Study of Magnetic Properties and Lattice Dynamics of the $Cd_x Co_{1-x}$ Ferrite System by Mössbauer Effect

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ABSTRACT

The magnetic properties and lattice dynamics of the spinel ferrite system $Cd_x Co_{1-x} Fe_2 O_4$ (x = 0.0, 0.1, . . . , and 1.) were studied in the temperature range between 78 to $800°K$. The results showed that the samples with x = 0.0 up to 0.5 are ferrimagnetic at room temperature, and a magnetic disorder transformation started to appear at x = 0.6. The Neel temperature was found to decrease with increasing cadmium concentration. The reduced hyperfine magnetic fields for the A- and the B- sites were found to follow the Brillouin function and One-Third-Power Law. The results showed also that the introduction of the Cd^{2+} ions decreased the f-value and Debye temperature, while the mean square velocity of the ^{57}Fe nucleus was not affected greatly specially at low and normal temperatures. The anisotropic energy, for $0.1 \leqslant X \leqslant 0.9$ was found to be of the order of 2×10^{-14} erg.

دراسة الخواص المغناطيسية والحركات الديناميكية

لشبكة التركيب البلوري

لمجموعة فريت الاسبنل

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تم في هذا البحث دراسة الخواص المغناطيسية والحركات الديناميكية والخواص الحرارية لشبكةالتركيب البلوري لمجموعة فريت الاسبنل كد كو ح أ ، حيث س = صفر ، ٠,١ ، ٠,٢ ، ٠٠٠ ، ١ باستخدام ظاهرة موسبأور ولقد اجريت قياسات الموسباور لكل عينه من عينات المجموعة في درجات حرارة تتراوح بين ٧٨ الى ٨٠٠ ك . هذا ولقد اوضحت النتائج ان العينات التي لا تزيد نسبة الكادميوم فيها عن٠,٥(س = ٠,٥)تكون في الحالة الفريغناطيسية في درجة حرارة الغرفة ثم تبدأ العينات في التحول الى الحالة البارامغناطيسية بزيادة الكادميوم عن هذه النسبة ، كما وجد ان درجة حرارة نيل تقل بزيادة نسبة تركيز الكادميون في الفريت . ولقد اظهرت النتائج ايضا ان العينات التي تحتوي علي نسبة تركيز الكادميوم اقل من٠,٤ ـ تتبع مجالاتها ـ المغناطيسية المختزلة لدالة بريلوين المميزة للحديد ذات العزم الزاوي ٢/٥ ، وكذلك تتبع قانون الاس ٣/١ الذي يصف الحالة المغناطيسية للتجويفات داخل الشبكية .

ومن نتائج هذه الدراسة ايضا امكن تعيين درجة حرارة ديباي واحتمال حدوث الامتصاص الرنيني ولقد وجد ان كل منهما يقل بالتدريج مع زيادة نسبة تركيز الكادميوم بينما يظل متوسط مربع سرعة نواه ذرة الحديد ٥٧ ثابتا تقريبا لا يتأثر بزيادة الكادميوم وخصوصا في درجات الحرارة المنخفضة . هذا ولقد تم كذلك حساب طاقة تباين الاوضاع داخل الشبكية للتركيزات من س = ١,٠ الى س = ٠,٩ ووجد انها تكون في حدود ٢ × ١٠⁻¹⁴ إرج

Introduction

The magnetic properties of several mixed ferrites with spinel-type crystal structure have been the subject of many investigations using different techniques [1-6]. An example of these ferrites is provided by the series of compounds with the general formula $Me\,Fe_2\,O_4$ where Me is a mixture of diamagnetic elements as Zn^{2+} or Cd^{2+} and transition elements as Ni^{2+} or Co^{2+}. In these compounds, the cations are distributed among octahedral (B) and tetrahedral (A) interstitial sites of a face-centred cubic oxygen lattice.

In a previous work [7] we applied the Mössbauer Effect technique for studying the magnetic properties of $Cd_X\,Ni_{1-X}\,Fe_2\,O_4$ series and in the present work we are dealing with the study of the magnetic behaviour of the series $Cd_X\,Co_{1-X}\,Fe_2\,O_4$ at different temperatures.

Experimental

Eleven samples for the ferrite system $Cd_X\,Co_{1-X}\,Fe_2\,O_4$, where $0 \leqslant X \leqslant 1$, were prepared by the usual ceramic sintering process [8], in steps of 0.1. Pure constituent oxides were mixed, pressed, prefired at $900^\circ C$ for 30 hours, then sintered at $1100^\circ C$ for 6 hours and were annealed in air. The ferrites formation were proved by X-ray diffraction. The lattice constant for each member was calculated and found to vary from 8.365 ± 0.019 Å for x = 0.0 to 8.676 ± 0.017 $^\circ A$ for x = 1.0. The Mössbauer Effect spectra were measured over the temperature range from 78 to $800^\circ K$.

Results

Magnetic Properties

The room temperature Mössbauer Effect spectra of the samples with x = 0.0 up to 0.6 showed magnetic hyperfine patterns. The samples with x = 0.7 up to 1.0 showed paramagnetic doublets only. The values of the calculated hyperfine magnetic fields for the A and B- sites at different temperatures are plotted in Fig. 1, for sample with Cd concentration x = 0.3. The relation between Neel temperature (T_N) and x is plotted in Fig. 2. It was shown that as x increased, T_N decreased. The obtained value of Neel temperature for $CoFe_2\,O_4$ is exactly the same as the value reported by Schucle et al. [9] using static magnetic measurements.

The curves of $H_{eff}(T)/H_{eff}(O)$ versus T/T_N for both A- and B- sites (Fig. 3) follow the Brillouin function characteristic of iron with J = 5/2. These curves showed also that the hyperfine magnetic field at the ^{57}Fe nuclei in the B-site at a certain value of T/T_N decreased on replacing iron ions in the A-site by cobalt ions. The log-log plot of these values (Fig. 4) showed straight lines for both A- and B- sites verifying the One-Third-Power Law [10] which describes the substance magnetization for samples with $0 \leqslant X \leqslant 0.4$.
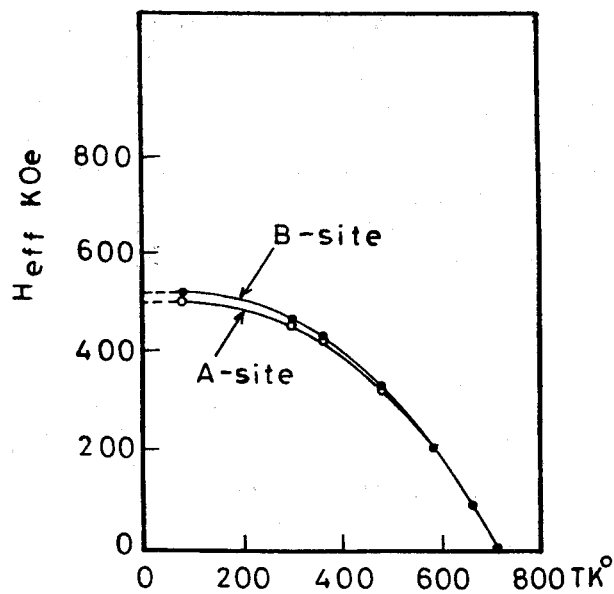
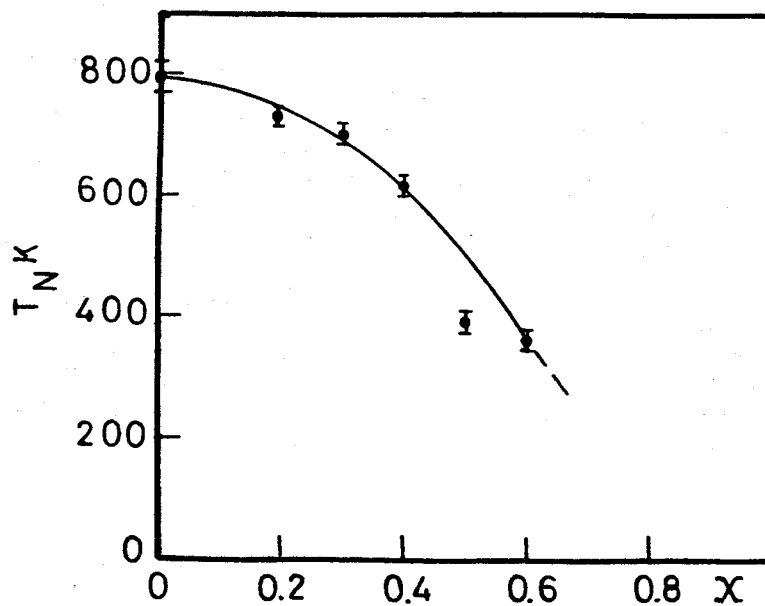*Fig. 1:* Variation of hyperfine fields in $Cd_{0.3} Co_{0.7} Fe_2 O_4$

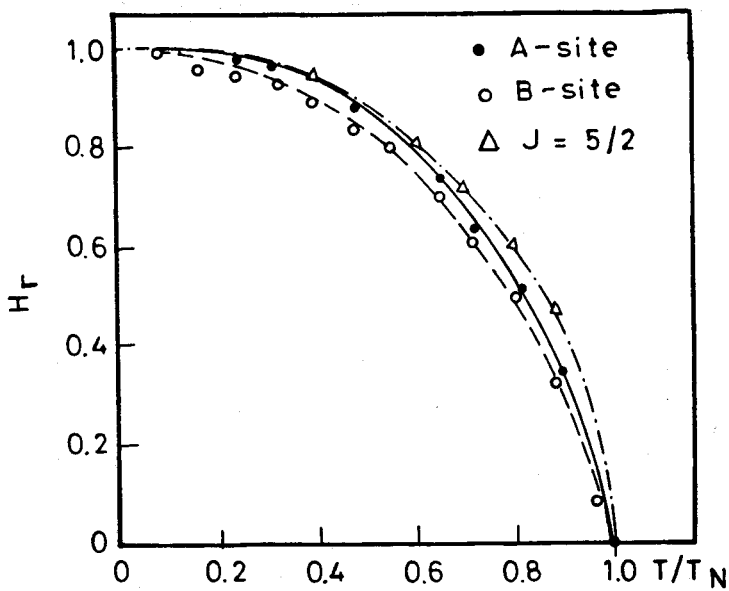*Fig. 2:* Variation of Neel temperature T_N of $Cd_x Co_{1-x} Fe_2 O_4$ system as function of x.

Fig. 3: The Brillouin curve for J = 5/2 with reduced hyperfine fields for
$Cd_{0.4}Co_{0.6}Fe_2O_4$ VS T/T_N

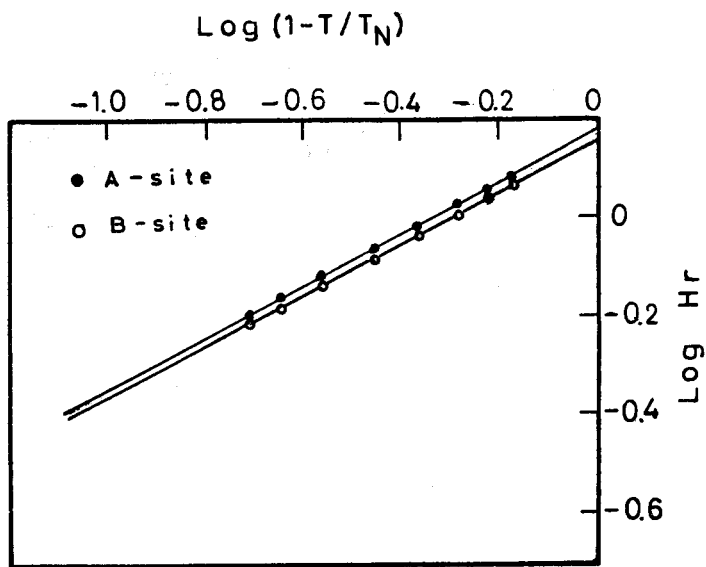*Fig. 4:* One-Third-Power Law, as applied for $Cd_{0.4}Co_{0.6}Fe_2O_4$ sample.

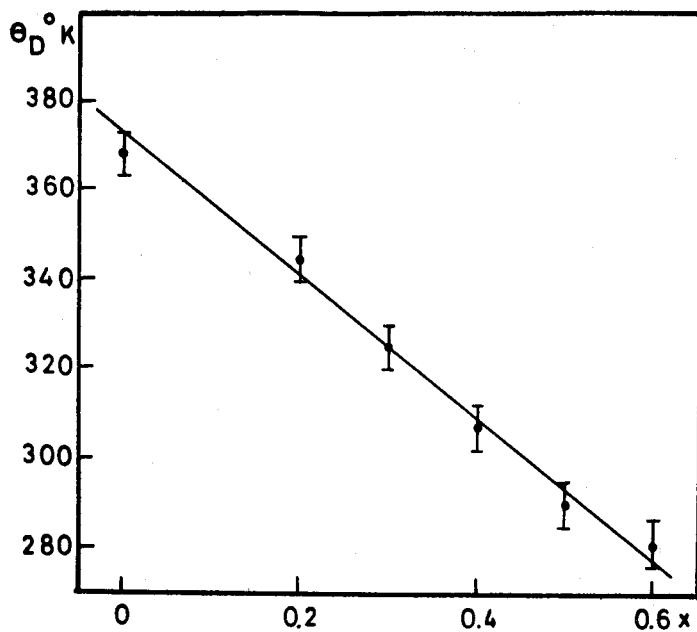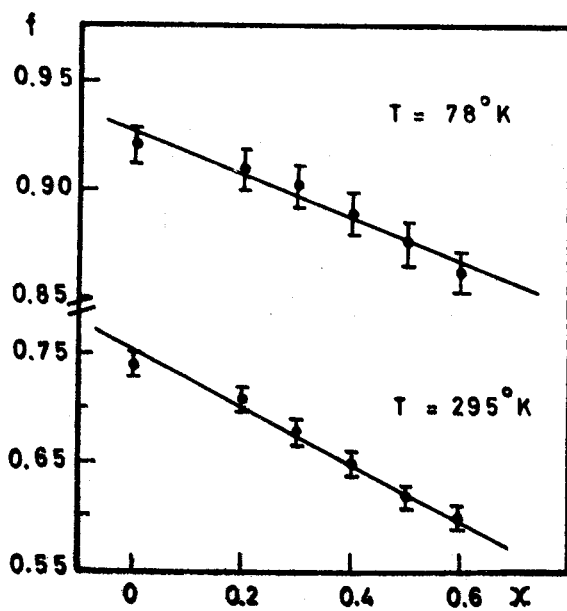*Fig. 5a:* Debye temperature for Cd – Co ferrite system versus x.

Fig. 5b: Variation of f-value with x at room and liquid nitrogen temperature.

Lattice Dynamics

In the Debye approximation for lattice vibrations, the f-value was used to calculate the Debye temperature θ_D, from the relation [11]:

$$\ln f \propto \ln A_{ex} \propto \frac{6E_rT}{K\theta_D^2}$$

Where A_{ex} is the experimental area, E_r is the free atom recoil energy, T is the absolute temperature and K is Boltzmann's constant. The value of θ_D was calculated for $0 \leqslant X \leqslant 0.6$, its variation with x is shown in Fig. 5a. The obtained values of Debye temperature of the system could be used to calculate the f-values at different temperatures. The values were found to decrease as the Cd-content increased, as shown in Fig. 5b.

The mean square amplitude of the vibration $\langle x^2 \rangle$ of the ^{57}Fe nucleus in the direction of emission of the gamma rays, averaged over the lifetime of its first excited state, is calculated from the relation: $f = \exp\left(-\langle x^2 \rangle / \lambda^2\right)$ and is found to increase by increasing the Cd − concentration (Fig. 6).

The mean square velocity $\langle v^2 \rangle$ of probe ^{57}Fe nucleus is calculated from the relation:

$$\ln f = 2 \frac{C^2}{\lambda^2} \frac{\langle x^2 \rangle}{\langle v^2 \rangle} \frac{\Delta E}{E_\gamma} \quad \text{where } \Delta E \text{ is the experimental value of isomer shift.}$$
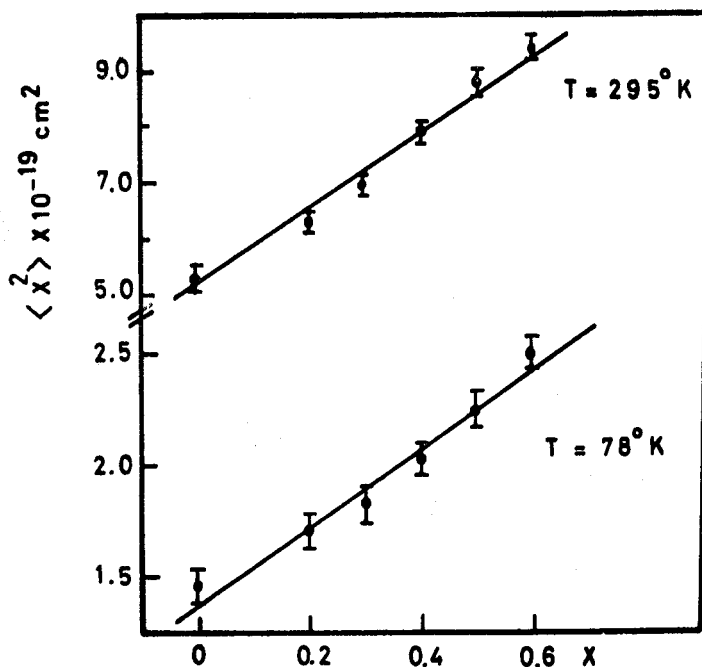

Fig. 6: Variation of the mean square displacement at room and liquid nitrogen temperatures versus x.

The variation of $\langle v^2 \rangle$ with temperature is shown in Fig. 7. This curve shows that $\langle v^2 \rangle$ is nearly constant for the A- site with varying Cd- content, while it differs slightly for the B- site, specially at high temperatures.

The anisotropic energy at room temperature is calculated from the spectrum of the sample with x = 0.6 where relaxation effects appeared due to magnetic disorder transformation, using the relation [12]:

$$A(T)/A_{max.} = \exp(-w/KT)$$

where A(T) is the relative amplitude of the central peak at temperature $T°K$, and A_{max} is the relative amplitude of the paramagnetic spectrum. The anisotropic energy w is found to be 2×10^{-14} erg.
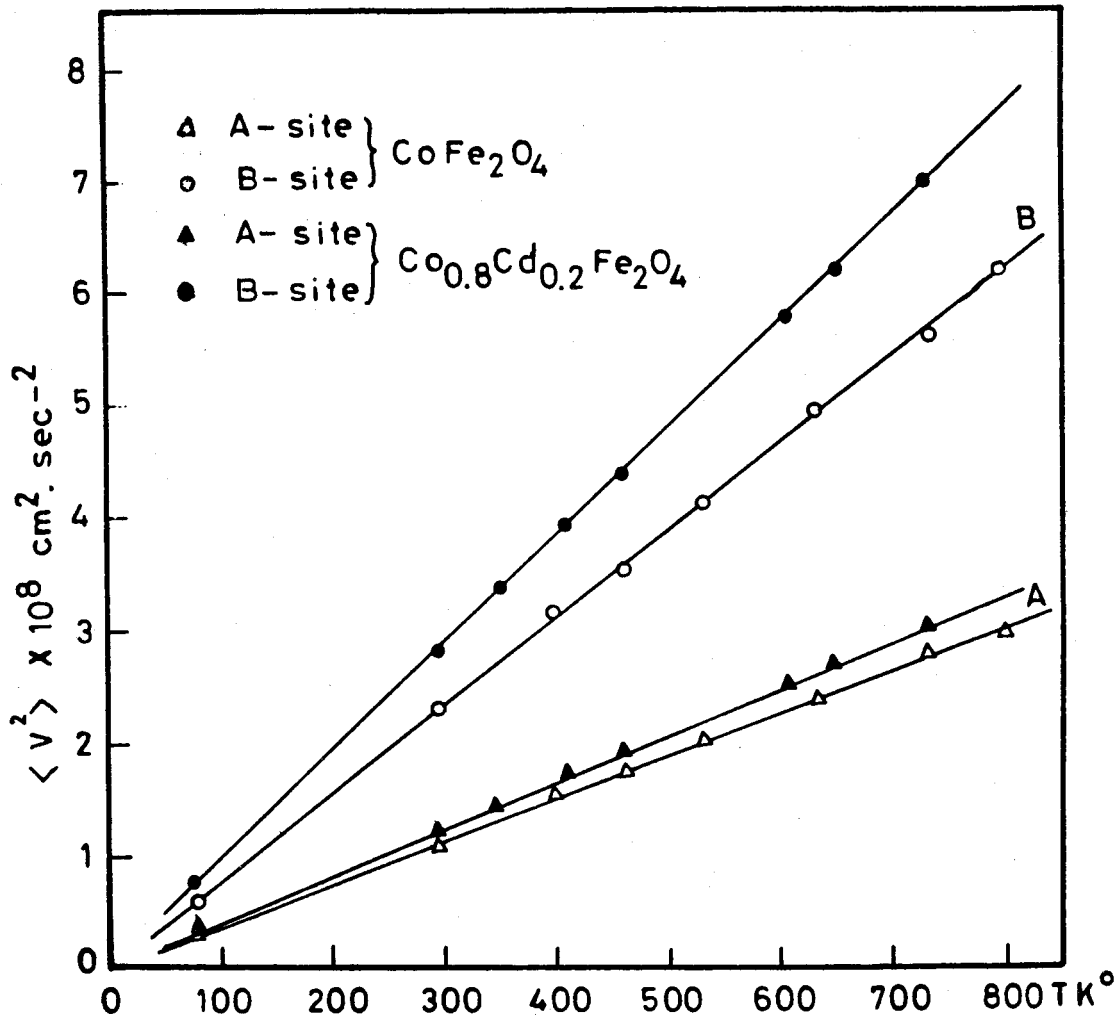

Fig. 7: Variation of the mean square velocity $\langle v^2 \rangle$ with different temperatures.

Discussion

The preceeding results showed that the compounds for $x = 0.0$ up to 0.6 are in a ferrimagnetic state at room temperature, for $x > 0.6$ the compounds are in the paramagnetic state. It is seen also that the nuclear magnetic field is smaller for the A-site Fe^{3+} ions than for the B-site ions, (Fig. 2). This can be due to the nature of the intersublattice magnetic bonds, beside the slight covalency of the tetrahedral iron ions. Since each tetrahedral iron ion will have on the average half of its intersublattice magnetic bonds with Co^{2+} and the other half with Fe^{3+} ions, while every octahedral Fe^{3+} ion will have on the average three quarters of the magnetic bonds with iron and one quarter with Co^{2+} [7]; so, it could be concluded that the $Fe^{3+} - O^{2-} - Fe^{3+}$ interaction is stronger than that of $Fe^{3+} - O^{2-} - Co^{2+}$.

The decrease of the B-site hyperfine magnetic fields at the Fe^{3+} nuclei at a certain value of T/T_N, on replacing iron ions in A-site by cobalt ions, can be interpreted also on the basis of the number of nearest magnetic neighbours where the $Co(A) - Fe(B)$ exchange interaction is less than $Fe(A) - Fe(B)$ interaction.

The increase of $\langle x^2 \rangle$ on increasing the Cd-concentration can be due to the increase of spacing of the B-site when it is distorted by the introduction of Cd^{2+} ions (radius 0.973 Å) in the nearest neighbour A-sites. Consequently the decrease in the values of f and θ_D on increasing the Cd-concentration.

REFERENCES

1. E. W. Gorter, Philips Res. Rep. *9*, 1 (1954).
2. Y. Yafet and C. Kittel, Phys. Rev. *87*, 290 (1952).
3. J. M. Daniels and A. Rosencwaig, Can. J. Phys. *48*, 381 (1970).
4. N. A. Eissa and A. A. Bahgat, Int. Conf. on the Mössbauer Effect, Corfu, Greece (1976). J. Phys., *37*, No. 12, C_6-575 (1976).
5. A. Lushmanov, S. Ligenza, M. Fayek and A. Koczarov, Phys. Stat. Sol., *A7*, 71 (1971).
6. L. K. Leung, B. J. Evans and A. A. Morrish, Phys. Rev., *88*, 29 (1973).
7. N. A. Eissa, A. A. Bahgat and M. K. Fayek, Hyperfine Interactions *5*, 137 (1978).
8. N. A. Eissa, A. A. Bahgat, A. H. Mohamed and S. A. Salah, J. Am. Ceram. Soc., *59*, 327 (1976).
9. W. J. Schuela, S. Shtrikman and D. Ireves, J. Appl. Phys. *36*, 3, 1010 (1965).
10. E. Callen and H. Collen, J. App. Phys. *36*, 3, 1140 (1965).
11. G. K. Wertheim, *Mössbauer Effect: Principles and Applications;* Academic Press, New York (1964).
12. L. May, *An Introduction to Mössbauer Spectroscopy*, Plenum Press, New York (1971).