in Fig. 1(c). The predicted on-resonance dips in the third-harmonic line tend to be obscured by the experimental laser spectrum but some evidence for them survives in the focused-beam data, Fig. 2(h). Numerical calculation taking the laser spectrum into account yields results for third-harmonic emission consistent with the observed $(P^{\omega})^2$ dependence shown in Fig. 1(b). In addition, the fraction of irradiated atoms excited to the $9d\,^2D_{3/2}$ level can be determined from the measured value of F and the result, $10^{-3}\times 10^{\pm 1}$, also indicates significant but not complete saturation.

The experimental results have been explained qualitatively on the basis of saturation involving power broadening and population of the two-photon-resonant state with hole burning being important in a certain range of fundamental power. While we believe these effects are dominant, a significant role may also be played by two-step transitions from the $9d\,^2D_{3/2}$ to $6s\,^2S_{1/2}$ level where one or both steps are stimulated.[9] Our observation of such effects in cesium vapor will be discussed elsewhere. Saturation effects will be important in schemes using resonant nonlinear interactions to enhance frequency-conversion efficiency.[9]

It is a pleasure to acknowledge conversations with John Hurrell, B. J. Orr, and Charles C. Wang. We thank Charles K. Miller for assistance with computing and one of us (J.F.W.) gratefully acknowledges the hospitality of the Center for Laser Studies of the University of Southern California during the preparation of this manuscript.

---

*Research supported in part by the U. S. Air Force Office of Scientific Research under Grant No. 72-2302.

[1]K. M. Leung, J. F. Ward, and B. J. Orr, Phys. Rev. A 9, 2440 (1974).

[2]I. D. Abella, Phys. Rev. Lett. 9, 453 (1962).

[3]Shaul Yatsiv, William G. Wagner, Gerald S. Picus, and Fred J. McClung, Phys. Rev. Lett. 15, 614 (1965).

[4]Charles C. Wang and L. I. Davis, Jr., preceding Letter [Phys. Rev. Lett. 35, 650 (1975)].

[5]B. J. Orr and J. F. Ward, Mol. Phys. 20, 513 (1971).

[6]See, for example, I. D. Abella, N. A. Kurnit, and S. R. Hartmann, Phys. Rev. 141, 391 (1966).

[7]Some characteristic times relevant to this experiment are as follows: The laser pulse length is 30 nsec FWHM; the lifetime of the $9d\,^2D_{3/2}$ level against fluorescent decay to the $6p\,^2P_{3/2}$ level is calculated to be 2000 nsec; the natural lifetime of the $9d\,^2D_{3/2}$ level is calculated to be 200 nsec which is consistent with the measured fluorescent decay time at low cesium density but this decay time is shortened to $T_1 = 35$ nsec by collisions at the density (10^{16} cm^{-3}) used in the present experiments; T_2 is estimated to be in the range 1–30 nsec. $T^{(2)}$ is calculated to be 5 nsec for 2×10^5 in a single mode with area 0.03 cm^2. The parameter governing the inhomogeneous linewidth is $(\gamma\Omega)^{-1} = 0.22$ nsec.

[8]B. D. Fried and S. C. Conte, *The Plasma Dispersion Function* (Academic, New York, 1961).

[9]See, for example, R. T. Hodgson, P. P. Sorokin, and J. J. Wynne, Phys. Rev. Lett. 32, 343 (1974); D. M. Bloom, James T. Yardley, J. F. Young, and S. E. Harris, Appl. Phys. Lett. 24, 427 (1974).

Two-Electron—One-Photon Transitions in Heavy-Ion Collisions*

W. Wölfli, Ch. Stoller, G. Bonani, M. Suter, and M. Stöckli
Laboratorium für Kernphysik, Eidgenössische Technische Hochschule Zurich, 8049 Zürich, Switzerland
(Received 9 June 1975)

Heavy-ion–atom collisions at medium energies (~0.8 MeV/amu) yield a considerable probability for multiple inner-shell ionization. In the Ni-Ni, Ni-Fe, Fe-Ni, and Fe-Fe cases, distinct lines in the x-ray spectra are observed, which must be interpreted as a correlated two-electron jump into the doubly ionized K shell followed by the emission of only one photon carrying away the total transition energy.

In heavy-ion–atom collisions at medium energies, multiple inner-shell vacancies may be produced. If, for instance, both electrons are removed from the K shell of either the target atom or the projectile during such an encounter, the remaining holes will be filled up by subsequent transitions of two electrons from higher-lying shells. Normally these jumps will be accompanied by the emission of two characteristic x rays and/or the emission of two Auger electrons. But according to the predictions of Heisenberg,[1] Condon,[2] and Goudsmit and Gropper[3] it is also possible that both holes may be filled up by a simultaneous transition of two electrons. In this case only one photon with an energy slightly larger than twice the K transition energy will be emitted.

We would like to report here the existence of this effect, which has been observed accidentally during the investigation of the noncharacteristic part of the x-ray spectra produced in Ni-Ni, Ni-Fe, Fe-Ni, and Fe-Fe collisions. The inverse effect, the one-photon–two-electron excitation, has already been observed in optical absorption spectra,[4,5]

The experiment was performed at the Eidgenössische Technische Hochschule Zurich EN tandem accelerator. Momentum-analyzed beams of $^{58}Ni^{6+}$ and $^{56}Fe^{6+}$, produced in a Middleton-type ion source, were used to induce the x rays in ^{58}Ni (1 mg/cm^2) and thick natural Fe targets. In the first experimental setup the x rays were measured with a 30-mm^2, 3-mm-thick, Si(Li) detector (resolution 160 eV at 5.9 keV) perpendicular to the beam axis. The runs were monitored either by measuring the beam current or, in the case of the thin Ni target, by counting the elastically scattered heavy ions with a cooled Si-surface-barrier detector placed at 45° with respect to the beam axis. This information was also used to determine the various x-ray production cross sections relative to the well-known elastic Rutherford-scattering cross section.

Typical x-ray spectra obtained at a Ni beam energy of 40 MeV are displayed in Fig. 1. To reduce electronic pileup effects to a negligible amount (<0.02%), the total count rate and the intensities of the characteristic $K\alpha$ and $K\beta$ lines of the target atoms and the projectile were adjusted with appropriate pure Al (99.999%) absorbers placed between target and detector. All four spectra exhibit at least one small but statistically significant peak (denoted by $X1, X2, X3, X4$) superimposed on the broad noncharacteristic x-ray continua. These peaks have the following remarkable property (see Table I): The energy of peak $X1$ is slightly larger than twice the Ni $K\alpha$ and that of peak $X3$ slightly larger than twice the Fe $K\alpha$ transition energy. There is also some evidence for further but even weaker lines. Here we note that the energies of the peaks denoted by $X2$ and $X4$ is slightly larger than the sum of the $K\alpha$ and $K\beta$ transition energies in the corresponding atoms. The following tests were made to ensure that these lines are not produced by any background effect:

(1) The targets were checked for impurities using the ultrasensitive proton-induced x-ray analysis method.[6] No trace elements giving charac-

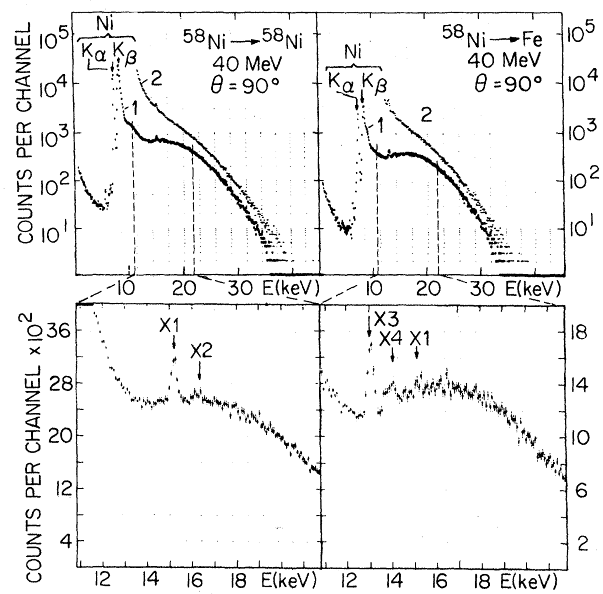

FIG. 1. Ni-Ni and Fe-Ni x-ray spectra. The upper figures show the total spectra. (Trace 1, measured spectrum; trace 2, spectrum corrected for absorption and detector efficiency.) In both cases a 720-μm Al absorber was used. The energy of the peaks denoted by $X1$ and $X2$ in the expanded part (lower) of the spectra agree with the following transition energies in the Ni atom: $E(X1) \approx 2E(K\alpha) + \Delta E_s$ and $E(X2) = E(K\alpha) + E(K\beta) + \Delta E_s$. Those of the peaks $X3$ and $X4$ are consistent with the corresponding transitions in the Fe atom.

teristic x rays at or in the neighborhood of the peaks under discussion were observed. Since the excitation cross section for protons is orders of magnitude larger and at the same time also the background radiation is much smaller than for Ni and Fe ions at these energies, the possibility of impurities can definitely be ruled out.

(2) γ rays produced by Coulomb excitation cannot be responsible for the peaks observed because possible γ-ray transitions have different energies.

(3) Electronic pileup effects can be excluded also, because of the following reasons: Taking into account that the total count rate was kept below 50 counts per second during all runs, it is impossible to explain the intensity of the observed peak by the well-known pulse-pair resolution ($\leqslant$ 2 μsec). Furthermore, since the $K\alpha$ lines are attenuated more than the $K\beta$ lines, one expects the $K\beta$-pileup peak to be the dominant effect. But in all four cases no peak has been observed at twice the $K\beta$ energy. In addition it was also verified experimentally that the energies of the peaks

TABLE I. X-ray energies in keV observed in Ni-Ni, Ni-Fe, Fe-Ni, and Fe-Fe collisions. All characteristic lines are shifted with respect to the theoretical values because of multiple vacancies in the outer shells of targets and projectile.

projectile target	x-ray emission angle	theoretical K_α -energy	Exp. K_α-energy	E(X1) and E(X3)	E(X2) and E(X4)	pile-up observed without absorber
Ni (40 MeV) Ni	90^o	7.477	7.530 ± 0.003	15.228 ± 0.010	16.174 ± 0.050	15.065 ± 0.02
Ni " Ni	30^o	7.727 7.477	7.739 ± 0.004 7.534 ± 0.004	 15.168 ± 0.025		
Ni " Fe	90^o	7.477 6.403	7.527 ± 0.004 6.471 ± 0.002	 13.080 ± 0.020	 13.820 ± 0.050	 12.917 ± 0.080
Ni " Fe	0^o	7.765 6.403	7.770 ± 0.010 6.465 ± 0.010	15.695 ± 0.030 13.080 ± 0.020		
Fe (41.5 MeV) Ni	90^o	6.403 7.477	6.456 ± 0.010 7.543 ± 0.010	13.025 ± 0.020	13.880 ± 0.070	
Fe " Ni	30^o	6.624 7.477	6.692 ± 0.010 7.531 ± 0.010	13.429 ± 0.010		
Fe " Fe	90^o	6.403	6.472 ± 0.010	13.048 ± 0.025	13.850 ± 0.100	
Fe " Fe	0^o	6.658 6.403	6.684 ± 0.010 6.460 ± 0.010	13.449 ± 0.025 13.098 ± 0.020		

$X1$ and $X3$ clearly are larger than those of the $K\alpha$ pileup peaks (see Table I).

(4) An investigation was made to determine whether these peaks exhibit a Doppler shift or not. For this purpose a second experimental setup, especially designed for x-ray angular distribution measurements, was used.[7] The spectra induced in the Ni target were taken at 90° and 30°, and those in the Fe target at 90° and 0°. The results, also listed in Table I, left no doubt that the observed peaks must be produced by radiative transitions in the target atom practically at rest as well as in the projectile.

Considering all results presented so far, it became clear that only the following two effects remained which can explain all properties of these peaks, namely a two-electron–two-photon or a two-electron–one-photon transition in the highly excited target and/or projectile atoms. Although the first effect is orders of magnitude more probable than the second one, it cannot explain the intensity of these peaks. The two photons emitted in this transition would have to be registered simultaneously by the detector. The probability for this is negligibly small in the present experiment because of the strong attenuation of the characteristic K lines (e.g., about 10^{-5} in the Ni-Ni and 10^{-6} in the Fe-Fe case) and the small solid angle of the detector (3.5×10^{-3} sr).

Therefore we must conclude that the observed peaks indicate the existence of a simultaneous two-electron jump accompanied by the emission of only one photon with an energy slightly larger than twice the corresponding K transition energies. This slight shift can be explained very easily by the reduced screening in the doubly ionized K shell. If the vacancies are filled by two L electrons then the transition energy is given by

$$E_x = 2E_{K\alpha} + \Delta E_s ,$$

for peaks $X1$ and $X3$; if an L and an M electron are involved, then

$$E_x = E_{K\alpha} + E_{K\beta} + \Delta E_s ,$$

for peaks $X2$ and $X4$. Neglecting the fine-structure splitting of the L and M shells, ΔE_s is about equal to the difference between the transition energies in a H-like atom. For the $K\alpha$ transition this difference is given by[8]

$$\Delta E_s = \tfrac{3}{8}\mathcal{R}[Z^2 - (Z-s)^2].$$

If we assume a screening factor of $s = \frac{5}{16}$, the following shifts are to be expected: for Ni ($Z = 28$),

$$\Delta E_s \cong 180 \text{ eV};$$

for Fe ($Z = 26$),

$$\Delta E_s \cong 165 \text{ eV}.$$

TABLE II. Cross sections and branching ratios of one-electron–one-photon ($K\alpha$), two-electron–two-photon ($K\alpha + \Delta E_s$), and two-electron–one-photon ($2K\alpha + \Delta E_s$) transitions. $K\alpha + \Delta E_s$ denotes the energy released in the first radiative electron transition to the doubly ionized K shell.

Projectile target	$\sigma(K\alpha)$ (b)	$\sigma(2K\alpha + \Delta E_s)$ (mb)	$\sigma(K\alpha + K\beta + \Delta E_s)$ (mb)	Ratio of $K\alpha$ to ($K\alpha + \Delta E_s$) transitions	Ratio of ($K\alpha + \Delta E_s$) to ($2K\alpha + \Delta E_s$) transitions
Ni Ni	4200 ± 400	4.5 ± 0.8	0.9 ± 0.5	80 ± 40	$(1.2 \pm 0.8) \times 10^4$
Ni Fe	Thick target			> 40 90 ± 40	$< 4.0 \times 10^4$ $(0.3 \pm 0.2) \times 10^4$
Fe	2900 ± 120	9.1 ± 2.0	1.9 ± 1.0	90 ± 50	$(0.4 \pm 0.3) \times 10^4$
Ni	1700 ± 250	1.6 ± 0.5	< 0.4	> 50	$< 2.0 \times 10^4$
Fe Fe	Thick target			80 ± 40	$(0.4 \pm 0.3) \times 10^4$

Both values are in good agreement with the measurements, as can be seen from Table I.

It is clear that if two vacancies can be filled up by a correlated electron jump then of course the two-electron–two-photon transition also must exist. Also in this case, because of the reduced screening, the energy of the x rays emitted during the first electron transitions are shifted by the same amount, producing a small satellite line adjacent to the undisturbed $K\alpha$ (or $K\beta$) line. Indeed an examination of the region in between $K\alpha$ and $K\beta$ lines clearly indicates the existence of this effect, which has already been reported by Richard, Hodge, and Moore.[9] Despite the limited resolution of our detector, it was possible to estimate the ratio of one-hole to two-hole production probability which, for instance, is about 80:1 in the Ni-Ni case, assuming equal fluorescence yields. The branching ratios between the two observed transition modes are compiled in Table II. The x-ray production cross sections are given only for the two thin-target cases. It is interesting to note that in the asymmetric Ni-Fe and Fe-Ni cases the correlated two-electron jumps into the K shell of the iron atom dominate, suggesting that the probability for the production of two holes is strongly Z dependent. The reason that the effect is also clearly visible in the Ni-Ni case can most probably be explained by the well-known enhanced ionization probability for symmetric systems.[10]

However we would like to point out that up to now no calculations exist with which the observed cross sections and/or branching ratios can be compared. We can only hope that the present results will stimulate new activities in a field which has been forgotten for almost fifty years.

The authors would like to acknowledge stimulating discussions with Professor W. Baltensperger and Dr. M. Simonius who also drew our attention to the existence of the effect discussed above.

*Work supported by the Swiss Foundation for Scientific Research.

[1]W. Heisenberg, Z. Phys. 32, 841 (1925).
[2]E. U. Condon, Phys. Rev. 36, 1121 (1930).
[3]S. Goudsmit and L. Gropper, Phys. Rev. 38, 225 (1931).
[4]R. P. Madden and K. Codling, Astrophys. J. 141, 364 (1965).
[5]H. A. Kuhn, *Atomic Spectra* (Academic, New York, 1970), 2nd ed., p. 304.
[6]G. Bonani, W. Wölfli, Ch. Stoller, and M. Suter, Laboratorium für Kernphysik, Annual Report, 1974 (unpublished), p. 206.
[7]W. Wölfli, Ch. Stoller, G. Bonani, M. Suter, and M. Stöckli, to be published.
[8]H. A. Bethe and E. E. Salpeter, *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1957), Vol. 35, p. 214.
[9]P. Richard, W. Hodge, and C. F. Moore, Phys. Rev. Lett. 29, 393 (1972).
[10]J. D. Garcia, R. J. Fortner, and T. M. Kavanagh, Rev. Mod Phys. 45, 111 (1973).