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THE EFFECT OF PRESSURE ON THE MOSSBAUER SPECTRUM OF Fe^{57} IN IRON METAL

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This paper reports on the development of a technique for conducting Mössbauer experiments[1] on materials under very high pressures and on the results obtained from a study of those changes produced by pressure in the Mössbauer spectrum of Fe^{57} in metallic iron. The effect of pressure on the Fe^{57} Mössbauer spectrum in iron metal is of interest for several reasons. All the nuclear parameters upon which the Fe^{57} spectrum depends can be determined from other experiments. Thus, the spectrum can be used as a probe into non-nuclear effects to which the spectrum is sensitive such as the electronic charge density and spin polarization at the nucleus. The Mössbauer spectrum of Fe^{57} can be used both to detect and to characterize the reported high pressure phase of iron metal.[2,3] Furthermore, the dependence of the spectrum on the magnetic field at the nucleus can be used to study the effect of compression on the ferromagnetism of α-iron. Few other high pressure experiments can yield such detailed information about behavior on an atomic scale which makes the Mössbauer effect a most useful experimental tool for high pressure research.

The theory of the Mössbauer effect and conditions for observation of recoilless radiation have been worked out quite thoroughly[4] and will not be discussed here. Two experiments observing Mössbauer spectra in solids at elevated pressures have been reported. Pound, Benedek and Drever[5] made a precise study of the shift in the photon energy (the chemical shift) produced by hydrostatic pressures up to 3 Kbar. They attributed most of the shift to the increase of the electron density at the nucleus but did not report any details of the fine structure of the spectrum. The authors with two coworkers studied the influence of pressure on the Mössbauer effect of Dy^{161} formed in situ in gadolinium metal[6]. The theoretical prediction made by Hanks[7] that higher pressure would permit observation of recoilless radiation not detectable at one atmosphere was demonstrated, and very dramatic changes

of the fine structure were found.

Since the 14-KeV radiation would be attenuated severely in passing through the walls of the pressure vessel, it was decided to contain the radiation source under pressure in order that the radiation passed through the wall of the pressure vessel only once. For simplicity, the source was a disk of iron metal .175 inch in diameter and .007 inch thick. Iron enriched to 99.9% in Fe^{56} was used in making the disk to minimize the absorption of the recoilless radiation within the disk.

The 14-KeV excited state of Fe^{57} was obtained from the 270-day half-life electron capture decay of Co^{57}. The long half-life of this decay controls the intensity of radiation which is essentially constant for a period of a few hours. To obtain the Fe^{57} in an iron rather than a cobalt environment, the Co^{57} was electroplated onto the iron disk; and the sample was annealled at 1000°C for two hours in a hydrogen atmosphere after electroplating. The sample preparation was done by the Nuclear Science and Engineering Corporation. A sample with 4 millicuries of Co^{57} plated on the .007 inch edge along one-half of the circumference was used for the measurements reported here. Assuming a uniform distribution of Co^{57} within .005 inch from the edge, the cobalt concentration should be less than 0.1%.

The iron disk was contained between a set of .250 inch face diameter Bridgman anvils by a ferric oxide coated ring of pyrophyllite .031 inch thick and .010 inch high. The Fe_2O_3 with which the ring was coated was enriched to 99.9% Fe^{56} to minimize absorption of the 14-KeV radiation. Details of the ring and anvils have been described elsewhere.[8] Pressure was applied with a 200-ton capacity hydraulic press through a calibrated, strain-gauge instrumented load cell. This permitted continuous monitoring of the load on the anvil faces, which was constant within at most 2% at any pressure.

No information is available about the distribution of pressure in an iron disk in this geometry, so pressures reported are average pressures on the anvil face. Experience in this geometry with silver chloride as a pressure medium indicates that about only 82% of the area of the anvil face is load bearing and the average pressure on the disk is about 20% higher than the average pressure on the anvil face. In future experiments, the uncertainty in the pressure can be reduced by replacing the solid metal disk with a circular section from the circumference and filling most of the volume with a well-studied pressure medium.

Difficulties in obtaining reproducible spectra experienced with the constant velocity spectrometer used in the Dy^{161} experiment suggested that a Mössbauer spectrometer using the velocity-sweep technique be developed. The low temperature spectrometer design of Shirley et al.[9] was modified for an external source for this reason. The absorber was made with a .001 inch thick foil of 19-9 stainless steel, enriched to 65% in Fe^{57}. The foil has a broad single absorption which permitted the components of the Fe^{57} spectrum in iron to be resolved. The absorber was connected to a loudspeaker through the moving element of a Sanborn 6LV1 velocity transducer in order to make the transducer sense all the motion of the absorber relative to the press on which the stationary element of the transducer was mounted. The output voltage of the transducer was directly proportional to the velocity of the absorber relative to the source.

A NaI(Tl) scintillation detector was mounted between the absorber and the loudspeaker to detect the radiation transmitted through the absorber. When a 14-KeV γ-ray was detected, a square pulse proportional to the output of the velocity transducer was generated and fed into a 400-channel pulse height analyzer. In this manner, a transmitted photon intensity against

photon energy spectrum was generated. Because a sinusoidal drive was used, this spectrum had to be normalized for variation in time spent in different velocity ranges. A typical normalized spectrum is shown in Fig. 1.

The spectrometer was calibrated with the one atmosphere spectrum using data of Dash et al.[10] Then, pressure was applied to the sample. Detailed spectra were taken at loads of 50, 60, 90, 105, 120, and 140 Kbar; the average pressure on the iron disk was probably 20% higher. At least two spectra were taken at each pressure; the average statistical error per channel was at most 0.5% of 100% transmission. The observed intensity of absorption decreased from 13% for the most intense peak of the uncovered sample at 1 atm to about 2% for the same peak in the 140-Kbar spectrum. The decrease is due to attenuation of the recoilless radiation by the ring relative to other radiation observed at the detector and no information could be obtained about the variation of the recoil free fraction with pressure. The loss of intensity at 160 Kbar was so great that no absorption greater than 0.5% could be detected.

At pressures up to 120 Kbar, these spectra consisted of six lines appropriate to Fe^{57} in ferromagnetic α-iron. In some of these spectra, weak inner lines were poorly resolved. The 105-Kbar spectrum, shown in Fig. 1, is typical of these spectra. These spectra were analyzed in terms of three parameters: A, measuring the magnetic splitting as defined in Eq. (1); B, measuring the electric quadrupole splitting as defined by Eq. (2); and v_c, the velocity of the center of gravity of the spectrum with respect to the stainless steel absorption. μ_o is the magnetic moment of the ground state of Fe^{57}.

$$A = -\mu_o H \tag{1}$$

$$B = \frac{1}{4} e^2 qQ \tag{2}$$

Q is the electric quadrupole moment of the 14-KeV state of Fe^{57}, and H and q are the magnetic field and the electric field gradient at the iron nucleus, respectively. These parameters can be determined from the position of the four outer lines of the spectrum according to Eqs. (3)-(5). v_i is the velocity of the ith line numbered from the lowest energy line. The values

$$A = (v_6 - v_1)/5.430 \quad (3)$$

$$B = (v_1 + v_6 - v_2 - v_5)/4 \quad (4)$$

$$v_c = (v_1 + v_2 + v_5 + v_6)/4 \quad (5)$$

obtained from these parameters are given in Table I. A and v_c are plotted as functions of pressure in Figs. 2 and 3, respectively.

At 140-Kbar (Fig. 4), a seventh line appeared in the spectrum near zero velocity (at -0.127 ± 0.064 mm/sec) in addition to six lines which are characteristic of α-iron. The constants calculated for the six line spectrum are A = 1.87 ± 0.02 mm/sec, B = 0.1 ± 0.1 mm/sec, and v_c = +0.025 ± 0.035 mm/sec. These values seem consistent with values for α-iron at lower pressures, although the variation with pressure is not so smooth as at lower pressures. In particular, the chemical shift is positive with respect to 105 Kbar and 120 Kbar, and A has dropped abruptly. More precise data are needed on this point. The positions of the two inner lines of the six line spectrum calculated with these parameters agree quite well with the observed absorptions. The additional line can not be explained in terms of radiation of higher multipolarity from an α-iron lattice site. The seventh line is most easily explained in terms of a second iron atom environment such as the high pressure phase of iron.

The observed variation of the magnetic splitting is compared in Fig. 2 with the more precise results obtained in a nuclear magnetic resonance experiment to 65 Kbar by Litster and Benedek.[11] The agreement is quite good.

Table I.

Pressure Kbar	A mm/sec ±0.02	B mm/sec ±0.1	v_c mm/sec
.001 (1 atm)	1.97	0.0	+ 0.095 ± 0.032
50	1.93	0.0	+ 0.057 ± 0.035
60	1.92	0.0	+ 0.120 ± 0.060
90	1.95	0.0	- 0.007 ± 0.032
105	1.95	0.0	- 0.069 ± 0.032
120	1.93	0.2	- 0.113 ± 0.032

The origin of this field has been discussed by Freeman and Watson,[12] and Benedek and Armstrong[13] have treated the pressure variation in terms of changes in volume and saturation magnetization. Because of the volume dependence, the pressure dependence of the magnetic field at the nucleus can not be used alone to measure the pressure dependence of the ferromagnetic coupling.

α-iron is a cubic lattice system for which electric field gradients at the nucleus are prohibited by symmetry for the undistorted lattice. Observation of non-zero values of B at the higher pressures achieved can be explained in two ways. A pressure gradient, such as that observed in silver chloride in this geometry, might distort the lattice sufficiently for the observed splitting. The distortion should increase gradually with pressure and might be obscured at low pressures by the broad absorption line of the stainless steel foil. However, the thickness of the sample from which the 14-KeV radiation can be detected is small, and a very large gradient would be required. A phase transition to a lattice system of lower symmetry, such as the hcp lattice suggested by Jamieson for the high pressure phase of iron,[14] also could produce quadrupole splitting.

The variation of the chemical shift with pressure is shown in Fig. 3 together with an indication of the variation obtained by Pound et al.[5] at lower pressures. Except for the 140 Kbar point, there is a gradual shift of the spectrum to lower energy which increases with pressure. However, as the spectrometer does not measure the absolute velocity directly, the precision of this measurement is not high. A minor variation in the voltage of the square pulse corresponding to zero velocity shifts the entire spectrum. This contribution can be checked by observing the location of the ends of the velocity spectrum on the pulse height analyzer; however, the precision in this correction will be of the order of a channel width, 0.063 mm/sec. This might

account for the apparent change in direction of the shift observed at 140 Kbar.

The dependence of the chemical shift on the 4s electron density at the nucleus has been discussed by Walker, Wertheim and Jaccarino.[15] According to their Fig. 1, the change of the chemical shift from 0.10 mm/sec to -0.11 mm/sec relative to stainless steel, observed from 1 atm to 120 Kbar, corresponds to an increase of about 8-10% in the 4s electron density at the nucleus for a $3d^{8-x}\ 4s^{x}$ electron configuration. This corresponds closely to the decrease in the volume of the iron lattice at 130 Kbar observed in the dynamic high pressure investigation of Brancroft et al.[2]

The seventh line observed in the spectrum at 140 Kbar is not at a position of a normally forbidden transition of the α-iron spectrum and it can be explained in terms of a second environment for Fe^{57}. The high pressure phase, which has been observed in both static and dynamic high pressure work,[2,3,14] would be such a second environment. Jamieson and Lawson have suggested that this phase is hexagonal close packed from x-ray measurements.[14] In static high pressure experiments,[2,14] a sharp transition is not observed, which could explain the coexistence of a six line (bcc) spectrum and an apparent single line (hcp) spectrum. The coexistence of these phases has been observed at 170 Kbar in x-ray studies by Jamieson.[16]

The single Mössbauer line indicates that Fe^{57} may not be aligned in the hexagonal phase. This might indicate a paramagnetic medium; however, a single line spectrum also has been observed for Fe^{57} in a number of magnetic alloys and as a dilute impurity in antiferromagnetic chromium. This effect might be attributed to a rapid relaxation of the nuclear substates. Recently, Clogston and Jaccarino have discussed the observation of unsplit Fe^{57} Mössbauer spectra in some magnetic transition metal alloys in terms of delocalization of the magnetic moments in these materials.[17]

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Figure Captions

Figure 1. 105-Kbar spectrum, typical of the α-iron spectra. The statistical error is indicated on every tenth channel. The bars indicate the position and theoretical intensities of the absorption lines. The positions of the two inner lines are calculated.

Figure 2. The variation of the magnetic splitting parameter with pressure. The straight line is calculated from the nuclear magnetic resonance results of Litster and Benedek.[12]

Figure 3. The variation of the chemical shift with pressure, compared with the results of Pound, Benedek and Drever[6] (dashed line) obtained at lower pressures.

Figure 4. 140-Kbar spectrum showing seven lines. The statistical error is indicated on every tenth channel. The bars indicate the position and theoretical intensities of the absorption lines. The position of lines 3 and 5 are calculated assuming a six line spectrum.

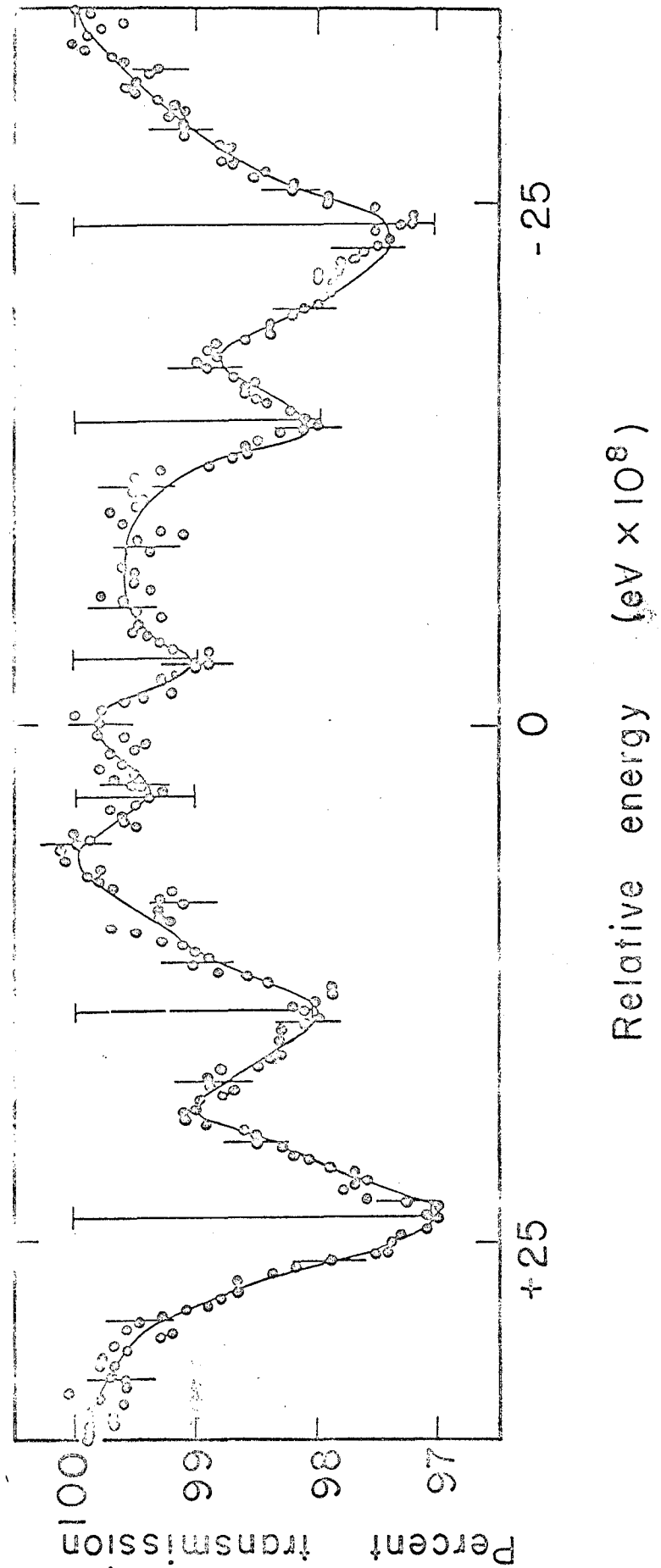

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Fig. 1

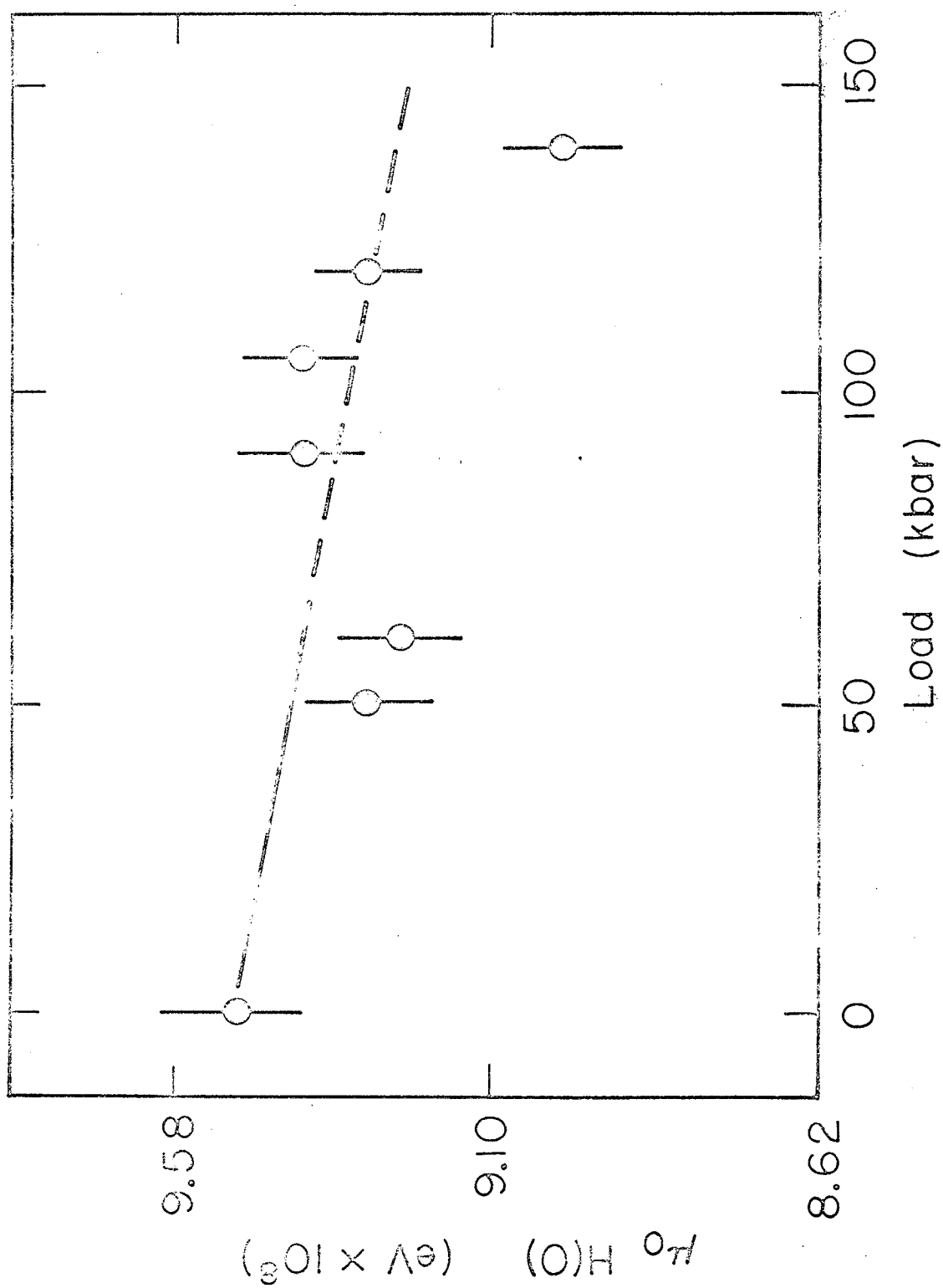

Fig. 2

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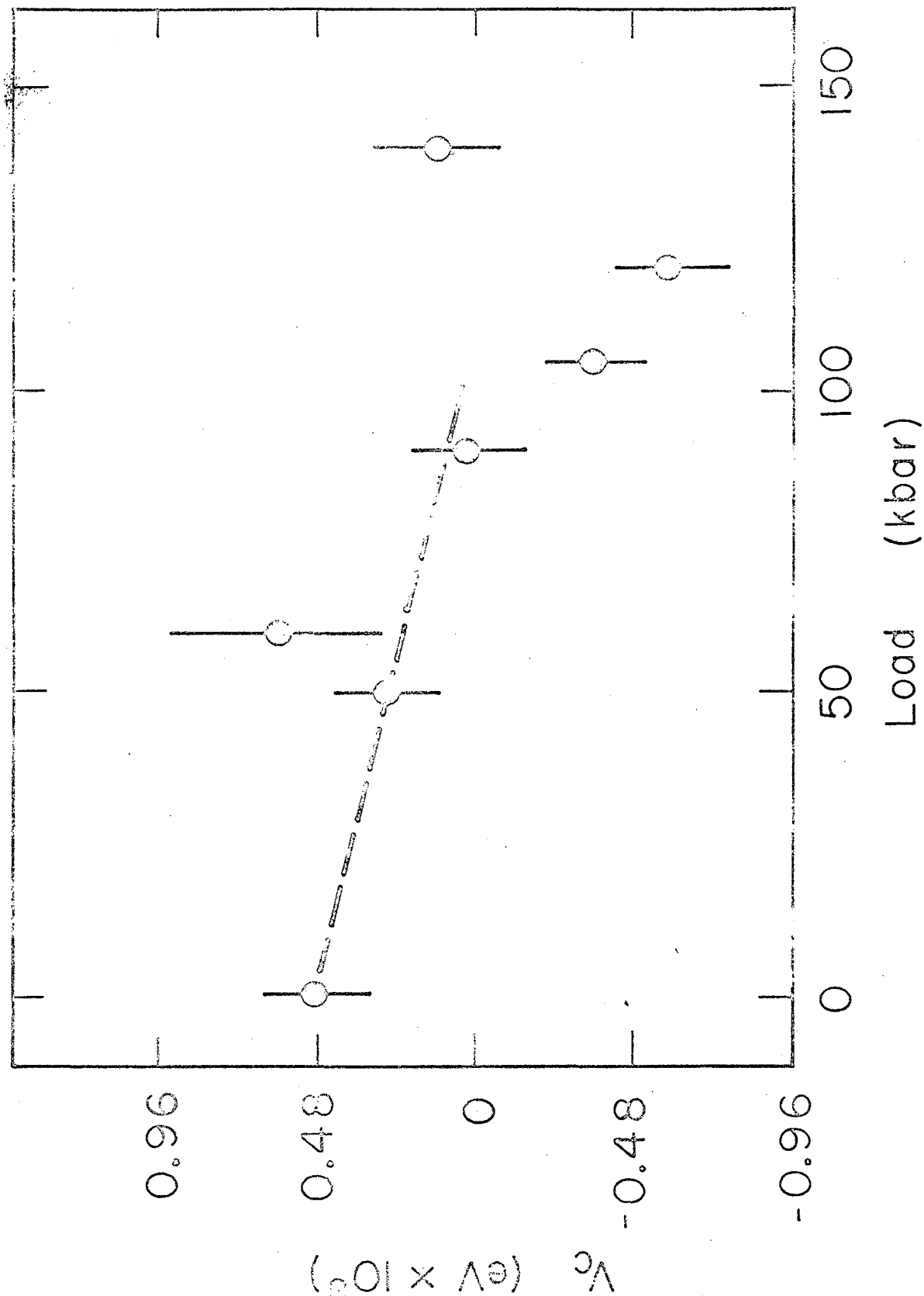

Fig. 3

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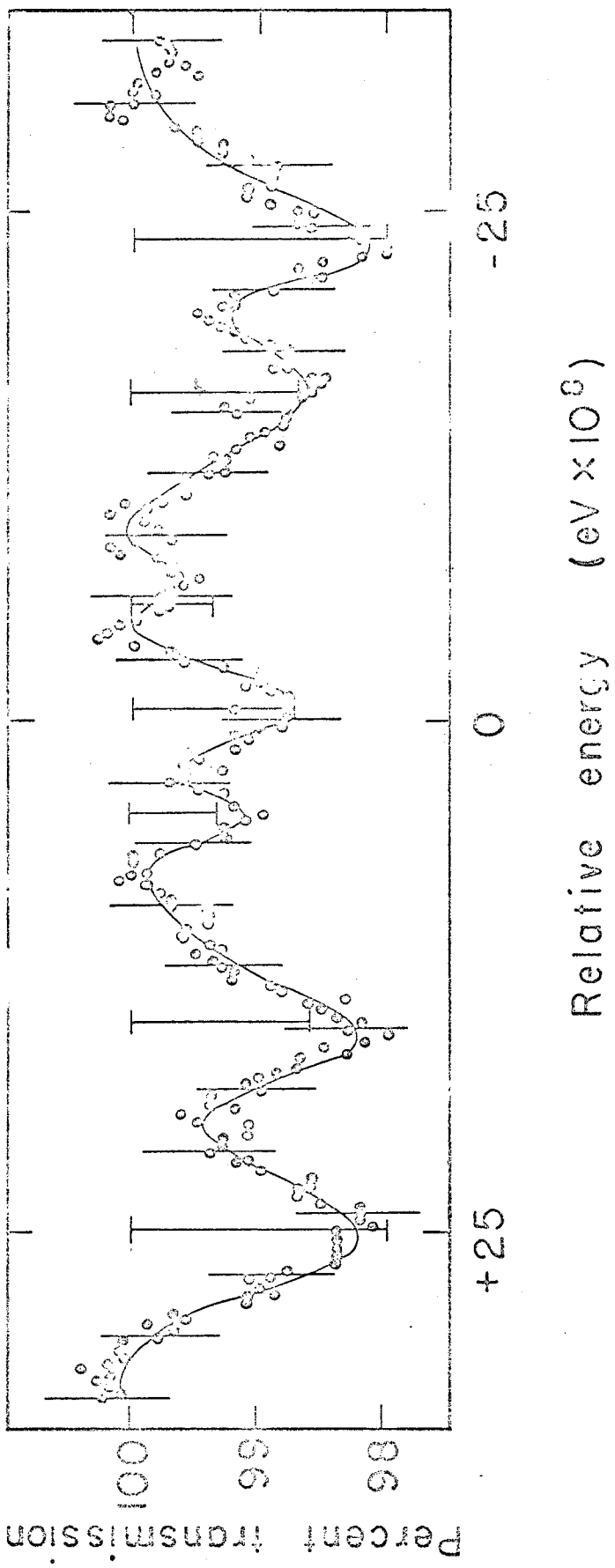

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Fig. 4