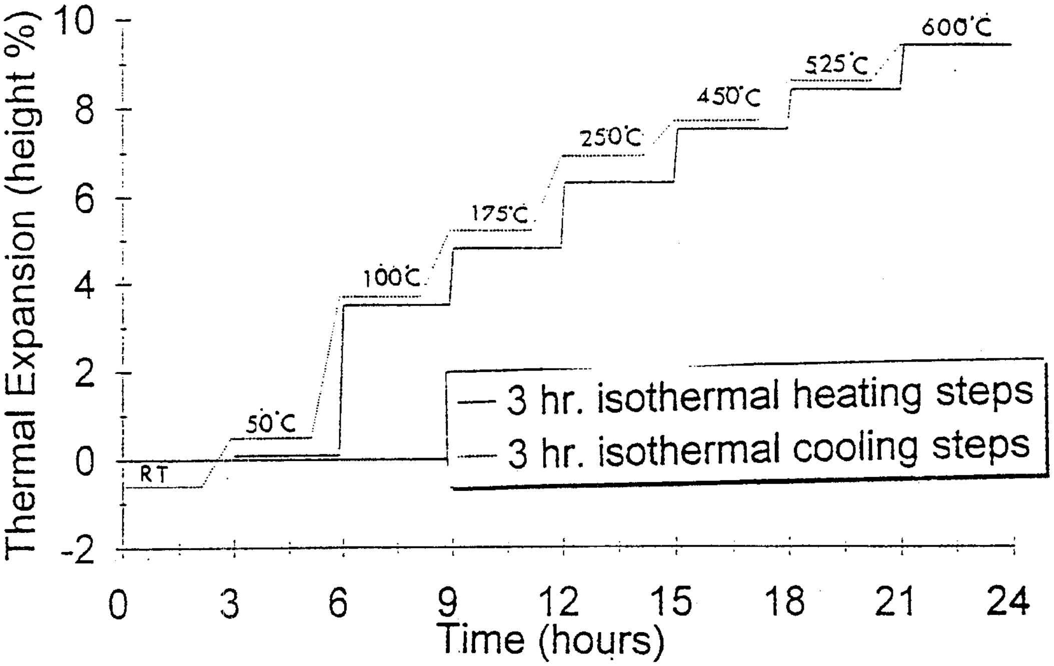


Fig. 3. Isothermal measurements of 3 hours for phlogopite mica at room temperature (RT), 50°C, 100°C, 175°C, 250°C, 450°C, 525°C, and 600°C. The hysteresis effect is characteristic of the mica on heating and cooling.

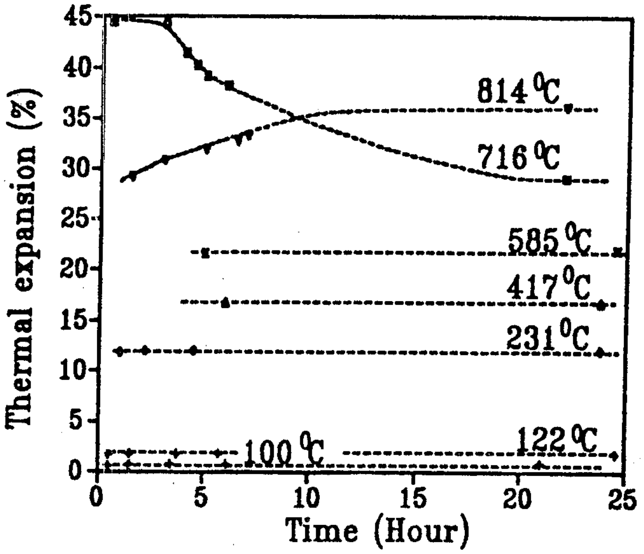


Fig. 4. Isothermal studies of phlogopite mica at temperatures from 100°C. The enhanced thermal expansion is stable at 585°C after 24 hours.

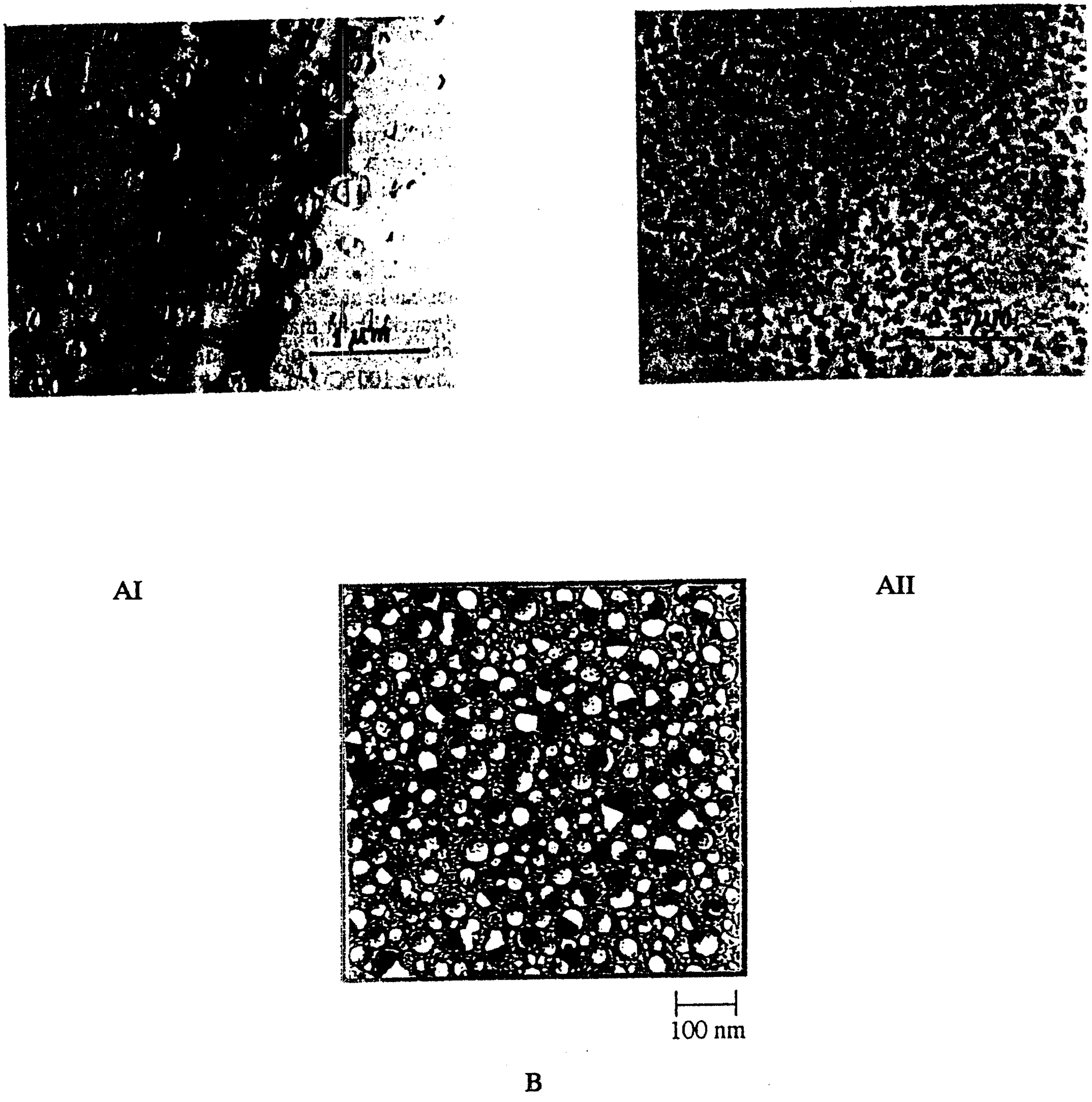


Fig. 5A. TEM bright fields showing the evolution of water bubbles in a phlogopite mica during heating

AI. First heating at 310°C.

AII. Room temperature after the first heating up to 365°C.

B. Low temperature solidification of Xe (or Kr) in cavities in muscovite mica as observed in TEM using liquid N (or He) stage.

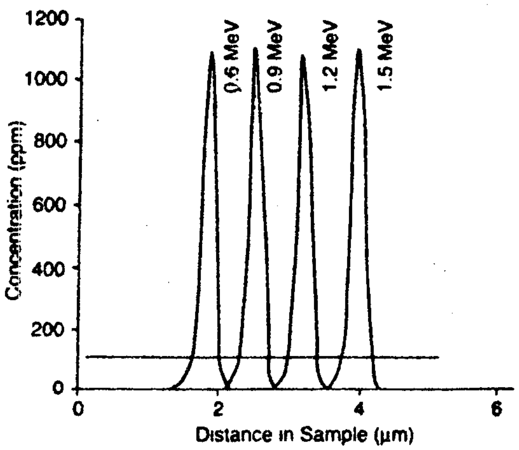
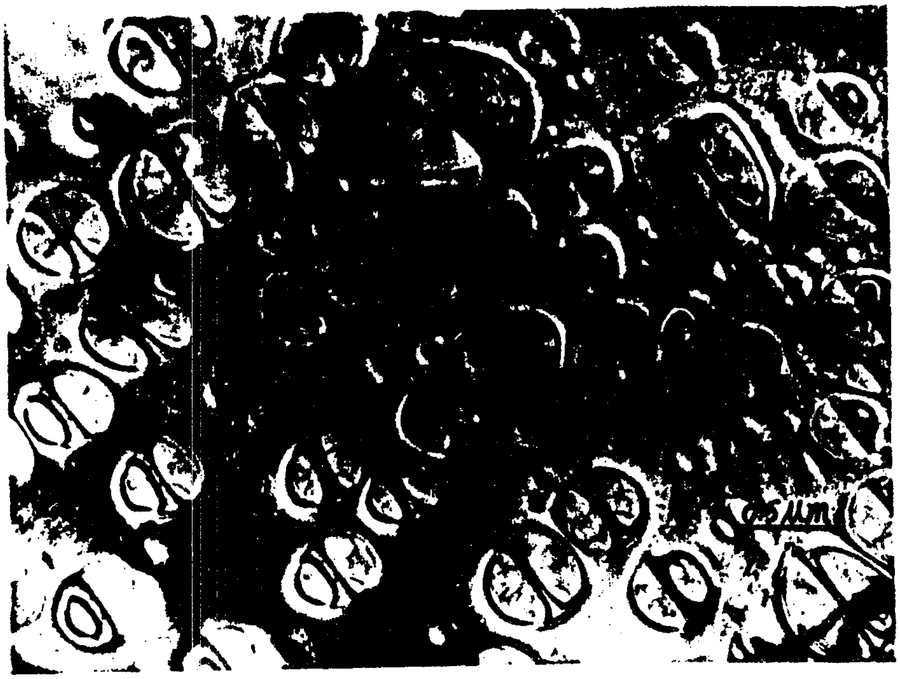


Fig. 6. Implanatation profile for He gas in muscovite mica calculated using TRIM-91 for 0.6, 0.9, 1.2, and 1.5 MeV energies. A total of 10^{16} ions/cm^2 of Xe has been implanted into the muscovite, so that 100 ppm of He was present, averaged over the 5-μm thickness.



Lenticular Flaws in Implanted Muscovite Mica

Fig. 7. Area of Helium-implanted muscovite mica with 10^{16} atoms/cm^2 as viewed in the TEM at room temperature. Sample was prepared by adhesive tape striping after implantation. Some areas show fewer bubbles.

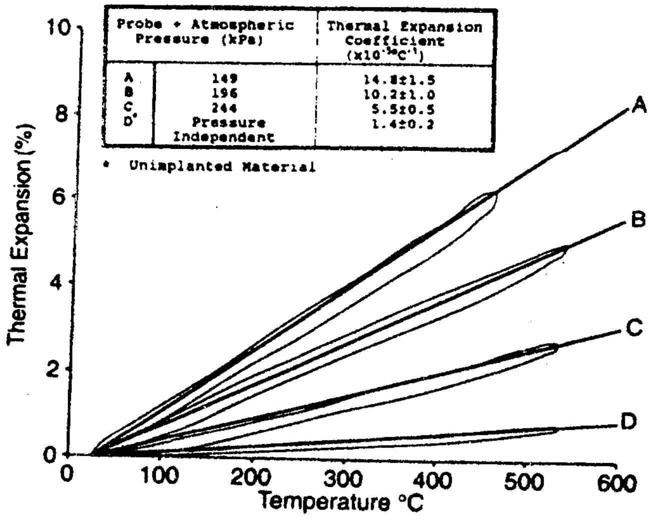


Fig. 8. Thermal expansion of He-implanted muscovite mica measured using TMA. The thermal expansion increases by a factor of about 10 at the lowest applied pressure and depends on the applied pressure of the TMA probe. There is a hysteresis loop, the lower curve corresponding to an increase of temperature, and the upper curve to cooling. The hysteresis loop for unimplanted mica is instrumental error.

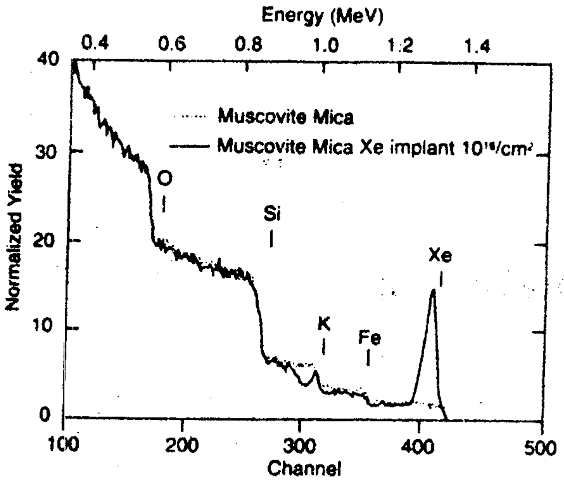


Fig. 9. Rutherford backscattering of muscovite mica before and after implantation of Xe at 180 keV and $10^{16}/cm^2$. The Xe peak is clearly identified and corresponds to a quantity in close agreement with the implanted fluence. There is a decrease in the implanted spectrum corresponding to potassium.

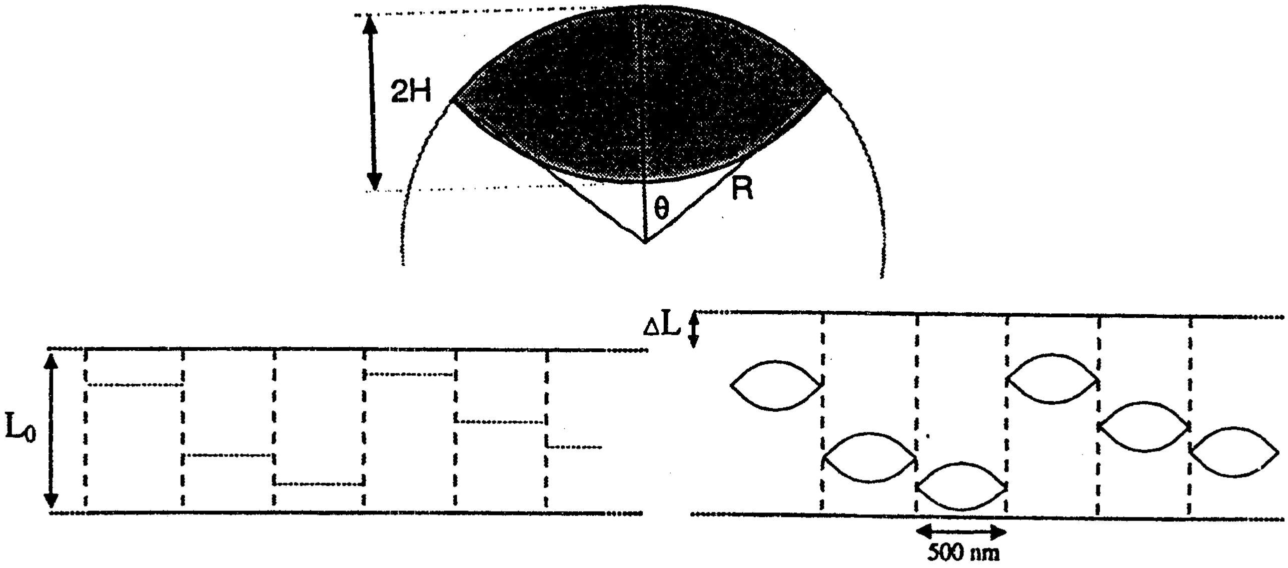


Fig. 10. Simple model of lenticular flaw behavior in a phlogopite mica

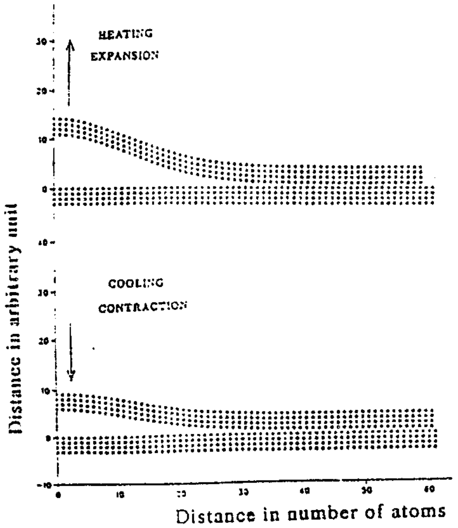


Fig. 11. Illustration of the large perpendicular expansion induced by a small longitudinal movement

Table I

LAYER STRUCTURES CRYSTALS		
		INTERCALANTS
$H_2Zr(PO_4)_2$ H_2O	$Na_2Ti_3O_7$,$K_2Ti_4O_9$,$KTiNbO_5$	alkylamines
$VOPO_4$ $2H_2O$	$M_2\{M^{IV}(PO_4)_2\}$,xH_2O	arylamines
$NbOPO_4$ $3H_2O$		N-oxides
KT_1 NbO_5	$M_2\{M^{IV}(AsO_4)_2\}xH_2O$	S-oxides
KNb_3 O_8	$KNiAsO_4$,$NaNiAsO_4$	P-oxides
$HTiNbO_5$	KV_3O_8, hewetite	fatty acid amines
$HMnAsO_4$ H_2O	$KNb_3O_8K_4Nb_6O_{17}$ ...	urea derivatives
ZrS_2	$Ag_6Mo_{10}O_{33}$ ...	alcohols
Nb Se_2		ketones
MoS_2	buserite	amino acids
	uranium mica, $Ca(UO_2)(PO_4)_2$,xH_2O	H_2O
	sabugalite, uvanite	benzene
	clathrates: $Ni(CN)_2NH_3$,xH_2O	
	$Ni(CN)_2NH_3(xC_bH_b)$	
	(This list is not complete)	

The variable water (or benzene) expresse din the formulae corresponds to different degrees of intercalation.

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