TIME INDEPENDENCE OF CHARGE STATES PRODUCED FOLLOWING ELECTRON CAPTURE IN Co57

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In a number of Mössbauer effect (ME) experiments using sources embedded in insulators, multiple emission lines have been observed which have been interpreted in terms of the formation of a metastable multiply charged ionization state.[1-9] These states are thought to be formed as a consequence of Auger processes following nuclear decay, and to have mean lifetimes (in favorable cases) comparable to those of the nuclear level in which the ME is observed.

We are engaged in a series of studies of such processes through the measurement of ME spectra at various delay times following the formation of the resonant level. In this Letter we report results on Co^{57} as an impurity in the oxides CoO and NiO, both of which have been studied extensively using the ME.[1,8-10] The experimental results on both systems have been discussed in terms of metastable Fe^{57} electronic charge states with lifetimes comparable to the 140-nsec mean life of the 14-keV nuclear level. Effects on this time scale should be easily observable in delayed-coincidence ME experiments. Our measurements show no evidence whatever for such time effects. It is thus clear that reinterpretations of many experiments interpreted in terms of this type of model are required.

The ME resonance of Co^{57} embedded in CoO was first studied by Wertheim,[1] who found (at room temperature) two partially resolved lines which could not be understood in terms of quadrupole splitting or magnetic hyperfine effects. The line positions (isomer shifts) led to the hypothesis that the lines arose from Fe atoms in +2 and +3 charge states. This identification was confirmed by low-temperature measurements of the magnetic hyperfine splitting in the antiferromagnetic regime below 292°K. Wertheim proposed that the Fe^{+2} line arose from stable states, whereas the Fe^{+3} line was produced as a result of Auger processes fol-

lowing electron capture in Co^{57}. Such higher charge states have often been observed in gases, where multiple ionization as high as +30 occurs.[11] Metastable states had not been previously inferred in solids. This proposal was discussed in detail by Pollak[12] who concluded that, following electron capture in Co^{57}, Auger processes rapidly produce (within a few nsec or less) a population of about 5% Fe^{+2} and 95% Fe^{+3}. From the approximate equal intensity of the two ME resonance peaks observed by Wertheim, Pollak inferred the mean life of the Fe^{+3} state in CoO at 300°K to be 140 ± 20 nsec.

We have tested this conclusion directly by performing delayed-coincidence ME measurements on sources of Co^{57} in CoO and NiO. The CoO source was prepared by reducing $Co(NO_3)_2$ to which $Co^{57}Cl_2$ had been added, in argon at 1000°C for 4 hours. The resulting brown-green powder was packaged in an argon atmosphere in a sealed Al holder for the measurements. X-ray studies on a nonradioactive sample of CoO identically prepared showed no diffraction rings not ascribable to CoO. The NiO source was similarly prepared by reduction of $Ni(NO_3)$ in argon at 1000°C for 4 hours.

Our measurement technique was similar to that of Lynch, Holland, and Hamermesh[13] and Wu et al.[14] Two photomultipliers were used to detect the 123- and 14-keV gamma rays from Co^{57}. The 123-keV gamma ray was used to start a time-to-amplitude converter, which was stopped by the arrival of a 14-keV gamma ray, thereby producing a pulse with height proportional to the elapsed time interval. Four single-channel analyzers selected four voltage (and thereby time) intervals which were used to control the particular quadrant of a RIDL 400-channel analyzer in which the pulses were stored. In each quadrant the particular channel in which a pulse was stored was determined by the instantaneous velocity of a single-line Fe^{57}-en-
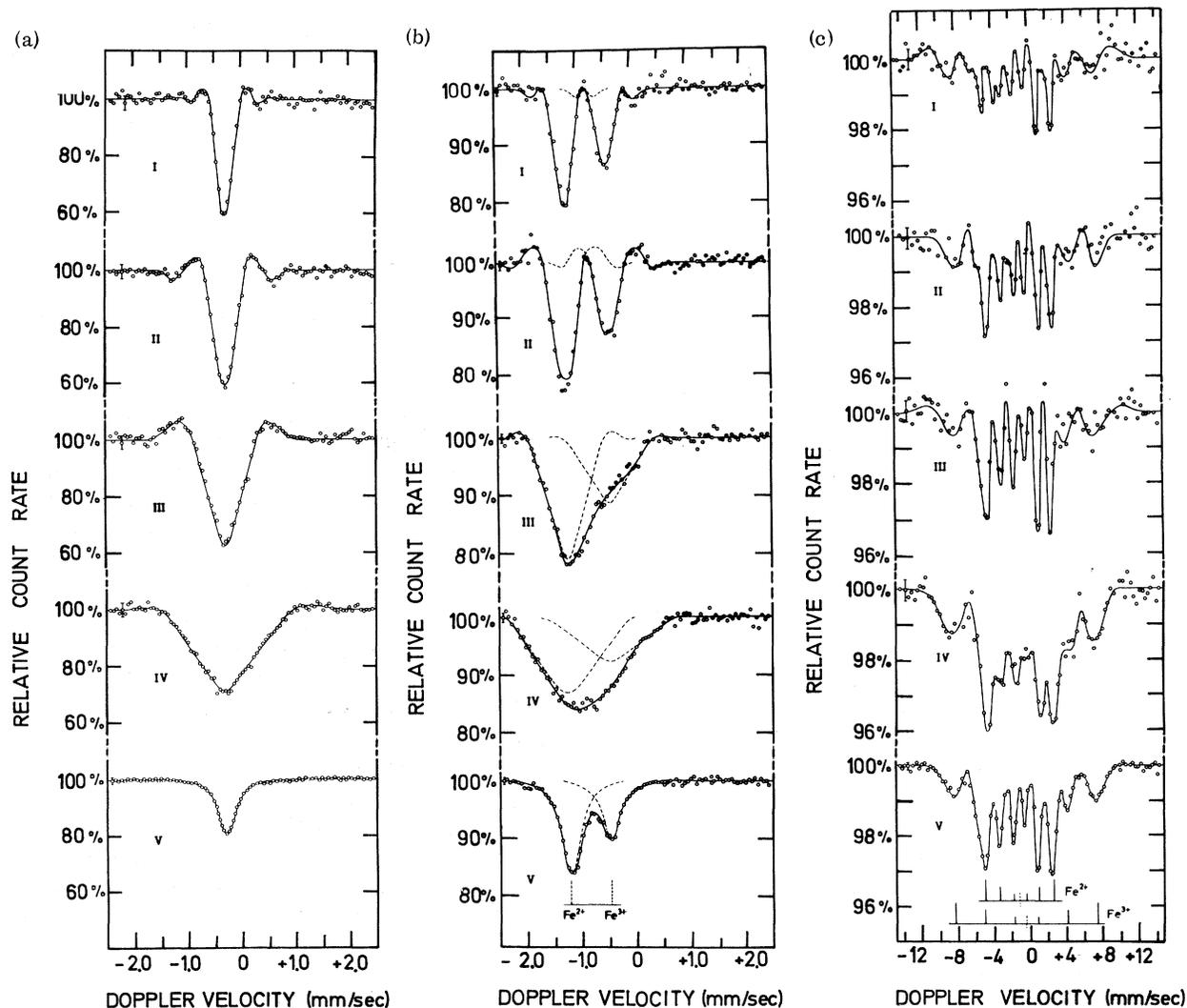
FIG. 1. Delay-coincidence Mössbauer spectra for various delay times using sources of (a) Co^{57} in Cu, (b) Co^{57} in CoO, and (c) Co^{57} in NiO, and a single-line absorber. The Cu source demonstrates the line-shape changes associated with "time filtering." In the latter two sources no evidence for metastable multiple-charge states is found, in contrast to predictions. In the three figures the time-delay intervals used are (from top to bottom) (I) 146-200 nsec, (II) 86-146 nsec, (III) 43-86 nsec, (IV) 4-43 nsec, (V) reference spectrum without coincidence. In (b) the resonances in CoO are decomposed using the line shapes of (a), thereby automatically including the line broadening and oscillations arising from "time filtering."

riched potassium ferrocyanide resonant absorber. Thus four resonance spectra could be obtained simultaneously corresponding to the four selected time-delay intervals. Time calibration and background corrections were determined directly from decay curves of the 14-keV level. The sources were made sufficiently weak that the random counting rate was about 3% for the longest delay times, and about 1% for the shortest delay times. The data were corrected for this background.

Figures 1(a), 1(b), and 1(c) present series of room-temperature resonance spectra at various delay times using sources of Co^{57} in Cu, Co^{57} in CoO, and Co^{57} in NiO. The delay-time intervals used were (from top to bottom) 146-200 nsec, 86-146 nsec, 43-86 nsec, and 4-43 nsec. The last resonance in each series is taken without coincidences and represents a time-average spectrum.

The time-average spectrum of CoO shows two well-resolved lines corresponding to Fe^{+2}

and Fe^{+3} occurring at -1.21 ± 0.01 and -0.46 ± 0.01 mm/sec with relative intensity ratios $I^{+3}/I^{+2} = 0.61 \pm 0.02$. In the coincidence spectra "time-filtering" effects[13,14] are clearly evident through pronounced line broadening at short times and oscillation of the resonance strength as a function of velocity. These effects may be calculated directly. We have found, however, that because the calculation is complicated by the greater than the natural absorber linewidth, a more convenient procedure is to determine experimentally the "time-filtered line shape" for each timing interval using an unsplit source of Co^{57} in Cu. The decomposition of the CoO data [Fig. 1(b)] assumes for each delay-time interval the line shape found for the Cu source [Fig. 1(a)] and the line positions and intensities determined from the time-average CoO spectrum. The effect of the "negative absorption" associated with time filtering is particularly evident in the CoO resonance in the time interval 43-86 nsec.

The decomposition shows the relative intensity ratio I^{+3}/I^{+2} to remain constant at 0.61 ± 0.04 for all delay times studied. This is in marked contrast to the Pollak model,[12] on which the intensity ratio would be expected to vary between $I^{+3}/I^{+2} = 5.0$ in the time interval 4-43 nsec and $I^{+3}/I^{+2} = 0.43$ in the time interval 146-200 nsec.

In order to test further the conclusion of the time independence of the intensity ratios, measurements were made at higher temperature (123°C) where the time-average intensity ratio $I^{+3}/I^{+2} = 1.27 \pm 0.05$. Again no time-dependent changes in intensity were observed. Measurements without coincidence were made at a number of different temperatures. The intensity ratios at each temperature were in agreement with the careful measurements of Bhide and Shenoy.[9,15]

These results lead to at least two possible interpretations: (a) Several Fe charge states are established on a time scale fast compared to the 140-nsec Fe^{57} mean lifetime and thereafter remain metastable for times long compared to the lifetime of the nuclear state, but sufficiently short so as to remain undetected by conventional chemical techniques. (b) The charge states are rapidly established as chemically stable entities. These possibilities were investigated by preparing absorbers containing $\frac{1}{2}$ and 1% Fe in CoO. One absorber was prepared from ferric iron [$Fe(NO_3)_3$] and the other from

ferrous iron ($FeCl_2$). Each absorber was found to exhibit two resonance lines at velocities corresponding to Fe^{+2} and Fe^{+3}. However, the absorber prepared from ferric Fe showed a considerably stronger resonance corresponding to Fe^{+3} than the one prepared from ferrous Fe. Thus Fe^{+3} can be stabilized in CoO.

The several ME lines observed in CoO, therefore, are not associated with metastable charge states created following electron capture, but result from the local chemical environment of Fe in CoO. This environment can be effected by the sample preparation, as is evidenced by changes in the relative intensities in samples prepared from ferric and ferrous Fe. The dependence upon sample preparation is particularly apparent in the work of Bearden, Mattern, and Hart,[10] who failed to obtain any evidence for Fe^{+3} in CoO. The chemical mechanism stabilizing Fe^{+3} in the CoO lattice is as yet obscure. Excess oxygen located interstitially is one possibility, but oxygen solubility measurements[16] show that only a few percent excess oxygen at most can exist in the lattice in equilibrium. A possibly more plausible explanation involves ferric ion stabilization by cation vacancies. Vacancy concentrations of a few percent can occur in CoO.[16] If one assumes a vacancy to stabilize the +3 state in any Fe atom located on a nearby Co site, then quite small concentrations are sufficient to account for the Fe^{+3} abundances typically found at room temperature. At high temperature, on this model, the increased mobility of vacancies[16] is responsible for the great increase in the abundance of Fe^{+3} ions. On this model the failure of Bearden, Mattern, and Hart[10] to observe Fe^{+3} suggests precise stoichiometry in their samples. We wish to emphasize, however, that no quantitative explanation is thus far available for the stability of Fe^{+3} in the CoO lattice.

Co^{57} in NiO behaves in a manner closely analogous to Co^{57} in CoO, the major difference being the much higher Néel temperature of 523°K in NiO. We have made delayed-coincidence measurements on a source of Co^{57} in NiO at room temperature. The results are shown in Fig. 1(c) and are identical to those found in CoO in that no evidence for time effects was obtained, in contrast to the large effects expected. Our time-average results at several temperatures were in agreement with those of Bhide and Shenoy.[8]

NiO and CoO are semiconducting oxides in

which stoichiometry is notoriously difficult to achieve. The stability of Fe^{+3} as an impurity in these materials is perhaps not too surprising. Experiments interpreted in terms of metastable multiple-charge states have been reported on several other materials which, in addition to not being oxides, are good insulators and in which, therefore, metastable charge states may be expected to remain stable for long periods.[3-7] Measurements on a number of such systems are in progress utilizing shorter lived nuclear levels as well as Fe^{57}.

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ZERO-POINT SPIN DEVIATION IN ANTIFERROMAGNETS

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Spin-wave theories of antiferromagnets predict a zero-point spin deviation of a few percent from the completely ordered state. Attempts have been made to observe this effect by using nmr measurements in the antiferromagnetic state to find the effective field acting on the nuclei of the magnetic ions. The largest part of this field is $A\langle S\rangle$ where $A\vec{S}\cdot\vec{I}$ is the hyperfine interaction and $\langle S\rangle$ is the time-averaged electronic spin. The value of A is usually taken from esr data on magnetically dilute salts and hence $\langle S\rangle$ can be deduced. This procedure has been followed in some recent investigations of Mn^{2+} antiferromagnets with the results given in Table I. The predicted deviations are not observed; the experimental values are consistently higher than expected. The observation of $\langle S\rangle/S > 1$ is clearly anomalous and several authors[1-3] have suggested that the assumed value of A may be in error. In this Letter we propose that $A(Mn^{2+})$ is in fact larger in the antiferromagnetic state due to the transfer of unpaired electron spin from one magnetic ion to the next.

There is experimental evidence that such transfers can be appreciable. For example,