# Low-Temperature Specific Heat of Face-Centered Cubic Ni-Co Alloys*

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Low-temperature calorimetric measurements have been made on some fcc Ni-Co alloys. The observed variation of electronic-specific-heat coefficient with the average number of valence electrons per atom, $n_e$, for this system is in a remarkably good agreement with that for the Ni-Fe system in Ni-rich alloys over a significantly large $n_e$ range. Based on these measurements and the validity of the rigid-band model, an approximate shape of the $3d$ band is proposed for fcc alloys.

## INTRODUCTION

FOR binary alloys of transition elements, low-temperature calorimetric measurements have demonstrated the remarkable feature that the electronic-specific-heat coefficient $\gamma$ is determined by the average number of valence electrons per atom, $n_e$, rather than the identities of the constituent elements. This is well illustrated by Cheng *et al.*[1] for various bcc alloys ($4<n_e<9$) of the $3d$ series. Since the variation of the experimentally determined $\gamma$ values may be regarded as reflecting the variation of the density of states, even without detailed knowledge of the enhancement effect due to the electron-phonon interaction,[2] these results are usually interpreted by the rigid-band model, which assumes a universal density-of-states curve for the $3d$ band. Consequently, the low-temperature calorimetry becomes an important technique for studying the shape of the $d$ band.

For various fcc alloys of $3d$ transition elements covering the $n_e$ range 7.5 to 10, earlier calorimetric measurements by Gupta *et al.*[3] revealed complications associated with their anomalous magnetic properties at low temperatures. Presumably, the measured $\gamma$ value consists of an additional magnetic contribution, and can no longer be simply related to the density of states at the Fermi level. Therefore, in the $\gamma$-versus-$n_e$ plot, a rather complicated picture was obtained instead of a common curve representing all systems. They concluded by suggesting an approximate shape of the $d$ band, based on Ni-V and Ni-Fe systems at $n_e\sim7.5$–$9.2$ and 9.2–10, respectively. However, it has been recognized that the rigid-band model is not likely to be applicable if the two constituent elements of an alloy, such as Ni-V, have a large $n_e$ difference.[4,5] It is of interest, then, to make a further test of this approximation by comparing it with the data of other suitable alloys. For this purpose, the Ni-Co system was thought to be particularly suitable. Ni and Co form a continuous fcc solid solution between $n_e\sim9.3$ and 10,[6] which is also covered by the Ni-Fe alloys. Another interesting point for this comparison arises from the expectation that the rigid-band model might break down near the end of the $d$ band. In this case, different types of $\gamma$-versus-$n_e$ curves should be observed in Ni-rich alloys of these two systems. Walling and Bunn[7] have previously reported a set of data on Ni-Co alloys. Unfortunately, no conclusive comparison could be made, since there were apparently significant uncertainties in their results. Even for pure Ni, their $\gamma$ value is much too low as compared with that well determined by other investigators.[3,8] With these considerations, new calorimetric measurements on fcc Ni-Co alloys have been carried out in this work.

## EXPERIMENTS AND RESULTS

Six fcc Ni-Co alloy specimens, containing 6, 10, 20, 33.4, 50, and 65 at.% Co, respectively, were prepared, either by induction-melting or by repeated arc-melting, from materials with nominal purity of 99.9%. After an homogenizing anneal at 1200°C for three days, metallographic examination showed each specimen to consist of a single phase. The specific-heat measurements were

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[1] C. H. Cheng, C. T. Wei, and P. A. Beck, Phys. Rev. **120**, 426 (1960).

[2] T. M. Srinivasan, H. Claus, R. Viswanathan, and P. A. Beck, in *Phase Stability in Metals and Alloys*, edited by P. S. Rudman, J. Stringer, and R. I. Jaffee (McGraw-Hill Book Co., New York, 1967), p. 151.

[3] K. P. Gupta, C. H. Cheng, and P. A. Beck, J. Phys. Chem. Solids **25**, 73 (1964).

[4] J. Friedel, Nuovo Cimento Suppl. **7**, 287 (1958).

[5] J. L. Beeby, Phys. Rev. **135**, A130 (1964).

[6] *Constitution of Binary Alloys*, edited by M. Hanson and K. Anderko (McGraw-Hill Book Co., New York, 1958), 2nd ed., p. 485.

[7] J. C. Walling and P. B. Bunn, Proc. Phys. Soc. (London) **74**, 417 (1959).

[8] J. A. Rayne and W. R. G. Kemp, Phil. Mag. **1**, 918 (1956).

TABLE I. Atomic fraction $f$ of Co, hyperfine field $H_e$ at Co nuclei, and various parameters $A$, $\gamma$, and $\beta$, in Eq. (1), for fcc Ni-Co alloy specimens. The $H_e$ values are estimated from the calorimetric work of Arp *et al.* (Ref. 11).

| $f$(at.%Co) | 6 | 10 | 20 | 33.4 | 50 | 65 |
|---|---|---|---|---|---|---|
| $H_e$(*kOe*) | −88 | −94 | −106 | −120 | −143 | −162 |
| $A$($10^{-4}$cal°K/mole) | 0.11 | 0.22 | 0.55 | 1.2 | 2.5 | 4.2 |
| $\gamma$($10^{-4}$cal/mole°K$^2$) | 16.0 | 15.4 | 13.6 | 13.0 | 12.4 | 12.8 |
| $\beta$($10^{-4}$cal/mole°K$^4$) | 0.094 | 0.067 | 0.044 | 0.039 | 0.044 | 0.044 |
| $\theta_D$(°K) | 367 | 410 | 472 | 492 | 472 | 472 |

made between 1.6 and 4.2°K in a He$^4$ cryostat.[9] The 1958 He$^4$ scale was used to calibrate the carbon thermometer (Allen-Bradley, $\frac{1}{10}$ W, 56 Ω) for measuring the temperature of specimen.

For these alloys, the low-temperature specific heat can be expressed as

$$C=\beta T^3+\gamma T+AT^{-2}, \tag{1}$$

in which the terms on the right are, respectively, the lattice, electronic, and hyperfine contributions. The last term arises from the interactions between the nuclear magnetic moment $\mu$ of the Co$^{59}$ nuclei and the hyperfine field $H_e$. (This contribution from Ni nuclei is negligible, owing to its very small nuclear magnetic moment.) It is calculated from the equation[10]

$$\frac{A}{T^2}=\frac{fNk}{3}\frac{(I+1)}{I}\left(\frac{\mu H_e}{kT}\right)^2, \tag{2}$$

where $f$ is the atomic fraction of Co in the alloy, $N$ is Avogadro's number, $k$ is the Boltzmann constant, and $I$ is the nuclear spin. The values of $H_e$ are estimated from an earlier calorimetric work of Arp *et al.*[11] on Co-Fe and Co-Ni alloys, assuming a linear relationship between $H_e$ and $n_e$ (Table I). Their measurements were made below 0.7°K, where the hyperfine contribution dominated the total specific heat, but no reliable $\gamma$ values were obtained.

For each specimen, as shown in Fig. 1, the experimental data fall on a straight line in a plot of $(C-AT^{-2})/T$ versus $T^2$. The $AT^{-2}$ term is only a small correction above 1.6°K, even for alloys with high Co content. The intercept at $T=0$°K and the slope of the straight line give the values of $\gamma$ and $\beta$, respectively (Table I).

## DISCUSSION

The $\gamma$ values of fcc Ni-Co alloys from this work are plotted against $n_e$ in Fig. 2, along with literature data for various fcc alloy systems.[3,7] As suspected, the thin dashed curve (I), representing the Ni-Co results by Walling and Bunn,[7] is systematically lower. Using the

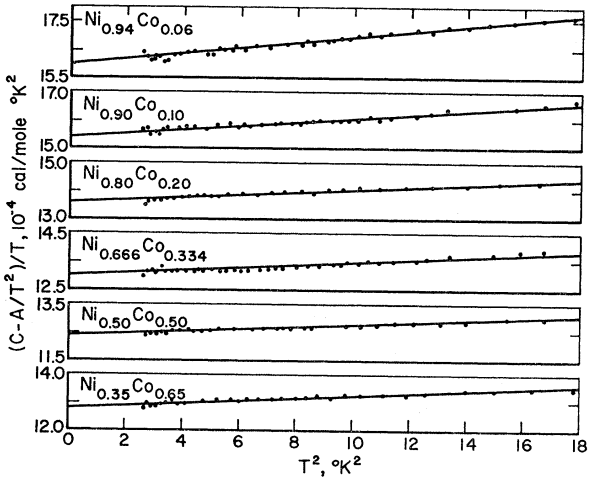


FIG. 1. $(C-A/T^2)/T$ versus $T^2$ for fcc Ni-Co alloys. The hyperfine contribution correction is based on $H_e$ values estimated from Ref. 11.

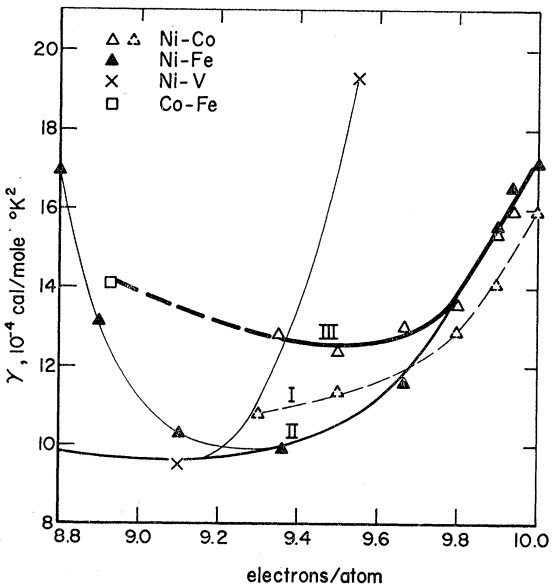


FIG. 2. $\gamma$ versus $n_e$ for various fcc alloys of 3*d* series. (I) Ni-Co [Walling and Bunn (Ref. 7)]; (II) Ni-V and Ni-Fe [Gupta *et al.* (Ref. 3)]; (III) Ni-Co (this work) and Co-Fe [Cheng *et al.* (Ref. 1)].

[9] The procedure and the apparatus used for the work performed at the University of Illinois are described in Ref. 1. A similar cryostat has been built at Battelle Memorial Institute, Columbus, Ohio.

[10] W. Marshall, Phys. Rev. **110**, 1280 (1958).

[11] V. Arp, D. Edmonds, and R. Petersen, Phys. Rev. Letters **3**, 212 (1959).

new data, one has good agreement between the Ni-Co and Ni-Fe alloys in the $n_e$ range from 10 (pure Ni) down to 9.8, which corresponds to 20 at.% Co or 10 at.% Fe in Ni. These concentrations are significantly large, since there are only about 0.6 holes per atom in the Ni-rich alloys (nearly filled $d$ band). Theoretically, the rigid-band model is applicable only if the influence of the solute atoms (the screening effect) can be treated as a small perturbation.[4] The experimental observations are thus rather surprising. In this connection it is of interest to refer to the recent work of Srinivasan and Beck[12] on the applicability of the rigid-band model for $3d$ band in bcc alloys.

Below $n_e=9.8$, the two systems start to deviate. The medium solid line (II) in Fig. 2, given by Gupta *et al.*,[3] is based on the results of strongly ferromagnetic Ni-Fe and nonmagnetic Ni-V alloys ($n_e<9.5$). Just beyond the smooth joining point at $n_e\sim9.2$, both systems have drastically increased $\gamma$ values, possibly arising from magnetic contributions. This, however, makes the smooth curve somewhat uncertain. In addition, the differences in $n_e$ between the constituent elements in these two systems are 2 and 5, respectively, whereas in Ni-Co it is only 1. Hence the rigid-band behavior should be more closely approximated in the latter system. In conclusion, we would therefore suggest the heavy curve (III) in Fig. 2, based on Ni-Co alloys, as the better approximation of the $d$-band shape. This curve is further extrapolated tentatively by dashed line to one fcc $Co_{0.93}$ $Fe_{0.07}$ alloy with $n_e=8.93$, which has previously been measured by Cheng *et al.*[1] All these Ni-Co and Co-Fe alloys are strongly ferromagnetic. However, it should be pointed out that martensitic transformation from fcc to hcp structure on cooling to low temperatures is certainly possible for the Co-rich alloys.

Based on this curve, there are two more points worth mentioning. First, beyond $Co_{0.93}$ $Fe_{0.07}$, it connects smoothly to the common curve for bcc alloys,[1] indicating the continuity of the $d$ band through the phase boundary. Secondly, the $\gamma$ value for fcc Co, which has not been determined so far, can be predicted to be close to $14\times10^{-4}$ cal/mole °K², a value much higher than that for the low-temperature stable hcp Co ($11\times10^{-4}$ cal/mole °K²).[13,14]

The Debye temperatures $\Theta_D$ for all Ni-Co alloys, as listed in Table I, are calculated from the lattice specific-heat coefficient $\beta$. These values have uncertainties of the order of 5% because the $T^3$ term here is only a small contribution to the total measured specific heat. However, in a plot of both $\Theta_D$ and $\gamma$ as a function of Co content (Fig. 3), it is obvious that the variations of these two parameters are closely correlated and opposite to each other, indicating the relation between the presence of conduction electrons and the lattice vibrations. Similar results have been observed in bcc V-Fe and V-Ru alloys[15] and in hcp Mo-Ru and Mo-Rh alloys.[16]

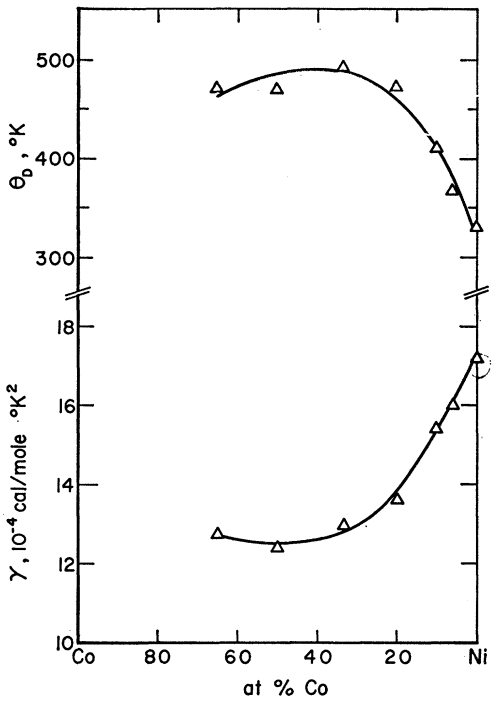


FIG. 3. $\gamma$ and $\Theta_D$ versus Co concentration for fcc Ni-Co alloys. The data for pure Ni are obtained from Ref. 3.

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[12] T. M. Srinivasan and P. A. Beck, Ann. Acad. Sci. Fennicae A VI, 163 (1966).
[13] M. Dixson, F. E. Hoare, T. M. Holden, and D. E. Moody, Proc. Roy. Soc. (London) A285, 561 (1965).
[14] W. Proctor, R. G. Scurlock, and E. M. Wray, Phys. Letters 20, 612 (1966).
[15] F. Heiniger, E. Bucher, and J. Muller, Physik Kondensierten Materie 5, 243 (1966).
[16] James C. Ho and R. Viswanathan, J. Phys. Chem. Solids (to be published).