

## Nuclear Magnetic Specific Heat of Ferromagnetic Iron Alloys with Sb and Re

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The effective field at the nuclei of Sb and Re solute atoms in Fe was determined by low-temperature specific heat measurements. For Sb,  $H_{\text{eff}} = 170 \pm 8$  kOe; for Re,  $H_{\text{eff}} = 610 \pm 35$  kOe.

INFORMATION has become available recently on the effective field  $H_{\text{eff}}$  at the nuclei of several non-magnetic solutes in ferromagnetic solvent metals. Such data were, for instance, obtained by Mössbauer-effect, nuclear magnetic resonance, calorimetric, and  $\gamma$ -ray anisotropy methods for V, Al, Cu, Sn, In, Sb, and Au in Fe. Reliable data for  $H_{\text{eff}}$  are of particular importance, since the theoretical interpretation of the effect is still quite tentative.

In the present work, calorimetric measurements were made to determine the effective field at Sb and Re nuclei in Fe. The calorimetric method has the advantage that it requires only a knowledge of the well-determined dipole moments in the ground state. For the nuclides concerned these values are as follows: For  $\text{Sb}^{121}$ ,  $\mu = 3.3417$ ; for  $\text{Sb}^{123}$ ,  $\mu = 2.5334$ ; for  $\text{Re}^{185}$ ,  $\mu = 3.1437$ ; and for  $\text{Re}^{187}$ ,  $\mu = 3.1760$ , in nuclear magnetons.

An iron alloy containing 10 at. % Re and one containing 5.4 at. % Sb were prepared by melting in argon atmosphere. Both alloys were homogenized by annealing in vacuum for three days at  $1200^\circ\text{C}$ . The Fe-Re alloy had, in addition, a one-day anneal at  $800^\circ\text{C}$ . In the case of the Fe-Re alloy, for which the nuclear magnetic specific heat was quite large, the measurements could be carried out in the temperature range of 1.3 to  $4.2^\circ\text{K}$  using a calorimeter described previously.<sup>1</sup> In the case of the Fe-Sb alloy the nuclear magnetic specific heat was much smaller and, consequently, the measurements had to be extended to much lower temperatures. For these measurements in the range of 0.4 to  $3.6^\circ\text{K}$  a He<sup>3</sup>

cryostat was used, which also has been described elsewhere.<sup>2</sup>

The experimental data are shown in Fig. 1. The two experiments with the Fe-Sb alloy were in excellent agreement with each other. Table I gives the coefficients  $\alpha$ ,  $\beta$ , and  $\gamma$  for the two alloys in the equation  $C = \gamma T + \beta T^3 + \alpha T^{-2}$ , calculated from the measured data by a least-squares method. The values of  $H_{\text{eff}}$ , given in the table, were calculated from the coefficients  $\alpha$ , using the following relationship:

$$\alpha = \frac{N_c}{3k} H_{\text{eff}}^2 \left\langle \frac{I+1}{I} \mu^2 \right\rangle_{\text{av}},$$

where

$$\left\langle \frac{I+1}{I} \mu^2 \right\rangle_{\text{av}} = \sum_i A_i \frac{I_i+1}{I_i} \mu_i^2,$$

with  $N_c$  the atomic fraction of solute in the alloy and  $A_i$ ,  $I_i$ , and  $\mu_i$  the fractional natural abundance, the spin, and the nuclear dipole moment, respectively, of isotope  $i$  of the solute. The summation is to be extended over all isotopic species in the element concerned.

The Debye temperatures  $\theta_D$  were calculated from  $\beta$  in the usual manner.  $\theta_D$  for the alloys is lower than that obtained by the same method for Fe ( $445^\circ\text{K}$ ). The Debye temperature for Fe calculated from elastic constants,  $\theta_D = 477^\circ\text{K}$ , is still higher.<sup>3</sup> The latter discrepancy is apparently due to the spin wave contribution to the low-temperature specific heat.<sup>3</sup> The electronic specific heat for the Re alloy is somewhat lower than that

TABLE I. Results from low temperature specific heat measurements.

Alloy	$\gamma \times 10^4$ (cal mole <sup>-1</sup> deg <sup>-2</sup> )	$\beta \times 10^4$ (cal mole <sup>-1</sup> deg <sup>-4</sup> )	$\theta_D$ (°K)	$\alpha \times 10^4$ (cal mole <sup>-1</sup> deg)	$H_{\text{eff}}$ at solute nucleus (kOe)
Fe <sub>0.90</sub> Re <sub>0.10</sub>	$10.4 \pm 0.2$	0.066	413	5.17	$610 \pm 35$
Fe <sub>0.946</sub> Sb <sub>0.054</sub>	$13.0 \pm 0.2$	0.067	411	0.172	$169 \pm 8$

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<sup>1</sup> C. H. Cheng, C. T. Wei and P. A. Beck, Phys. Rev. **120**, 426 (1960).

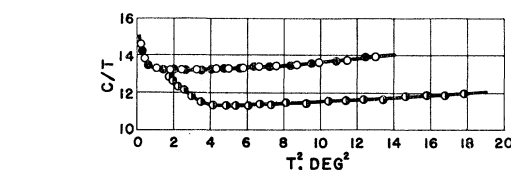


FIG. 1.  $C/T$  in units of  $10^{-4}$  cal mole<sup>-1</sup> deg<sup>-2</sup> vs  $T^2$  in  $^\circ\text{K}^2$  for an Fe<sub>0.946</sub>Sb<sub>0.054</sub> alloy (○ experiment No. 1, ● experiment No. 2) and for an Fe<sub>0.90</sub>Re<sub>0.10</sub> alloy, ○. In the low-temperature region so many data points were accumulated in the two experiments that only some of these can be shown in the graph. However, these give a clear indication of the degree of consistency attained.

<sup>2</sup> O. V. Lounasmaa and R. A. Guenther, Phys. Rev. **126**, 1357 (1962).

<sup>3</sup> J. A. Rayne and B. S. Chandrasekhar, Phys. Rev. **122**, 1714 (1961).

for iron,<sup>1</sup> as expected on the basis of the electron concentration,<sup>1</sup> while for the Sb alloy it is slightly higher. These differences are well outside of the experimental error.

It is interesting to observe that for Re in iron the effective field is of the same order of magnitude as that previously found for Au in iron,<sup>4</sup> but that the value for Sb is much smaller. On the basis of  $\gamma$ -ray anisotropy measurements, Samoilov *et al.*<sup>4</sup> give  $H_{\text{eff}} \geq 280$  kOe for

<sup>4</sup> B. N. Samoilov, V. V. Sklyarevskii and E. P. Stepanov, J. Exptl. Theoret. Phys. U.S.S.R. **38**, 359 (1960) [translation: Soviet Phys.—JETP **11**, 261 (1960)].

Sb in Fe. According to a note added to their paper by those authors, this should be corrected to  $H_{\text{eff}} \geq 180$  kOe, which is not inconsistent with the value obtained in the present work.  $H_{\text{eff}}$  for Re in Fe apparently has not been previously measured.

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## Relation between Absorption and Emission Probabilities in Luminescent Centers in Ionic Solids

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It is pointed out that the Einstein relationship between spontaneous emission probability and induced absorption probability for radiative transitions is not generally valid for impurity centers in condensed media. An alternative approach to the problem is available by which estimates of the possible discrepancies can be made. Several mechanisms are discussed, particularly the Jahn-Teller effect, which depend on the existence of the phonon field and the lattice relaxation following absorption of a photon. In some simple cases, such as the *F* center in KCl and LiF, the decay time predicted from the integrated absorption cross section may differ by an order of magnitude from that observed. In other simple and cubic systems, where the atomic symmetries are appropriate, the discrepancy may be even larger. In noncubic crystals similar discrepancies may be expected.

### I. ABSORPTION AND LUMINESCENCE IN ATOMIC SYSTEMS

BECAUSE of the common occurrence of absorption and luminescence of light in physical systems, and because of similar characteristics of these two phenomena, it has long seemed natural to discuss them in terms of related concepts. The development of the Bohr theory of the atom, together with the Planck radiation law, made it possible for Einstein<sup>1</sup> to establish simple relationships between absorption and emission parameters in atomic systems. In his famous work Einstein considered a simple two-state system and showed that when such a system is in equilibrium with a set of Planck oscillators (i.e., a radiation field), the principle of detailed balancing leads to a predicted spontaneous emission probability per unit time,  $A_{21}$ , which is related to the induced absorption (or emission) probability per unit energy density per unit time, times unit frequency,  $B_{12}$  ( $=B_{21}$ ), by the expression

$$A_{21} = \frac{1}{\tau_{21}} = \frac{8\pi h \nu_{12}^3}{c^3} B_{12}, \quad (1)$$

where  $h\nu_{12}$  is the energy separation between the two states. The frequencies of absorbed and emitted light ( $\nu_{12}$ ) are equal in this case.

Quantum-mechanical considerations applied to simple systems lead to the same conclusions.<sup>2,3</sup> Semiclassical radiation theory is sufficient to compute the (induced)  $B$  coefficient, and although it does not predict the existence of spontaneous emission, quantum electrodynamics does; therefore, although the Einstein relationship *must* be used in connection with semiclassical theory to predict  $A_{21}$ , it is not necessary if the problem is treated by quantum electrodynamics, and so in principle one could forget it. In connection with isolated atomic systems, the two schemes may be used equivalently; however, as we shall see, in solids there are particular precautions which must be taken.

In the simple atomic case, either of the above schemes yields the following results for allowed (electric-dipole)

\* Research supported in part by a grant from the U. S. Air Force Office of Scientific Research.

<sup>1</sup> A. Einstein, Physik. Z. **18**, 121 (1917).

<sup>2</sup> L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), Chaps. 10 and 14. W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, New York, 1954), 3rd ed.

<sup>3</sup> E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935), Chap. 4.