and we proceed to find $b(n',\mathbf{k}';n,\mathbf{k})$. From (A11) we have

$$(\mathcal{H}^0-E_{n\mathbf{k}}{}^0)\theta_{n\mathbf{k}}=(E_{n\mathbf{k}}{}^0-\mathcal{H}^0)\zeta_{n\mathbf{k}}-U'\Psi_{n\mathbf{k}}{}^0. \quad \text{(A17)}$$

Taking the scalar product with $\Psi_{n'\mathbf{k}'}{}^0$ gives

$$(E_{n'\mathbf{k}'}{}^0-E_{n\mathbf{k}}{}^0)b(n',\mathbf{k}';n,\mathbf{k})$$
$$=(E_{n\mathbf{k}}{}^0-E_{n'\mathbf{k}'}{}^0)\langle\Psi_{n'\mathbf{k}'}{}^0|\zeta_{n\mathbf{k}}\rangle-\langle\Psi_{n'\mathbf{k}'}{}^0|U'|\Psi_{n\mathbf{k}}{}^0\rangle, \quad \text{(A18)}$$

or

$$b(n',\mathbf{k}';n,\mathbf{k})=-\langle\Psi_{n'\mathbf{k}'}{}^0|\zeta_{n\mathbf{k}}\rangle+\frac{\langle\Psi_{n'\mathbf{k}'}{}^0|U'|\Psi_{n\mathbf{k}}{}^0\rangle}{E_{n\mathbf{k}}{}^0-E_{n'\mathbf{k}'}{}^0}. \quad \text{(A19)}$$

Substituting the expression into (A16) and using (A3), we have

$$\mathfrak{M}(n',\mathbf{k}';n,\mathbf{k})=\langle\Psi_{n'\mathbf{k}'}{}^0|U'|\Psi_{n\mathbf{k}}{}^0\rangle. \quad \text{(A20)}$$

The effect of the core motion is identically cancelled out. This is seen to be consequence of the first-order perturbation nature of the argument which in turn is a consequence of the phonon approximation. There is no communication among the two scattered states and the other states as would occur in higher order.

PHYSICAL REVIEW VOLUME 157, NUMBER 3 15 MAY 1967

Evidence for Interstitial Cobalt in Indium by Mössbauer Spectroscopy

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(Received 20 December 1966)

The Mössbauer effect for Fe^{57} in indium was measured from helium temperature to near the melting point. Contrary to a previous report, we found no evidence for large anharmonic effects. The high Debye-Waller factor indicates interstitial solution of Co^{57} in indium metal.

In the early period of Mössbauer investigations, the resonance effect for Fe^{57} believed to be dissolved in indium was investigated[1,2] and an anomalous result reported: The Debye-Waller factor was quite small (≈ 0.5) at low temperature, and showed very little temperature dependence over the temperature range from near absolute zero to the melting point of indium. Since this result has been widely accepted and quoted as evidence for extreme anharmonic behavior,[3] we felt it desirable to reinvestigate the question. Our results, in contrast to the original ones, show a normal temperature dependence for the Debye-Waller factor, and hence no indications of large anharmonicity. The large Debye-Waller factor at elevated temperature is consistent with the assumption that the cobalt (and its daughter iron) are in interstitial positions in indium.

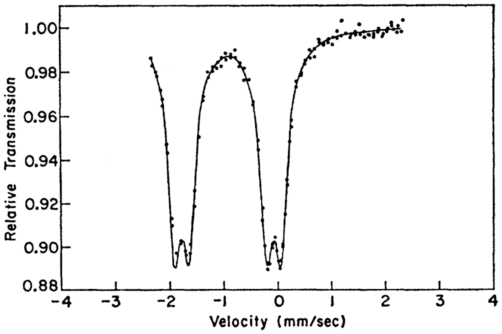

FIG. 1. Mössbauer absorption spectrum of a Co^{57} in In source at 80°K, and an absorber of $\mathrm{Na_2Fe(CN)_5NO\cdot 2H_2O}$ at room temperature.

Since the solid solubility of iron and cobalt[4] in indium is extremely small (not measurable by conventional methods), the Mössbauer effect can be studied only by a "source" experiment, i.e., by dissolving carrier-free Co^{57} in indium and studying the γ rays of the Fe^{57} arising from the decay of the Co^{57}. To ensure that the Co^{57} was indeed in solution, we used a method of preparation different from that of the original investigators. Co^{57} was electroplated onto an indium foil, which was then compacted and heated to 900°C in hydrogen to ensure reduction of any oxide and the formation of a homogeneous *liquid* solution.[5] The sample was then cooled quickly, and again converted to foil by compression between steel plates followed by cold rolling. The ratio of 14-keV γ rays to Fe K x rays was consistent with the assumption that the cobalt was indeed homogeneously distributed through the material.

The Mössbauer spectrum observed for this source (Co^{57} in indium at 80°K) versus a quadrupole-split absorber of $\mathrm{Na_2Fe(CN)_5NO\cdot 2H_2O}$ at room temperature is shown in Fig. 1. From the spectrum the following values can be deduced: isomer shift $\delta=-0.91\pm0.01$ mm/sec and quadrupole splitting (peak separation) for

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Fe^{57} in In, $\Delta E_Q = 0.28 \pm 0.02$ mm/sec. With the same source and absorber both at room temperature, the isomer shift is -0.78 ± 0.01 mm/sec. Unfortunately, the previous investigators did not publish a spectrum or report isomer shift or quadrupole splitting, so that a comparison with their work in regard to these parameters is not possible. The slight difference in the peak heights is insensitive to temperature, but changed with mechanical working of the sample. This indicates the presence of a texture (nonrandom distribution of crystallite orientations).

We determined the Debye-Waller factor as a function of temperature, using the "black absorber" technique.[6] The absorber was prepared from lithium and ammonium fluoroferrates and contained 10 ± 1 mg/cm^2 of Fe^{57}. It absorbed $\sim 97\%$ of the resonant γ rays. The incomplete blackness of our absorber and the effects of Compton scattering and self-absorption in the source and source holder were roughly corrected for by multiplying the raw f values by 1.04. We feel that the relative f values are quite accurate. However, the background correction was only made crudely. Therefore, the uncertainty in the absolute values is about $\pm 7\%$. The precautions necessary to achieve more precise f values are not justified since the indium lattice is anisotropic and the source had an undetermined amount of texture.

Our results, shown in Fig. 2, indicate that the temperature dependence of the Debye-Waller factor for Fe^{57} in indium is quite normal in comparison with that observed for other solutes, e.g., gold and copper.[7] We see no evidence for marked anharmonic effects. One somewhat surprising feature, however, is that the magnitude of the effect is larger than that expected on the basis of a simple model in which the iron simply substitutes for indium, without change in force constants. Such a model[8] predicts a room-temperature value of about 0.15–0.2. Since the iron atom is much smaller than the indium atom, it would be expected to be less strongly held in place than an indium atom, and the room-temperature value of f should be even lower. A plausible interpretation is that the cobalt (and daughter iron) is in ***interstitial*** rather than substitutional solution in indium. If the iron atoms are indeed crowded into interstitial positions, one might expect that the restoring forces acting on them would be larger than the forces between indium atoms and thus account qualitatively for the relatively large Debye-Waller factor. Seith and Keil[9] interpreted the high diffusivity of gold and silver in lead in terms of an interstitial diffusion mechanism. Recently, theoretical and experimental work[10,11] confirmed the idea that noble metals dissolve interstitially in metals like lead, tin, cadmium, and indium. The theoretical arguments also apply to cobalt.

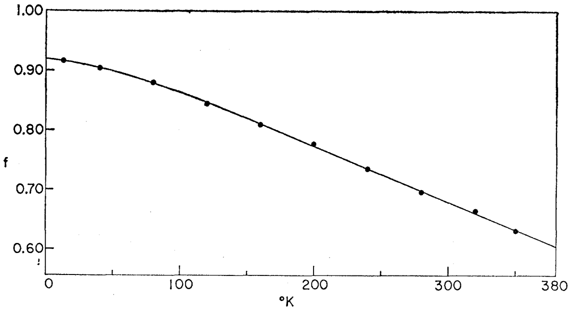

FIG. 2. Debye-Waller factor f as a function of temperature in °K.

The time scale in Mössbauer spectroscopy is the mean lifetime of the excited state τ which determines the linewidth (for the 14.4-keV state of Fe^{57}, $\tau \approx 10^{-7}$ sec). Diffusion broadening of the resonance line will become significant when the mean jump frequency ν of the resonance atom in the lattice approaches $1/\tau$.[12] Since interstitial diffusion can have a rather low activation energy of motion, one might expect to observe some line broadening of this origin. We have not observed significant line broadening up to 147°C (melting point of In$=156$°C) indicating $1/\tau \gg \nu$. From the diffusion equation for interstitials $\nu = ZF \exp(-E_m/kT)$, where Z represents the number of equivalent neighbor sites and F the frequency of vibration, a lower limit of the activation energy of motion $E_m > 0.5$ eV is estimated.

ACKNOWLEDGMENT

Discussions with Dr. A. H. Muir, Jr. and Dr. H. Wiedersich are appreciated.

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